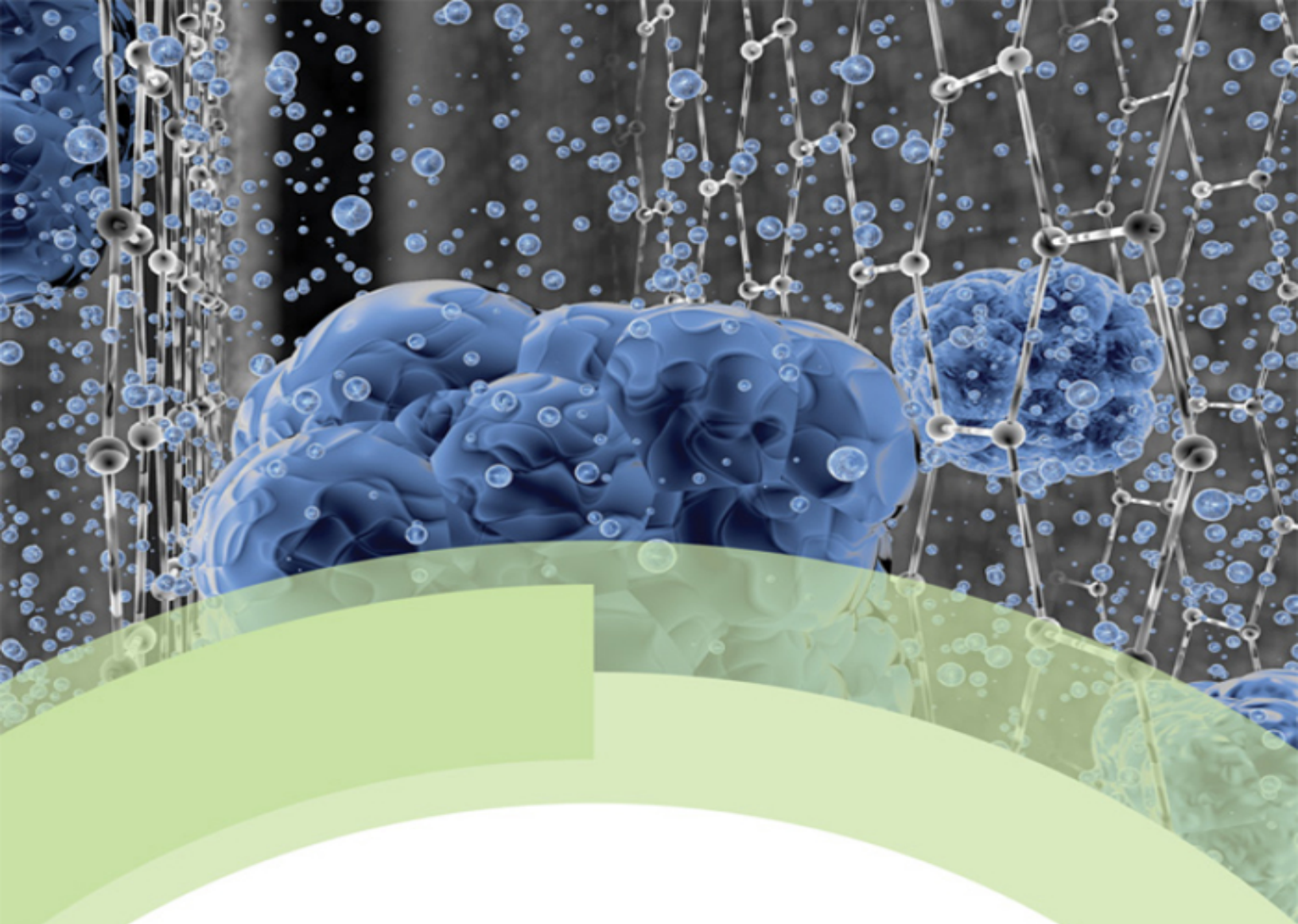




Chemistry in the Environment

Emerging Nanotechnologies for Water Treatment

Edited by Yanbiao Liu, Chong-Chen Wang and Wen Liu



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Emerging Nanotechnologies for Water Treatment

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Preface

In Chinese idioms, the supreme good is like water. Water (H_2O) is a very fantastic substance for us. For a long period of time, humans have been considering how to improve the water environments of our planet. We three got acquainted because of water. The area we work in is environmental engineering for water treatment. Purification of contaminated water is a way to maximize its value. For example, *good water can produce good wine*. We have devoted all our lives to such a great cause.

In the 1950s, Richard Phillips Feynman's great speech “*There's Plenty of Room at the Bottom*” opened a precedent for nanotechnology. In my (Wen Liu) class of “Environmental Nanotechnology”, I always tell Feynman's story to the students. They are guided to explore the essence of the micro- and nano-world, and meanwhile, to appreciate the romance of a scientist's life. Actually, literature, art and science are inherently interrelated. It is so exciting that technology is where it is today, so we can learn more about the “bottom”. We are delighted that we can provide Emerging Nanotechnologies for Water Treatment for you all.

A link is needed to connect the macro-scale water world and micro-scale nano world. A metaphor for this link could be seen in the “knot” mentioned in Makoto Shinkai's animated movie, *Your Name*. Today, we happily find that nanomaterials act as knots in this way. It's our great pleasure to show you this connection caused by nanotechnology. Since we share a common enthusiasm in this topic, we got together to prepare this book. There is an old saying that the friendship between gentlemen is as pale as water, while we believe it is thicker than water. We also offer our acknowledgement to Dionysios D. Dionysiou, who is the Editor-in-chief of this series of Royal Society of Chemistry books, and whose name is similar to that of Dionysus, the ancient Greek god associated with wine.

In the future, we will continue to be proud of water and nanotechnology. Contaminated water treated using nanotechnology is the ultimate goal pursued by us, and thus the water quality is significantly upgraded.

Yanbiao Liu, Donghua University, China

Chong-Chen Wang, Beijing University of Civil Engineering and
Architecture, China
Wen Liu, Peking University, China

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Chapter 1

Functionalized Metal Nanoclusters for Biosensing Applications

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1.1 Introduction

Nanoscale materials are the foundation of many diagnostic technologies.¹ The unique physical and chemical properties of nanomaterials are often not possible to achieve in their corresponding bulk state and therefore, such nanoscale properties of these nanomaterials have been explored in many biomedical applications.^{2–4} For instance, the localized surface plasmon resonance (LSPR) and electrochemical properties of noble metal nanoparticles (NPs) such as gold (Au) and silver (Ag) have been explored in sensing, diagnosis and therapy.^{5–8} For biomedical applications such as sensing and imaging, the material should be highly photostable, nontoxic and optically sound. In this context, fluorescent organic dyes remained as

one of the front runners for many years however, their poor photo-stability renders researchers to consider potential alternatives that will not only have extremely high fluorescence properties like organic dyes but also have good photo-stability in solution as well as in the solid state. Fluorescent nanomaterials such as semiconductor quantum dots (QDs) have been explored as one such alternative in the last few decades.^{9–11} These QDs are extremely photostable, exhibit color-tunable fluorescence and have high fluorescence quantum yield. Though one key issue of exploring these QDs in biomedical application is their intrinsic toxicity which originates due to the presence of toxic metals such as $\text{Pb}^{2+}/\text{Cd}^{2+}/\text{Hg}^{2+}$ as key constituents. Indeed, several functionalization strategies have been developed to reduce the toxicity of QDs however, none of them appears to provide a long-term solution.^{12,13}

Consequently, the focus of research was shifted to the development of new non-toxic nanomaterials with controlled fluorescence properties. In this context, metal nanoclusters (MNCs) have emerged as a rising star in the fluorescent nanomaterial community.^{14,15} They consist of a few to hundreds of metal atoms at the core with an average size less than 2 nm. Because of their ultra-small size, these MNCs exhibit many unique physical and chemical properties such as HOMO–LUMO transition, fluorescence, chirality, intrinsic magnetism, high catalytic activity, *etc.*^{16–21} Because of such molecular-like properties, which are not generally seen in their larger counterparts (*i.e.*, nanoparticles; size 3–100 nm), MNCs are considered to bridge the gap between atoms and nanoparticles. All these intriguing molecular-like properties allow MNCs to be used in various areas including optoelectronics, photovoltaics, catalysis, sensing, imaging and so on.^{22–28}

In the last two decades, research on MNCs has advanced tremendously. In particular, various synthesis methodologies have been developed to achieve MNCs with high atomic precision, functionalization strategies have advanced to improve the properties of MNCs and subsequently, their properties have been explored in various avenues. Because of such advancements in the field, several review articles were published over the last few years. These review articles focused on the total synthesis, synthesis mechanism,²⁹ optical and fluorescence properties of MNCs,^{26,30} sensing,²⁵ catalysis²² and biomedical applications of MNCs.^{31,32} Some

excellent review articles are also well documented that summarize a brief overview of the nanocluster field and their potential in various applications.^{14,15,23,26} However, a concise review article that is particularly focused on the biosensing applications of MNCs is missing in the literature. Biosensing is an important research field, with numerous applications in the health and environment sectors. Over the last few years, several published articles suggested that MNCs could be the ideal biosensor material due to their excellent biocompatibility and optical properties. They have been used to detect biologically relevant small molecules (*e.g.*, H₂S, H₂O₂, cysteine, glutathione, dopamine and so on) and biomolecules (*e.g.*, proteins, DNA, RNA, ATP and so on).^{33–40} Therefore, a focused review on the development of functional MNC-based biosensors would be of great interest. In this chapter, we summarize the state-of-the-art biosensing applications of MNCs. In particular, this chapter is focused on sensors based on the absorbance, fluorescence and electrochemical properties of MNCs. A brief discussion on the current challenges and an outlook on the future research challenges of these functional MNCs are also presented.

1.2 MNC-based Optical Biosensors

Biosensors relying on the optical properties of materials have certain advantages over other prevailing methods, such as high sensitivity, rapid detection and low cost of spectroscopic assays. Being ultra-small in size, MNCs not only show distinct absorbance bands in their UV–vis spectra but also exhibit size- and composition-dependent tunable fluorescence properties that are highly sensitive to the environment. In this section, we summarize recent advances in the application of MNCs as new fluorescent probes for analytical sensors and biological imaging.

1.2.1 Detection of Small Biomolecules

Amino acids such as cysteine (Cys), lysine (Lys), histidine (His), *etc.* play a vital role in biological systems. The lack of any of these amino acids or the excess presence of them could lead to severe diseases and therefore the selective detection of these amino acids is of great importance in biomedical research. As an example, elevated levels of Cys are associated

with diseases like hypoglycemic brain damage, schizophrenia, *etc.*,^{41,42} while low levels of Cys are involved in liver injury, skin damage, and weakness or even Huntington's disease.⁴³ With the aim of detecting Cys, various MNCs and their composites have been developed. Trace level of Cys can enhance the photoluminescence (PL) properties of MNCs through the passivation of their defect states. Based on this mechanism, red-emitting bovine serum albumin protected AuNCs have been used to detect trace level of Cys in human blood serum. Recently, an aggregation-induced emission (AIE)-type AuNCs-based Cys sensor has also been constructed under alkaline conditions (pH 11). At elevated pH, the PL intensity of the AIE-type AuNCs is generally enhanced. When Cys was added at an alkaline pH, the PL of these NCs was significantly quenched. By this method, it was not only possible to achieve an ultra-low limit of detection (LOD) but also high selectivity over another ten amino acids and glutathione (GSH).⁴⁴ Such a high selectivity for Cys and homocysteine (Hcy) was also observed when AuNCs–NBD (4-chloro-7-nitro-2,1,3-benzoxadiazole (NBD-Cl)) was used as a chemosensor.⁴⁵ Due to the high specificity of NBD toward Cys and Hcy, the AuNCs–NBD probe was successfully applied for monitoring and imaging intracellular Cys and Hcy in HeLa cells. Recently, a Förster resonance energy transfer (FRET) assembly using GSH capped AuNCs and carbon dots as a ratiometric probe for cysteine detection was developed, which may be employed in the future for the diagnosis of cysteine-related diseases.⁴⁶ Like Cys, fluorescent AuNCs were also used to detect other important amino acids like histidine or lysine in biological fluids. For histidine detection, the PL of the NCs was often quenched by bivalent metal ions such as Cu^{2+} or Ni^{2+} . Due to the strong chelating efficiency, upon exposure of free histidine, these metal ions could be removed from NC surface and as a result, the PL of the AuNCs was restored.^{47,48} A ratiometric fluorescent sensor based on GSH-stabilized AIE-type AuNCs was also reported for the detection and sensing of lysine and Cys.⁴⁹

A FRET-based sensing platform was also employed for the detection of hydrogen sulfide (H_2S) in both *in vitro* and *in vivo* systems using chitosan-functionalized AuNCs.³³ Hydrogen peroxide (H_2O_2), which is a key

messenger in redox signaling, enzyme activity and various cell signaling pathways, is another important analyte often detected using fluorescent MNCs.³⁴ In particular, various protein- (or enzyme) functionalized MNCs were frequently used to detect H_2O_2 . Upon addition of H_2O_2 , the PL intensity of these protein-protected MNCs was quenched primarily due to the surface oxidation followed by aggregation. Such quenching strategies were used for intercellular H_2O_2 sensing and imaging of living macrophage cells using BSA-protected AuNCs.³⁵

In addition to the functionalized AuNCs, other MNCs such as AgNCs with strong PL properties could be regarded as effective biosensors. For example, Lan *et al.* prepared highly fluorescent AgNCs by conjugating 12 cytosine bases as templates and an 8-OHdG aptamer as the specific binding target to detect 8-OHdG in cells.⁵⁰ Likewise, various GSH protected AgNCs were used to selectively detect dopamine in human urine samples³⁶ as well as urea and glucose based on a target-triggered pH change of the solution using enzyme-catalyzed reactions.⁵¹ Recently, Chen *et al.* developed a smart and multifunctional DNA template of double standard (ds)-DNA-hosted AgNCs for the label-free and sensitive detection of ATP. This proposed strategy was also extended to the application of DNA detection.³⁷

The biosensing applications of MNCs were further extended to non-noble metal NCs. In particular, the fact that the PL of CuNCs could be quenched by trace amounts of hydrogen peroxide (H_2O_2),⁵² has been explored to construct a facile H_2O_2 –glucose detection strategy. In the case of CuNCs based glucose sensors, glucose oxidase (GOx) was often used as the support material. In the presence of GOx, glucose is oxidized by oxygen and results in the formation of H_2O_2 . Based on the PL quenching mechanism, several powerful analytical platforms for glucose detection were reported.^{53,54} In addition, a FRET-based biosensor using a MnO_2 nanosphere–CuNCs complex was reported for the detection of GSH. In this hybrid complex, CuNCs work as the donor while the MnO_2 nanosphere was used as the acceptor. Due to FRET, the PL of the CuNCs was quenched. The presence of GSH in the complex solution could digest the MnO_2 nanosphere into

Mn^{2+} and thus restore the PL of the CuNCs. In fact, GSH can not only selectively recover the quenched PL of CuNCs but also improve the PL (25 times) through host–guest interactions between GSH and CuNCs.³⁹ Using fluorescent CuNCs, a novel fluorescent “turn-on” detection was also reported for the detection of urea in real biological samples.⁵⁵ Yang *et al.* used ovalbumin–CuNCs to detect both vitamin B₁ and doxycycline where the PL of ovalbumin–CuNCs was quenched by vitamin B₁ and restored by doxycycline because of different affinities toward those analytes.⁵⁶

1.2.2 Detection of Proteins and Enzymes

Alongside small molecules, MNC-based sensors have been exploited for the detection of biomolecules such as proteins and enzymes. For example, Qi *et al.* developed an inner filter effect (IFE) based method for the fluorometric detection of alkaline phosphatase (ALP) using fluorescent AuNCs.⁵⁷ For this purpose, they used *p*-nitrophenyl phosphate (PNPP) that is hydrolyzed by ALP to *p*-nitrophenol (PNP), the absorbance of which was similar to the AuNCs. Due to competitive absorbance between PNP and AuNCs, the PL of the AuNCs was quenched. By this mechanism, they were successfully able to detect ALP in serum solutions. On the other hand, a simple fluorescence sensor array based on two different metal ions (Zn^{2+} and Cd^{2+}) and three different protein-protected AuNCs was reported by Wu and co-workers.⁵⁸ Based on the difference in PL response, they were able to detect nine different proteins with different concentrations and identified five different bacteria. Recently, Zhang *et al.* developed a novel strategy for the simultaneous determination of protein kinase A and casein kinase II using artificial peptide-protected blue-emissive CuNCs and red-emissive AuNCs.³⁸ These artificial peptides retained their activity after the synthesis of both AuNCs and CuNCs. In the absence of protein kinase, the peptides on the surface of NCs were digested by carboxypeptidase Y, resulting in surface oxidation followed by PL quenching of the NCs. However, the PL of the NCs was retained in the presence of protein kinase A and casein kinase II (Figure 1.1). Interestingly, the excitation wavelength of both the NCs was similar and therefore, by single excitation, they were quantitatively determining protein kinase A and casein kinase II.

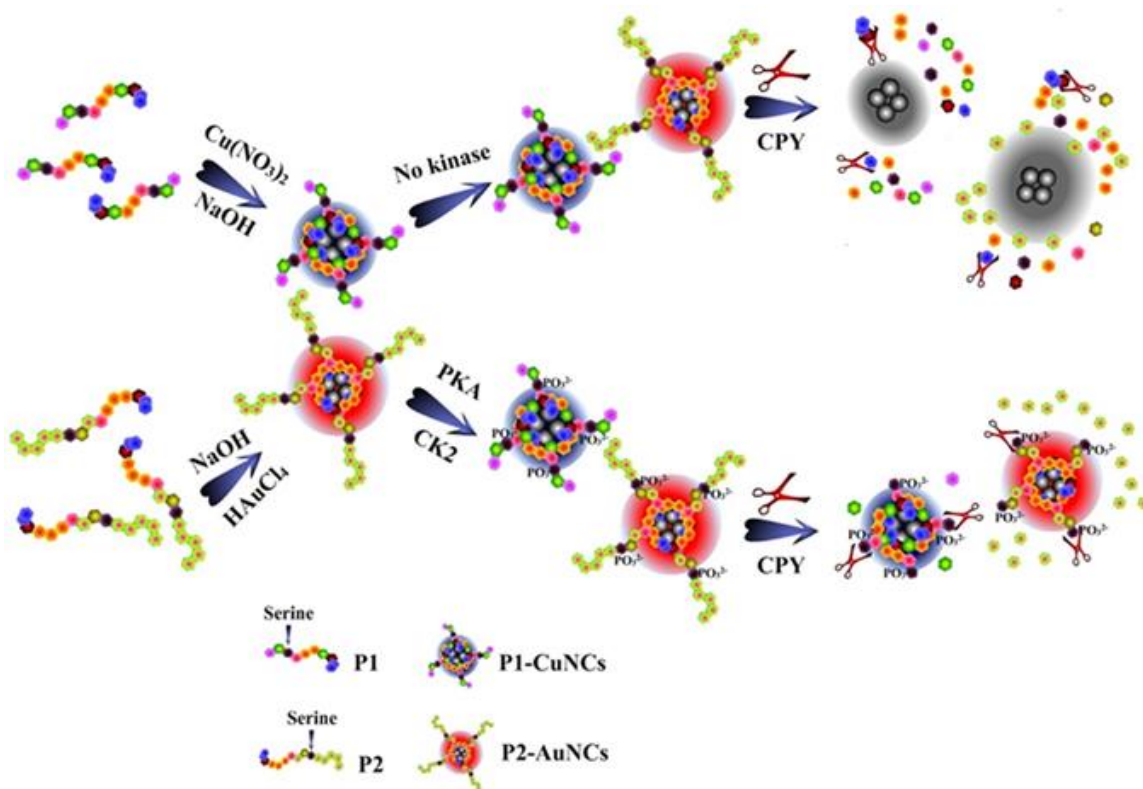


Figure 1.1 Schematic representation of the different peptide-NCs biosensor for the simultaneous detection of protein kinase A (PKA) and casein kinase II (CK2) based on the blocking effect of phosphate groups on carboxypeptidase Y (CPY) digestion. Reproduced from ref. ³⁸ with permission from American Chemical Society, Copyright 2016.

Along this line, Chen *et al.* developed a sensitive and facile fluorescent method for the detection of actin based on enzyme-responsive DNA-AgNCs.⁵⁹ Deoxyribonuclease I (DNase I) was used for digestion purposes. In the presence of DNase I, ds-DNA was degraded and formed shorter complexes. As a result, the PL of the DNA-AgNCs was quenched. The presence of actin prevented the digestion of ds-DNA due to a stable complex formation between actin and DNase I. By this method, a LOD of as low as $0.03 \mu\text{g mL}^{-1}$ was achieved. Recently, based on the specific recognition ability of the aptamer (APT), a fluorescent APT-AgNCs probe was reported for the detection of mucin 1 (MUC1). The method showed a linear detection range of 0.1–100 nM for MUC1 with a LOD of 0.05 nM.⁶⁰ Li *et al.* designed a DNA-AgNCs molecular beacon (AgMBs) for transcription factors (TFs) analysis on the basis of the switchable

fluorescence of AgMBs. The detection ability was also verified by detecting multiple endogenous TFs in DLD-1 cells.⁶¹

Furthermore, enzymes such as hyaluronidase (HAase) were detected using luminescent GSH-protected CuNCs.⁶² The detection mechanism was based on the surface confinement effect. In the presence of hyaluronic acid (HA), the surface confinement effect of GSH–CuNCs was inhibited, blocking the enhancement of fluorescence. With the addition of HAase, HA was hydrolyzed into small fragments, and the fluorescence of GS–CuNCs was turned on because of the surface confinement effect. GSH–CuNCs can also be employed to evaluate the activity of pyrophosphatase (PPA).⁶³ Here, first the PL of the CuNCs was enhanced by Al^{3+} ions due to the AIE effect. However, owing to the stronger coordination between PPA and Al^{3+} ions, the surface coordinated Al^{3+} ions from the GSH–CuNCs were removed upon the addition of PPA, and thus PL was quenched. In another study, Ling *et al.* developed a ratiometric fluorescent sensor using poly(T)–CuNCs and 4',6-diamidino-2-phenylindole (DAPI) as output signals for the detection of uracil-DNA glycosylase (UDG) with a LOD of $5.0 \times 10^{-5} \text{ U mL}^{-1}$.⁶⁴ Cao *et al.* developed an integrated detection system for two opposite targets including small molecules (biotin) and proteins (streptavidin) using highly fluorescent CuNCs and magnetic separation techniques.⁶⁵

1.2.3 Detection of Oligonucleotides

The detection of oligonucleotides is essential as it is one of the primary biomarkers for monitoring human health. The PL properties of AuNCs were used for the quantification of dsDNA. In this context, one approach was based on a single heating and cooling cycle like in the polymerase chain reaction (PCR). In the presence of ds-DNA, the PL of the AuNCs increased. Through this straightforward technique, DNA was quantified in two different cancer cell lines, namely, HeLa and A549.⁶⁶ The other approach is based on reverse transcriptase PCR (RT-PCR), where luminescent AuNCs were used to assess gene profiles associated with apoptosis in HeLa cancer cells as well as to measure the expression of the glutathione *S*-transferase (GST) protein and the GST-tagged human granulocyte macrophage colony-

stimulating factor (GSThGMCSF) recombinant protein extracted from *Escherichia coli*.⁶⁷

Recently, a simple and low-cost method for the detection of telomerase activity was reported.⁶⁸ This sensing platform used DNA–AgNCs as a probe. The PL properties of the DNA–AgNCs were altered by introducing Mg^{2+} ions into the solution. The experimental results revealed that the DNA sequence and the secondary structure of the DNA had a huge influence on the metal ion-induced PL properties of the AgNCs and therefore such a phenomenon was explored as basis for the detection of telomerase activity. The effect of stem sequence on the PL properties of hairpin–AgNCs was studied by Guo and co-workers.⁶⁹ In this regard, they first designed DNA hairpin with a 20-base pair stem and subsequently used it as a template for the synthesis of AgNCs. The PL properties of the AgNCs varied with the elongation of stem length under an invariable GC content and distribution pattern. DNA–AgNCs was also used for the detection of miR-122 and norovirus RNA.^{70,71} In the presence of the target (norovirus RNA), the PL of the AgNCs was enhanced due to the binding of target chain with the secondary structure of the DNA. Based on this “turn-on” mechanism, the LOD of norovirus RNA was found to be as low as 18 nM. Fluorescent DNA–AgNCs was also explored as a general sensing platform for the detection of DNA and microRNA (miRNA). This new enzyme-free and label-free amplified nucleic acid detection platform was developed by combining the highly efficient signal-amplification capability of the catalytic hairpin assembly (CHA) reaction with the spatially sensitive fluorescent AgNCs.⁷²

Like AgNCs, various types of DNA were also used to fabricate CuNCs. It was found that while normal ds-DNA could be a powerful template for the synthesis of fluorescent CuNCs, the presence of abasic sites in the DNA could hinder their formation. Based on this observation, the effect of the abasic sites present on the DNA was detected using the PL properties of the as-synthesized CuNCs.⁷³ Hairpin DNA–CuNCs were also used to detect miRNA155 in solution as well as in spiked human serum samples.⁷⁴ In the presence of miRNA155, the PL of the CuNCs was not only enhanced at 510 nm but also had a red shift (~ 60 nm) due to the formation of a DNA–RNA adduct. Mismatched RNA failed to form a complex with DNA and thus was

selectively discriminated from the miRNA155. DNA-hosted CuNCs were also able to detect mismatched base types located in the major groove of DNA (Figure 1.2).⁷⁵ The PL of the CuNCs was used as a parameter for the detection of mismatch types at room temperature. Approximately a three-fold enhancement in fluorescence intensity of the CuNCs was observed with mismatched DNA when compared to matched DNA. This is because AC-mismatched (MM) duplexes provide an appropriate environment for the fluorescent CuNCs that increases the fluorescence quantum yield (two-fold) of the CuNCs formed by the AC-MM duplexes compared to that of the full duplexes.

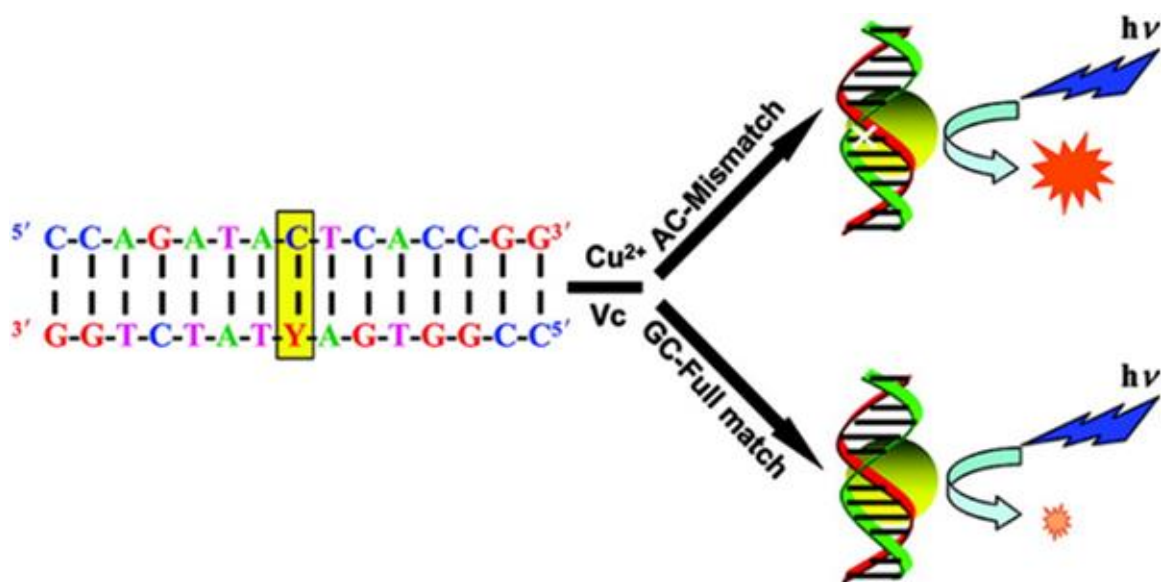


Figure 1.2 Schematic representation of a mismatch detection strategy using luminescent CuNCs. Reproduced from ref. ⁷⁵ with permission from American Chemical Society, Copyright 2012.

In a recent study, Wang *et al.* developed a simple and inexpensive method for the discrimination of nucleosides using the PL spectra of various nucleoside-templated CuNCs.⁷⁶ They used various nucleosides as templates for the synthesis of CuNCs and for the detection, they explored the advanced multivariate chemometrics analysis. Mismatch sequences in DNA were also probed using GSH-protected CuNCs.⁷⁷ Through fluorescence correlation spectroscopy, the binding affinity of CuNCs

toward DNA was determined and it was found to be dependent on the fraction of the GC pair. With these experimental findings, fluorescent CuNCs were found to be useful for the detection of MM DNA.

1.2.4 Detection of Diseases

Nanoparticles, particularly gold, remain one of the most explored materials that have been used for the sensitive, selective, and specific detection of various diseases. As ultra-small metal NCs possess many unique features such as PL, peroxidase and enzyme-like activity, metal NC-based detection of diseases has attracted immense interest. For example, recently the peroxidase-like activity of GSH-stabilized AuNC was explored to identify normal and cancer cells by accurately evaluating cellular GSH levels.⁷⁸ GSH is known to be an antioxidant and elevated levels of GSH are associated with the progression of various types of tumor. AuNCs serve as a catalyst for the oxidation of peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB) to produce a blue-colored product. However, being an antioxidant, increased levels of GSH inhibit the oxidation process. Based on this fact, the cellular GSH level was accurately determined and it was found that the GSH level of cancer cells was much higher than that of normal cells. Similarly, in another study, it was revealed that diseases could be monitored by sensing the protease activities with the help of AuNC-based nano-sensor platform as a biomarker that produces a direct colorimetric readout of disease state. To achieve this, a catalytic AuNC functionalized with GSH and biotinylated protease-cleavable peptides were first coupled to neutravidin (NAv) to form AuNC-NAv complexes. Following intravenous injection, these AuNC-NAv complexes specifically reached the disease site through blood stream and were digested by proteases secreted from diseased cells. In this way, AuNCs were filtered out through the kidneys due to their small size (≤ 2 nm). Therefore, a urine sample from the tumor-bearing mice was collected to monitor the disease state and the presence of AuNCs was used as an indicator of disease state. In the urine sample, the peroxidase-like catalytic activity of AuNCs was measured using the oxidation of the peroxidase substrate TMB by H_2O_2 . Direct colorimetric readout of the collected urine revealed that the mean urinary signal for tumor-bearing mice was 13-fold higher relative to healthy

mice and the urine samples from tumor-bearing mice were blue in color and could be read using the naked eye after the addition of the chromogenic peroxidase substrate, TMB.⁷⁹

Recently, an array-based sensing method was developed using fluorescent AuNCs, which could effectively discriminate the serum of hepatoma patients from those of healthy volunteers using different fluorescence responses.⁸⁰ The same group also constructed a “chemical tongue” sensor array based on fluorescent AuNCs to discriminate the sera of Alzheimer's disease (AD) patients from those of osteoarthritis patients, or of healthy people.⁸¹ Such direct effects of AuNCs also open a new avenue for the medicinal applications of AuNCs and they have been used for the detection of Parkinson's disease (PD) in mice.⁸² AuNCs have also been used for the early and sensitive detection of human immunodeficiency virus (HIV) infection using an antibody–antigen–antibody sandwich immunoassay format.⁸³ In this context, an immunocomplex was prepared by exploiting the interaction of the captured antibody with the HIV-1 p24 antigen followed by secondary biotinylated anti-p24 antibodies. The immunocomplex was attached to the streptavidin-conjugated AuNCs and causes changes in the PL intensity due to the strong noncovalent chemistry between biotin and streptavidin. An ultrasensitive nano-biosensor for detecting vascular endothelial growth factor (VEGF) disease was also developed by using supra-particle CuNCs consisting of multimerized VEGF165 aptamer joints with a single stranded (ss) DNA-based linker in the middle and polythymine sequences on both the 3' and 5' ends as a template. The sensing strategy was designed based on the target-induced structure switching mode of the aptamer. In the presence of VEGF165, this nanostructure depicted the visible wavelength shift and enhancement in the PL intensity due to self-assembly induced emission and AIE phenomena.⁸⁴

1.2.5 Labeling and Imaging

Due to the ultra-small size, biocompatibility, and high photo-stability, a number of research works have reported biological labeling and imaging applications based on fluorescent MNCs. For example, a new approach was developed using self-assembled AuNCs with carborane amino derivatives (AuNCs–CB) for the treatment of boron neutron capture therapy (BNCT).

BNCT is a powerful binary anticancer therapy in which boron compounds containing the ^{10}B isotope gather selectively in cancer cells. Subsequent irradiation with thermal neutrons produces an excited $^{11}\text{B}^*$ nucleus that undergoes a rapid fission reaction and results in the emission of high energy α -particles ($^4\text{He}^{2+}$), $^7\text{Li}^{3+}$ ions and low energy γ -rays. These emitted particles and ions are responsible for the selective damage of cancer cells. From their study, it was observed that the self-assembled AuNCs–CB nanocomposite was efficiently delivered to targeting tumor cells through enhanced permeability and retention (EPR) effects and nanometer size effects (Figure 1.3). The water-soluble amino derivative nido-carborane ($[7\text{-NH}_2(\text{CH}_2)_3\text{S-7,8-C}_2\text{B}_9\text{H}_{11}]^-$) efficiently facilitated the fluorescence enhancement of AuNCs through self-assembly, which is essential for cell imaging. The ^{10}B isotope of carborane, on the other hand, fulfills the requirement of BNCT treatment for the destruction of tumor cancer cells.⁸⁵ The fact that the presence of various reactive oxygen species (ROS) and enzymes in the cellular environment often causes quenching of MNC fluorescence and has been exploited to improve cellular imaging. In this context, a new strategy was developed by choosing chitosan (CS) as the coating agent on the surface of *N*-acetyl-L-cysteine (NAC) protected gold nanoclusters (AuNCs@NAC–CS) to improve resistivity toward ROS (H_2O_2) and enzyme (trypsin) in cellular environments. From the *in vivo* experiment on normal mice, it was observed that AuNCs@NAC–CS showed fluorescence signals in the liver and kidney of mice 6 h post-injection, and that the intensity gradually decreased after because of the highly efficient clearance characteristics of ultra-small MNCs. The study revealed that AuNCs@NAC–CSs exhibit good potential applications in long-term imaging in live-cells and tumor cells with low cytotoxicity.⁸⁶ In another study, a 3D gold nanocluster framework (GNCF) was fabricated through self-assembly of GSH–AuNCs using Sn^{2+} ions as an inter-nanocluster cross-linker. Self-assembled GNCF showed significantly improved luminescence signals as evident from their PL quantum yield change from $\sim 3.5\%$ to $\sim 25\%$. The excellent colloidal stability and high PL of GNCF in aqueous media make it a unique platform for bioimaging applications. Both GNCFs and GNCs were tested for cytotoxicity and cell viability in two different cell lines (NIH3T3 and A549 cells) and no

noticeable cytotoxicity was observed in the case of GNCFs. Rather, it exhibited higher viability with brilliant fluorescence in the cell cytoplasm compared to that of GNCs.⁸⁷

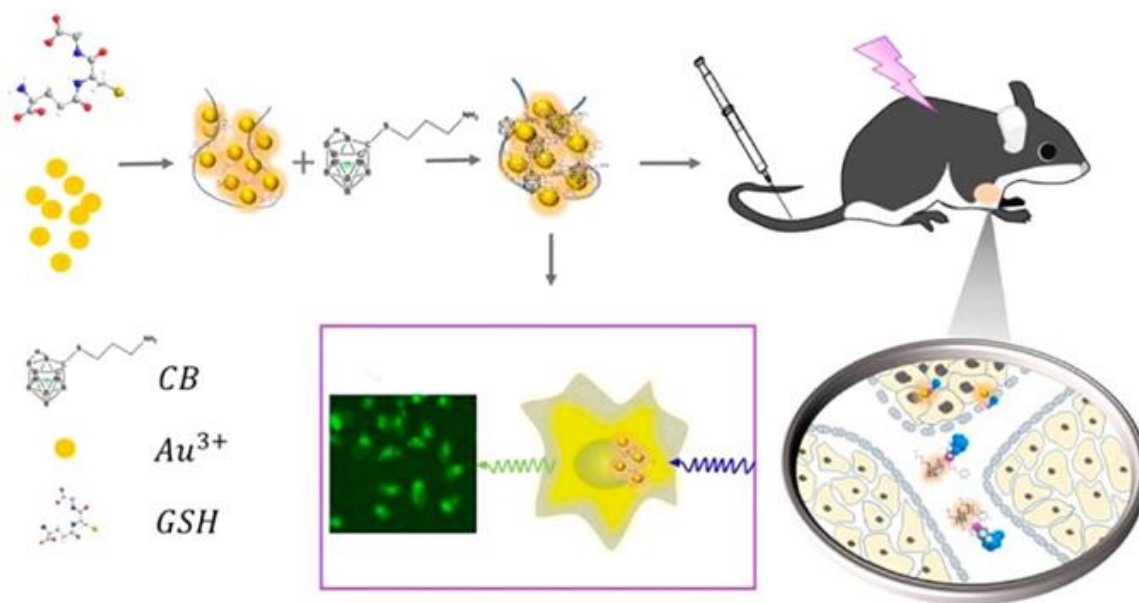


Figure 1.3 Schematic illustration of the bioimaging process for cancer cells using self-assembled AuNCs–CB. Reproduced from ref. ⁸⁵ with permission from American Chemical Society, Copyright 2017.

There are two types of ROS: weakly ROS (wROS) (H_2O_2 , O_2^- , *etc.*) and highly ROS (hROS) ($\cdot\text{OH}$, ONOO^- , OCl^-), responsible for several human diseases like cardiovascular disorders, cancer, Alzheimer's disease and related neurodegenerative diseases.⁸⁸ Mainly hROS are highly capable of oxidizing nucleic acids, proteins, lipids, *etc.* and cause serious damage in living cells.^{89,90} For the quantitative detection of hROS in a cellular environment, a luminescent AuNC-based platform was developed. In this regard, negatively charged GSH–AuNCs was first modified with positively charged thiol quaternary ammonium salt (QA), Tat protein and oligoarginine peptide (R_9). The resulting R_9 –AuNCs showed better cellular uptake and better efficiency in intracellular hROS detection. The experimental study of R_9 –AuNCs in living cells and zebrafish demonstrate

their excellent biocompatibility with long-term imaging both *in vitro* and *in vivo*.⁹¹

In a recent study, Au NCs stabilized using zwitterionic molecules (ZwMe) were explored as imaging agents in subcutaneous (s.c.) and orthotopic U87MG glioblastoma-bearing mice using advanced multimodal imaging techniques and the results were compared to well-defined Au₂₅GSH₁₈.⁹² In another study, red luminescent AuNCs were developed using a low cost, biocompatible, biodegradable, and nonallergenic plant protein namely, pea protein isolate (PPI). It was demonstrated that the AuNCs–PPI composites were readily self-assembled using a simple dialyzing process. When these AuNCs–PPI composites were successfully coated with red blood cell (RBC) membranes, the resulting hybrid materials, namely AuNCs–PPI@RBC, showed a long blood circulation lifetime. As a result, the AuNCs–PPI@RBC also showed *in vivo* targeting of the tumor site with an excellent imaging capability.⁹³

An innovative FRET-based fluorescent quenching method followed by reappearance of fluorescence in the presence of tumor markers was proposed for the simultaneous detection of multiple tumor markers including alpha-fetoprotein (AFP) and carcinoembryonic antigen (CEA). Two different DNA sequences namely, Probe A and Probe C-templated AgNCs (defined as A-AgNCs and C-AgNCs) respectively were prepared and then blended with polydopamine nanosphere (PDAN) to form PDAN@AgNCs nanocomposites, which is fluorescence inactive. However, in the presence of target tumor markers AFP and CEA, the AgNCs were released from PDAN and formed fluorescence-active complexes with the target molecules. This approach provides a new way to analyze multiple tumor markers for the early diagnosis of cancers.⁹⁴

Anterior gradient protein 2 homolog (AGR) is a potential tumor biomarker responsible for tissue development and regeneration. Therefore, the detection of AGR is an urgent requirement to suppress the cancer cell growth. However, intracellular detection of AGR is rarely reported. Recently, modified AGR aptamer (MA) with a sequence of 50 bases 5'-CGG GTG GGA GTT GTG GGG GGG GGT GGG AGG GTT TTTT CCC CCC CCC CCC-3' was used as a template for AgNCs synthesis. The MA@AgNCs nanocomposite exhibited an enhanced PL peak at 565 nm,

with a high quantum yield (QY = 87.43%), excellent stability (PL intensity retains for weeks) and good thermostability, making it a good candidate in the field of protein tracking, cell imaging and cancer diagnosis. Interestingly, these MA@AgNCs were used for the detection of AGR in breast cancer (MCF-7) cells.⁹⁵ Green emitting luminescent AgNCs (CSH-AgNCs) were also synthesized using a peptide extracted from the C terminal of the heavy chain of silk fibroin (CSH) *via* a one-pot, green synthesis method. The stable and bright luminescent CSH-AgNCs were effectively applied for cell imaging in murine preosteoblast MC3T3-E1 cells.⁹⁶ In another study, water soluble, highly green luminescent CuNCs with exceptionally high quantum yield (QY = 44.67%) were synthesized using poly(vinyl pyrrolidone) (PVP) as a template and ascorbic acid (AA) as a mild reducing agent. The strong green luminescence with large stokes shift, tolerance toward high ionic strength, antioxidation properties, good photo-stability and biocompatible nature of the prepared CuNCs@PVP probe was explored in cell imaging, environmental monitoring and human security. From experimental studies it was shown that CuNCs@PVP selectively responded during living cell imaging of human monocytic leukemia cells (THP-1 macrophages) and had good selectivity for the detection of trinitrophenol (TNP) over other nitro compounds. TNP can not only easily contaminate soil and groundwater but is also used in explosives. Thus, the quantitative detection of TNP is very essential for the betterment of human society. CuNCs@PVP nanocomposites were highly beneficial for solving the above two problems of environmental and human security by detecting TNP quantitatively.⁹⁷ Another interesting nanomaterial, radiolabeled ⁶⁴Cu-CuNCs loaded with temozolomide (TMZ) was synthesized and subsequently used for glioblastoma multiforme imaging and therapy.⁹⁸ A nanodrug containing blue-emitting transferrin (Tf)-templated CuNCs (Tf-Cu NCs) and doxorubicin (Dox) as a hydrophobic drug (abbreviated as Tf-CuNC-Dox-NPs) were developed for the targeted delivery of the anticancer drug Dox to cancer cells. FRET from the donor *i.e.*, blue-emitting Tf-CuNCs to the acceptor *i.e.*, Dox led to the enhancement of red emission of Dox. Interestingly, the blue emission of Tf-CuNCs was further recovered in the cytoplasm of transferrin receptor (TfR) overexpressed cancer cells and gradually released Dox into the nucleus. The

therapeutic efficacy of the nanodrug system was also examined on tumor-bearing Dalton's lymphoma ascites (DLA) cells of mice.⁹⁹ AIE-triggered luminescent CuNCs were synthesized in the presence of cysteine and chitosan, which revealed red and green PL at pH 4.5 and pH 7.4, respectively. Time-dependent live cell confocal microscopy studies clearly indicated an intracellular AIE phenomenon featured by MCF-7 cells at pH 7.4 that lead to bright green emission and a higher AIE efficacy than that of the HEK-293 cell line. Henceforth, the AIE feature of the pH stimuli-responsive CuNC provides a new basis for the differentiating of cell lines MCF-7 and HEK-293 based on their AIE kinetic rate differences.¹⁰⁰

1.2.6 Detection of Bacteria

The requirements of rapid bacterial detection and identification screening are crucial for environmental monitoring and human health maintenance. A novel strategy was developed for the rapid detection of *Escherichia coli* (*E. coli*) by employing an on–off–on-based BSA-stabilized luminescent AuNC. The PL of the AuNCs was quenched by the Cu^{2+} ions however, quickly recovered in the presence of *E. coli* bacteria, as Cu^{2+} quickly removed from cluster surface and simultaneously reduced by *E. coli* through copper-binding and redox pathways. Based on this absolute bacteria-responsive PL recovery phenomenon, a water sample containing trace amounts of pathogenic *E. coli* bacteria (~ 100 CFU per mL) was successfully detected within 0.5 h. Hence the rapid detection potential of *E. coli* bacteria using the luminescent AuNCs could be applicable in environmental monitoring and clinical diagnosis.¹⁰¹ Gram-positive pathogenic bacteria, namely *Listeria monocytogenes* (*L. monocytogenes*), is a considerable threat to humans as it causes listeriosis and meningitis diseases. A biosensor assay for the detection of *L. monocytogenes* was developed by immobilizing an antimicrobial peptide leucocin A on a glass surface followed by the *in situ* growth of 3-mercaptopropionic acid (MPA)-protected AuNCs. The biosensor assay was successfully tested on *L. monocytogenes* contaminated spiked milk samples. It was observed that the PL of the NCs was significantly enhanced in the case of contaminated sample as compared to the milk alone.¹⁰² Another novel nanoplatform (Au–BSA–antiSAIgG–PS) was developed from highly fluorescent BSA-protected AuNCs

functionalized with human antistaphylococcal immunoglobulin (antiSAIgG) and a photodynamic (PD) dye PhotosensTM (PS) for the selective detection and killing of the pathogenic bacteria methicillin-sensitive *Staphylococcus aureus* (*S. aureus*, MSSA) and methicillin-resistant *S. aureus* (MRSA). The Au–BSA–antiSAIgG–PS complex displayed three main theranostic modalities: (i) bio-specific detection by antiSAIgG targeting, (ii) eminent luminescence by Au–BSA NCs with high quantum yields (QY = ~14%) and (iii) PD inactivation due to the photosensitizer PhotosensTM. Both types of bacteria (MSSA and MRSA) were effectively destroyed upon PD treatment with the synthesized complex under 660 nm light irradiation.¹⁰³ Recently, CS-functionalized luminescent AuNCs, which have peroxidase-like properties, were prepared using UV irradiation. Three types of bacteria were chosen as model bacteria to investigate the sensing selectivity of the NCs. From the colorimetric assay, it was observed that *S. aureus* can be easily differentiated from *E. coli* and *Bacillus subtilis*. The peroxidase-like AuNC–chitosan composite detected *S. aureus* as low as 4×10^2 CFU per mL and *Staphylococcal enterotoxin B* as low as 1.0×10^{-12} g mL⁻¹ for naked-eye readout. Therefore, such colorimetric strategies could be a viable alternative to the conventional enzyme-linked immunosorbent assay method.¹⁰⁴

Highly luminescent, water-soluble dihydrolipoic acid (DHLLA)-protected AgNCs (DHLLA–AgNCs) were impregnated within agarose hydrogel. The hydrogel, with a high loading capacity and low background signal, was used to monitor pH over a wide range from 4.0–8.0. The PL of the hydrogel completely disappeared below pH = 5, which again reappeared with increasing pH. Based on this “off–on” signal switch, the change of pH levels during metabolic activity of some microorganisms could be monitored in the growth culture medium. To demonstrate the practicability of the AgNCs impregnated hydrogel, different concentrations of *E. coli* were spread on pH-sensitive agarose Luria–Bertani (LB) medium hydrogel plates. It was observed that red luminescent hydrogels reducing their intensity as the gradual growth and metabolism of *E. coli* progressed, significantly acidifying the plate. It was also anticipated that the prepared hydrogels could be able to monitor different species of bacteria effectively.¹⁰⁶

Recently, a AgNC-based fluorescent assay was developed for the detection of bacteria by integrating DNA-templated fluorescent AgNCs with an MNP–DNAzyme–AChE (MDA) complex, which was composed of three materials: (i) magnetic nanoparticles (MNP) as the separation unit, (ii) DNAzyme as the bacteria-specific recognition unit and (iii) acetylcholinesterase (AChE) as the enzyme unit. In that assay, the pathogenic bacteria *E. coli* could selectively target the MDA complex through bacteria-specific recognition units *i.e.*, DNAzyme.¹⁰⁵ The proposed sensing mechanism is been illustrated in [Figure 1.4](#). In the presence of bacteria, the DNAzyme part is cleaved into fragments and following magnetic separation, the PL of the AgNCs is restored. An analytical method was developed for the rapid detection of the notorious *Acinetobacter baumannii* (*A. baumannii*) pathogen from saliva using an alteration of the PL behavior of bimetallic GSH–AuAgNCs. The strong PL of the bimetallic NCs was selectively quenched by *A. baumannii* due to cluster agglomeration. It was envisaged that the rapid detection phenomenon of GSH–AuAgNCs toward specific bacteria might allow application in clinical diagnosis.¹⁰⁷ The enzyme micrococcal nuclease (MNase) is the extracellular nuclease of *S. aureus* that degrades the nucleic acid. In this context, a passive detection strategy was developed for the detection of MNase level, which estimated the pathogenicity of *S. aureus*. For this study, double stranded DNA (dsDNA) was used as the luminescent probe. The AT-rich dsDNA with a 3' protruding termini was chosen due to its high-selectivity toward both MNase and CuNCs. The results revealed that the bright yellow fluorescent long chain AT-rich dsDNA-templated CuNCs became nonfluorescent in the presence of MNase, as the enzyme MNase degrades the long, AT-rich dsDNA into mono or short oligonucleotide fragments. The proposed analytical method manifested a low LOD and high selectivity for MNase secreted by *S. aureus* and thus efficiently identified *S. aureus*.^{108,109}

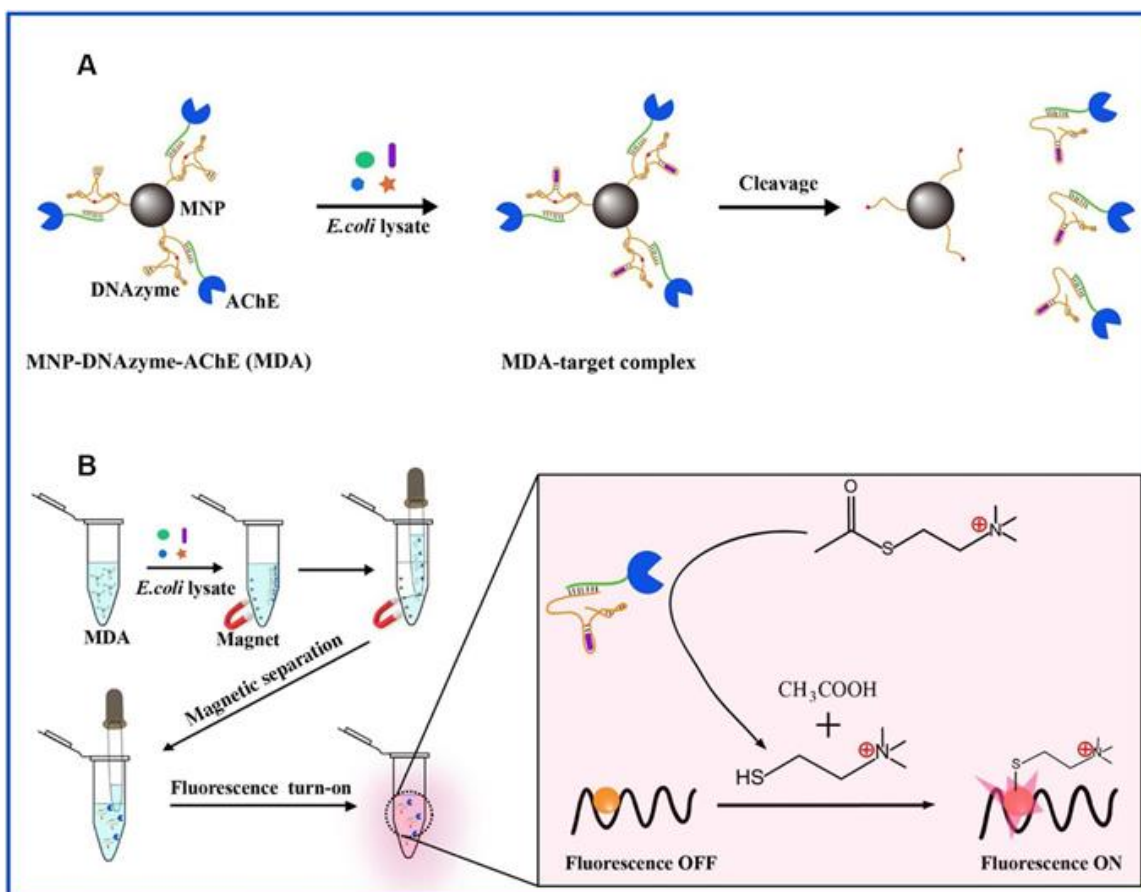


Figure 1.4 Schematic representation of DNA-templated fluorescent AgNC-based sensing system for pathogenic bacterial detection integrated with an MNP-DNAzyme-AChE complex. Reproduced from ref. ¹⁰⁵ with permission from Elsevier, Copyright 2018.

1.3 MNC-based Electrochemical Biosensors

It is now well-established that the redox properties of MNCs can be tuned by their size, shape and composition, making them an efficient electron transfer mediator for catalysts in the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Although electro-catalysis reaction for CO oxidation and oxygen reduction in fuel cells have been widely examined using platinum metal and platinum-based alloys, the slow reaction dynamics, high cost and limited supply of platinum compelled researchers to find an alternative material. Though the bulk gold metal as an alternative to platinum cannot satisfy the

expected catalytic efficiency, gold in the form of NPs showed unusual catalytic activity due to its high fraction of surface area. AuNCs, being ultra-small in size (≤ 2 nm), have even higher surface area than their larger counterparts (*i.e.*, NPs) and are therefore used extensively as electrocatalysts. Even in this confined dimension, AuNCs showed size-dependent electrocatalytic activity. To understand the size dependency, a series of AuNCs (Au_{11} , Au_{25} , Au_{55} and Au_{140}) with core sizes ranging from 0.8 to 1.7 nm (in diameter) were prepared using different types of phosphine and thiol ligands and oxygen electro-reduction was carried out. The electrocatalytic activity in oxygen reduction was found to be enhanced when the core size reduced from Au_{140} to Au_{11} .

Recently, several well-defined $\text{Au}_n(\text{SR})_m$ and related alloy NCs were tested as model catalysts for monitoring HER, OER, and ORR electrochemical reactions. Investigation of the catalytic activity of $\text{Au}_n(\text{SR})_m$ was carried out by synthesizing series of NCs with respect to different variables such as number of metal atoms, ligand functional groups, heteroatom species, charge state of cluster. To demonstrate the dependence of catalytic activity, the NCs were synthesized and tested as follows, (i) based on the number of metal atoms: $[\text{Au}_{25}(\text{PET})_{18}]^0$, $[\text{Au}_{38}(\text{PET})_{24}]^0$, $[\text{Au}_{130}(\text{PET})_{50}]^0$, $[\text{Au}_{144}(\text{PET})_{60}]^0$, and $[\text{Au}_{329}(\text{PET})_{84}]^0$; ii) based on ligand functional groups: $[\text{Au}_{25}(\text{PET})_{18}]^0$ hexanethiolate (C6T)-protected $[\text{Au}_{25}(\text{C6T})_{18}]^0$, and dodecanethiolate (C12T)-protected $[\text{Au}_{25}(\text{C12T})_{18}]^0$, iii) based on doping of heteroatom species: $[\text{Au}_{20.5}\text{Ag}_{4.5}(\text{PET})_{18}]^0$, $[\text{Au}_{23.7}\text{Cu}_{1.3}(\text{PET})_{18}]^0$, and $[\text{Au}_{24}\text{Pd}(\text{PET})_{18}]^0$ and iv) based on charge state of the cluster: $[\text{Au}_{25}(\text{PET})_{18}]^0$ and $[\text{Au}_{25}(\text{PET})_{18}]^-$. On the basis of the experimental data series, it was found that the catalytic activity increases upon minimizing the number of constituent atoms in the cluster, narrowing the thickness of the ligand layer, and doping using Pd substituents. In particular, $[\text{Au}_{24}\text{Pd}(\text{PET})_{18}]^0$ exhibited high potential in all the three electrochemical reactions (Figure 1.5).¹¹⁰

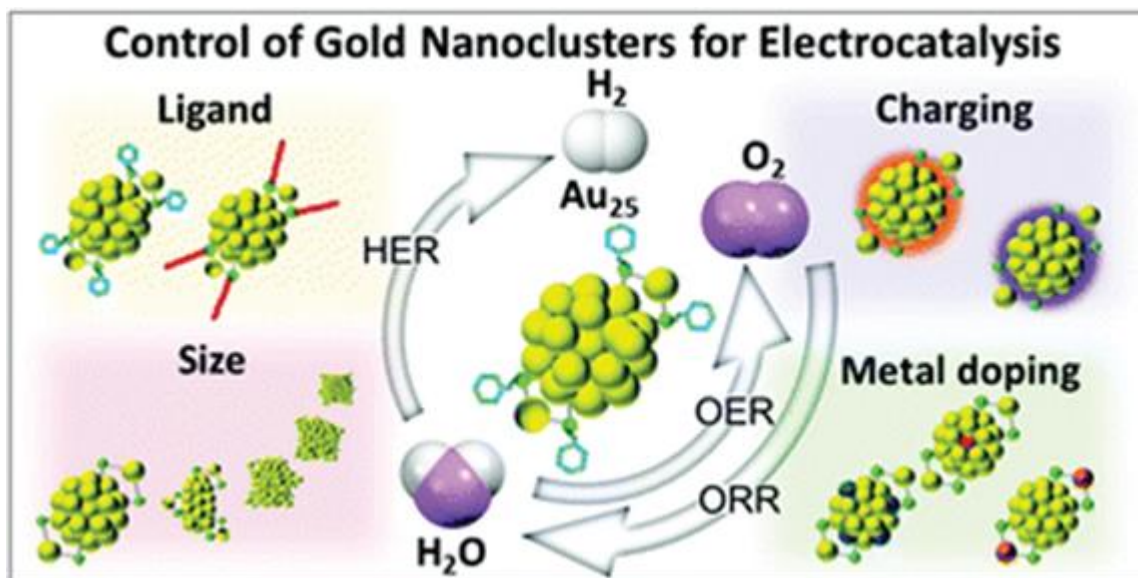


Figure 1.5 Schematics of the different parameters (size, ligand, doping and charge) of AuNCs and the corresponding electrochemical reactions investigated using AuNCs.

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Such types of NCs with strong electrochemical properties have often been explored in electrochemical sensing. The physical phenomenon behind the electrochemical sensing is the transformation of electrochemical information into an analytically useful signal, where a chemical (molecular) recognition system acts as a sensor and a device that converts the chemical response into a signal that can be detected by modern electrical instrumentations. Electrochemical measurement is a powerful analytical method that has been used for a wide range of applications including detecting faint bioelectricity and evaluating novel electrocatalysts. Numerous approaches such as electrostatic interaction,¹¹¹ electrochemical deposition¹¹² and mixing with components in a composite electrode matrix¹¹³ have been applied to deposit MNCs on electrode surfaces. The unique electronic and/or electrochemical properties of MNCs offer an alternative platform for the optical sensing of small molecules, enzymes, oligonucleotides and others. In the following sections, we will summarize the use of MNCs for electrochemical and electro-catalytic sensing.

1.3.1 Detection of Small Biomolecules

Phosphate-containing metabolites such as inorganic pyrophosphate (PPi), adenosine triphosphate (ATP), and adenosine diphosphate (ADP) are essential biomarkers for many diseases. By using the peroxidase-like catalytic properties of histidine-protected AuNCs (His–AuNCs), a new method has been developed for the sensing of phosphate-containing metabolites and monitoring of ALP activity. For the experiment, peroxidase substrates 3,3',5,5'-tetramethylbenzidine (TMB), 2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid ammonium salt) (ABTS), and *o*-phenylenediamine (OPD) were chosen to characterize the peroxidase-like catalytic activity of His–AuNCs. In the presence of H₂O₂, His–AuNCs catalyzed the oxidation of the above three colorless peroxidases to the corresponding products with blue, bluish-green, and yellow colors with distinct absorption maxima at ~652, ~416, and ~448 nm, respectively. Among the three peroxidases, His – AuNCs showed the highest catalytic activity toward TMB over a broad pH range (2.0–6.0) and a wide temperature range (15–45 °C). The His–AuNCs show peroxidase-like properties due to the formation of superoxide radicals (O₂^{·-}) and their ability to transfer electrons from TMB to H₂O₂. The phosphate-containing metabolites (PPi, ATP, ADP) severely hamper the peroxidase-like activity of His–AuNCs by preventing the generation of O₂^{·-} and electron transfer processes. ALP plays a vital role in restoring the inhibition process through hydrolysis of the phosphate-containing metabolites. This is how the novel nanomaterial (His–AuNCs) selectively senses the metabolites and ALP.¹¹⁴

In addition, a biomimetic mineralization method was introduced for the sensing of arginine (Arg) enantiomers using BSA-protected AuNCs (BSA–AuNCs)-based thin film glass nanopores. First, the inner wall of the glass nanopore was coated with positively charged poly(ethylene imine) (PEI) followed by electrostatic deposition of BSA, which not only helps to reduce Au(III) to Au(0) and as a capping ligand to form BSA–AuNCs thin film but also shows intense red emission in the film state as well as in solution. The BSA–AuNCs thin film nanopore, with a broad pH range, stability and high salt concentration tolerance, selectively interacts with Arg *via* ion pairing interaction between the guanidinium groups of Arg and the carboxyl groups (–COO⁻) of the BSA surface motif on the Au NCs. Therefore, the BSA–AuNCs film coated nanopore system creates its own identity for the

selective discernment of Arg enantiomers through monitoring of ionic current.¹¹⁵ A new electrochemical aptasensor platform has been successfully developed by embedding AuNCs into two-dimensional zirconium-based metal–organic framework (2D Zr–MOF) nanosheets (abbreviated as 2D AuNCs@521-MOF) for detecting cocaine. The as-synthesized 2D AuNCs@521-MOF consisting of a Zr–MOF with strong bio-affinity; 2D nanosheets with high specific surface area and AuNCs with good electrochemical activity leads to an effective platform for the immobilization of the inorganic phosphate functionalities bearing oligonucleotide molecules (including DNA or aptamer strands) which further facilitate the detection of cocaine.¹¹³

Human serum albumin (HSA), which is a natural carrier of bilirubin, was used to synthesize Au₁₈ nanoclusters (HSA–AuNCs) for the electrochemical detection of free bilirubin in serum samples. Basically, the HSA–AuNCs immobilized indium tin oxide (ITO) plate functions as a bilirubin detector while the AuNCs act as an electron transfer bridge between the ITO electrode plate and the HSA-attached bilirubin molecule, which shows a specific redox peak for bilirubin. To check the importance of AuNCs, an experiment was carried out where only HSA was immobilized on an ITO plate. However, this system was unable to produce any such redox peak for bilirubin. Therefore, the unique HSA–AuNCs-based platform could be considered one of the effective methods for the electrochemical investigation of free bilirubin levels in serum.¹¹⁶

A new type of ionic liquid-based platform was also prepared for the sensing of glucose using redox active, anionic Au₂₅ clusters protected with (3-mercaptopropyl) sulfonate (MPS–Au₂₅) and 1-decyl-3-methylimidazolium (DMIm) cations, possessing both ionic and electronic conductivity. By using the easily film forming capability of the highly viscous ionic liquid DMIm–Au₂₅ on an electrode, an enzyme electrode was prepared by incorporating glucose oxidase (GOx) in DMIm–Au₂₅, which exhibited high glucose binding affinity and fantastic electro-catalytic activity toward glucose oxidation; making DMIm–Au₂₅ a potential material for enzyme-based biosensors.¹¹⁷ Another interesting nanodevice was developed for the electrochemical sensing of glucose using ultra-small

AgNCs. Specifically, *N*-acetyl-L-cysteine (NALC) capped AgNCs $\text{Ag}_6(\text{NALC})_5$ undergo self-assembly into nanowires and long ribbons, followed by a 3D porous network structure in a mixed solvent of water and ethanol, which subsequently leads to enhanced affinity for the selective detection of glucose with high detection sensitivity and low limits of detection.¹¹⁸

Other metal NCs, such as atomically precise $\text{Cu}_6(\text{SG})_3$ NCs loaded on a TiO_2 support, resulted in CuNCs– TiO_2 composites that played a vital role in the electrochemical sensing of glucose.¹¹⁹ Another interesting material namely, mercaptobenzoxazole protected hexanuclear CuNCs or $\text{Cu}_6(\text{C}_7\text{H}_4\text{NOS})_6^-$, had a distorted octahedron structure where two copper atoms at opposite vertices are exposed, suggesting the possibility of cluster-based electrochemical detection of small molecules. Indeed, the $\text{Cu}_6(\text{C}_7\text{H}_4\text{NOS})_6^-$ cluster acted as a non-enzymatic chemical sensor for electrochemical detection of H_2O_2 .¹²⁰

Beyond the conventional MNCs, a hexagonal nickel NCs *i.e.*, $\text{Ni}_6(\text{C}_{12}\text{H}_{25}\text{S})_{12}$ when supported on carbon black, exhibited high electrocatalytic activity for the detection of AA. The sensitivity was much better when compared to its larger counterpart due to its tiny size and high surface area-to-volume ratio. The cluster composite had good sensitivity for the detection of AA with a broad linear range (1–3212 μM) and a low LOD of 0.1 μM .¹²¹ Another example is an electrochemical non-enzymatic nanocomposite based on palladium nanoclusters (PdNCs)-encapsulated electrochemically-activated graphene (EAGr). The PdNCs–EAGr nanocomposite displayed a wide linear range for H_2O_2 reduction from 1.0 to 1100 μM with a low LOD of $0.02 \pm 0.01 \mu\text{M}$ along with the successful determination of H_2O_2 in real sample of human urine.¹²² Similarly, a palladium nanocluster (Pd_{nano})-coated poly(*N*-methylpyrrole) (PMPy) film, abbreviated as PMPy– Pd_{nano} , when electrodeposited on a Pt electrode displayed good electrochemical behavior for the simultaneous determination of dopamine, uric acid and AA. The experimental study on real samples such as detection of dopamine in human serum, uric acid in

human urine and AA in injection samples also showed satisfactory results.¹²³

1.3.2 Detection of Proteins and Enzymes

Many disease states (*e.g.*, cancer) are associated with variations in the concentration of proteins. Therefore, protein detection is of utmost importance in the early diagnosis of diseases and the successful treatment of patients. In Section 1.2.2, we have mentioned how the PL properties of MNCs can be used for the detection of proteins. In this section, how the electrochemical properties of MNCs were successfully applied for the sensitive, convenient and precise detection of proteins will be discussed.

A key example in this regard is the development of a hybrid composite with both AuNCs and AgNPs into a single entity. Here, the photoelectrochemical properties of AuNCs were largely improved by integrating it with Ag@SiO₂ NPs. It was achieved by optimizing the distance between AuNCs and AgNPs by adjusting the thickness of the silica shell in the presence of AA as an electron donor. The hybrid AuNCs–Ag@SiO₂ nanocomposites were finally exploited as photoelectrochemical (PEC) biosensors for the sensitive detection of ALP activity based on generation of electron donors and AA from the catalytic hydrolysis of ascorbic acid phosphate (AAP) by ALP. The photocurrent responses of the AuNCs-based composite improved gradually with increasing ALP activity due to *in situ* generation of more AA.¹²⁴ BSA-protected AuNCs acting as a low potential luminophore were also used for the detection of procalcitonin (PCT) *via* an electrochemiluminescence (ECL) pathway. The BSA–AuNCs showed a low potential anodic ECL signal in a triethylamine (TEA) solution at 0.87 V and a longer signal stabilization time (~ 80 s). Therefore, to increase ECL intensity, the co-reactant Cu₂S snowflakes with high surface area and good conductivity were loaded with the cluster to obtain Cu₂S–AuNCs composites, which not only increased the ECL significantly but also helped in shortening the signal stabilization time to ~ 30 s through the generation of more cationic radicals TEA^{•+}. From the experimental results, it was observed that the ECL intensity of the biosensor increased upon the decrease of PCT concentration and reached a LOD of 2.36

fg mL⁻¹, which is within the allowable range for PCT. This excellent detection sensitivity up to femtogram levels of PCT was also tolerated in human serum samples.¹²⁵

An electrochemical signal amplification strategy was used for the detection of thrombin by cascade catalysis reaction of polyamidoamine dendrimer-templated AuNCs and glucose dehydrogenase (GDH). In particular, AuNCs were immobilized with excess thrombin aptamer (TBA II) and initiator strands (S1) to form AuNCs–TBA II–S1 bioconjugates, and further used for the ultrasensitive detection of thrombin.¹²⁶ Nevertheless, liposome-templated CuNCs (denoted as CNL) trapped upon CdS quantum dots (QDs) were also introduced for the PEC bioanalysis of human cardiac troponin T (cTnT) as a model target. In this case, the external surface of the CNL probes was first labeled with antibodies (represented as Ab₂–CNL) followed by sequential lysis treatments of confined liposomal labels for the release of CuNCs and countless Cu²⁺ ions. The released NCs and ions then interacted with the CdS QDs electrode to generate Cu_xS and blocked the photocurrent generation. As the photocurrent inhibition was associated with the released Cu²⁺ ions from the Cu NCs-loaded liposomal probe, a novel “signal-off” PEC immunoassay was fabricated with high sensitivity. In addition, a supplementary “signal-on” fluorescent detection could also be performed by measuring the luminescence intensity originating from the CuNCs.¹²⁷ Recently, an immunoprobe was developed by immobilizing BSA-stabilized CuNCs (BSA–CuNCs) with antibody labeled PtNPs and was subsequently used for electrochemical sensing of the model analyte prostate-specific antigen (PSA). The detection method was based on a triple signal amplification mechanism where BSA–CuNCs acted as a redox species with a current signal at 0.06 V, PtNPs were used as carriers to immobilize the antibody and enrich the BSA–CuNCs, and finally, the BSA–CuNCs exhibited good AA electrocatalytic detection further enhancing the current response.¹²⁸

1.3.3 Detection of Oligonucleotides

MNC-based techniques offer an alternative platform to the conventional methods of nucleic acid-based detection owing to their excellent

electrochemical properties. Examples of such methods include the detection of the *invA* gene of *Salmonella* using a AgNCs–sDNA–AuNPs nanocomposite biosensor.¹²⁹ *Salmonella* is an important foodborne pathogen, which causes several human foodborne diseases, *i.e.*, diarrhea, fever and abdominal cramps, *etc.* The sensitive detection was attributed to using AgNCs as the origin of the electrochemical signal and AuNPs as a carrier for signal amplification. Thus, the combined properties of the synthesized biosensor make it a potential tool for *Salmonella* detection.

Another important example is the development of a new platform of graphene stabilized AuNCs (GR–AuNCs) modified with a glassy carbon electrode (GCE) and the exonuclease III (Exo III) enzyme for the electrochemical biosensing of HIV DNA. HIV has been one of the most dreadful viruses during the last few decades. Early diagnosis of the HIV gene is thus a great concern to the scientific community. Due to good conductivity and a high specific surface area, GR–AuNCs nanocomposites provide more fixed sites for the cytosine (C)-rich aptamer to bind with Au atoms through Au–N bonds and thus showed a good electrochemical signal. In the presence of the target HIV DNA, the C-rich probe was digested leading to a reduction of signal intensity and further resulted in a signal-off electrochemical biosensor for sensitive detection of HIV DNA with a low LOD of 30 aM.¹³⁰

Based on the surface plasmon-enhanced electrochemiluminescence (SPEECL) phenomenon, a nanocomposite was developed for the detection of microRNA (miRNA-21) using DNA-templated AgNCs (DNA–AgNCs) as ECL emitters and AuNPs as surface plasmon resonance sources. It was observed that the SPEECL intensity depends on the separation distance between AgNCs and AuNPs and the electrodeposition time of AuNPs. After optimizing these factors, the as-prepared composite material responded well in the sensing of miRNA-21 with a broad linear range from 1 aM to 10^4 fM and a low LOD (0.96 aM).¹³¹

Another novel electrochemical biosensor was established by combining three-dimensional dendrimer polyamidoamine (PAMAM)-encapsulated AgNCs (denoted as AgDNCs), DNA-templated AgNCs (denoted as DNA–AgNCs) and probe DNA (pDNA) for the sensing of nucleic acids. Such hybrid pDNA–AgDNCs@DNA–AgNCs conjugates, when combined with

noncanonical lambda exonuclease (λ_{exo})-assisted target recycling (LNTR), were able to successfully detect Epstein–Barr virus (EBV)-related DNA that is responsible for several malignancies such as Hodgkin's disease, Burkitt lymphoma and nasopharyngeal carcinoma.^{132–134} Recently, Hu *et al.* developed a novel electrochemical assay for the label-free detection of terminal deoxynucleotidyl transferase (TdT) activity based on the unique electro-catalytic activity of the TdT-related DNA–AgNCs loaded on a graphene oxide (GO)-modified electrode.¹³⁵ Yang *et al.* demonstrated a label-free and highly sensitive method for the electrochemical detection of miRNA-199a using AgNCs.⁴⁰

Similar to gold and silver, CuNCs also displayed remarkable electrochemical properties that enable them to be applied in many fields such as catalysis, sensing, *etc.* For example, a DNA nanocrane-based CuNCs biosensor platform was developed for the sensitive electrochemical detection of miRNA-155.¹³⁶ This DNA nanocrane was constructed based on binding-induced DNA assembly as the manipulator and a tetrahedral DNA nanostructure (TDN) as the base. It has the capability of binding specifically to the target microRNA (miRNA-155) to trigger the assembly of DNA components to produce enormous amounts of AT-rich double-stranded DNA (dsDNA) on the vertex of TDN. It was evidenced that TDN could not only increase the probe spacing to generate more CuNCs but also supported a reduction in the collision probability of excited-state species CuNCs* to retain remarkable ECL emission, which is essential for an effective biosensor.¹³⁶

In addition to the many reports on nucleic acid-templated CuNCs synthesis based on ssDNA or DNA–DNA homoduplexes, DNA–RNA heteroduplex-templated CuNCs were explored for the electro-catalytic sensing and quantification of miRNA.¹³⁷ In this study, thiolated DNAs were first self-assembled on the surface of a gold electrode through Au–S bonds. Then, in the presence of the target miRNA, the DNA–miRNA heteroduplexes were formed through hybridization between DNA and miRNA. Finally, using DNA–miRNA heteroduplex templates, AA as reducing agent and Cu^{2+} as a precursor, CuNCs were synthesized on the electrode surface. The synthesized surface-tethered CuNCs had a high capability to catalyze H_2O_2 reduction, resulting amplified electrochemical

signals leading to the selective detection of miRNA. With an increase of miRNA concentration, more DNA–miRNA heteroduplex-templated CuNCs were formed on the electrode surface causing more reduction of H_2O_2 by CuNCs, leading to larger current increments in the electrochemical signal. The experiment revealed that the biosensor was suitable for the detection of miRNA in biological samples with a LOD up to 8.2 fM with good reproducibility of the electrodes.

1.4 Conclusions

In summary, the field of MNCs has matured over the course of the last two decades of research both in terms of synthesis and technological applications. At present, research on MNCs is developing in many directions particularly for emerging applications such as sensing and imaging. The unique physicochemical properties at confined dimensions (less than 2 nm scale) such as HOMO–LUMO transitions, strong PL, high electrochemical performance together with the core–shell like structure of MNCs, makes it possible for them to selectively interact with various types of specific analytes. The selectivity and specificity toward a particular analyte depend not only on the structure and composition of the MNCs but also their surrounding environment. For PL-based detection, both quenching and enhancement strategies have been explored. A recent emerging trend is the detection of various diseases and bacteria by means of the optical and catalytic properties of the MNCs. These properties depend on the size, structure and composition of the MNCs. Tailoring the size and structure provide further advantages in improving their properties and thus in their performance in biosensing applications.

MNC-based biosensing application strategies, however, also represent a formidable challenge. One potential challenge is the fabrication of highly luminescent MNCs. The introduction of the AIE phenomenon to the field of MNCs has improved the luminescence efficiency however, the number of AIE-type MNCs is currently limited. Furthermore, the number of studies focusing on electrochemical sensing of analytes is much lower than that of PL-based strategies. It would be of a great value to create a library of highly luminescent MNCs so that one can take advantage of their rich functionality

and high versatility in developing new strategies for the detection of various analytes. In particular, more focus should be given to the detection of various diseases and infectious bacteria, as well as understanding the sensing mechanism by experimental and computational methods. The field of MNCs is rapidly growing and the rising popularity of this field certainly promises the construction of more advanced strategies for detecting a wide variety of analytes by means of their unique nanoscale properties.

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Chapter 2

Label-free Surface-enhanced Raman Spectroscopy for Water Pollutant Analysis

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2.1 Introduction

A side-effect accompanying global population and economy growth is the explosive production and use of synthetic chemicals, which generally cannot be completely removed from natural and engineered water systems and can possibly make their way into drinking water supplies.^{1–3} For example, synthetic chemicals for household use, including personal care products, disinfectants, and caffeine, are directly discharged into municipal wastewater treatment plants (WWTPs). The portions of chemicals that “survive” the WWTPs will be subsequently released back into the natural water bodies *via* WWTP effluents ([Figure 2.1](#)).^{4–6} Similarly, toxic chemicals released from solid wastes in landfill sites, such as poly- and perfluoroalkyl substances (PFAS), may be carried to WWTPs *via* landfill

leachate. Due to their extreme recalcitrant and “non-sticky” nature, PFAS that are discharged into natural waters are likely to travel long distances and eventually enter drinking water sources.⁷ Pesticides, fertilizers, and antibiotics are extensively used in agricultural sector to improve the crop and livestock production. These chemicals can be washed into natural water bodies *via* agricultural runoff and raise concerns for drinking water safety in places that are close to agricultural fields.⁸ In addition, the inefficient treatment of industrial wastewater streams (*e.g.*, organic halogens generated from the bleaching step in the pulp and paper industry), the unintentional discharge of recalcitrant pollutants (*e.g.*, aqueous film-forming foam) from military training, and accidental leakage from chemical storage tanks (*e.g.*, gas stations) can also become point sources of organic micropollutants in water. The extensive discharge of synthetic chemicals into natural water environments and even drinking water sources has raised concerns related to chronic human exposure and the long-term health impacts.

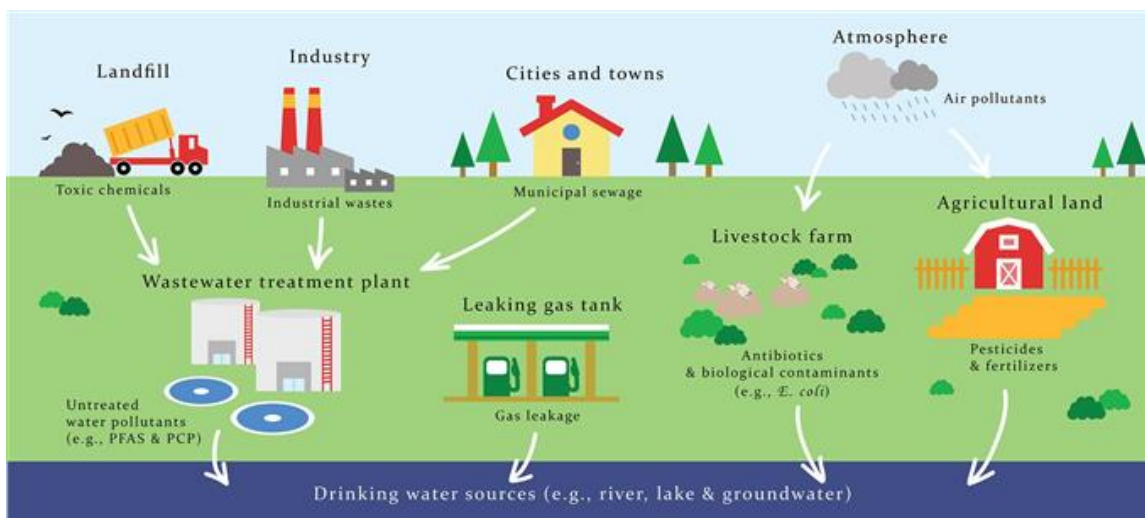


Figure 2.1 Schematic illustration of the generation of water pollutants and their transport routes to drinking water sources.

In addition to synthetic chemicals, biotoxins and pathogens have also been frequently detected in drinking water supplies and are recognized as threats to drinking water safety. For example, outbreaks of harmful algal blooms in drinking water sources (*e.g.*, the Taihu Lake in China) result in a

substantially increased level of microcystins (known as hepatotoxins), which make the water unsafe to drink and lead to large-scale drinking water shut down.⁹ Waterborne pathogens, including bacteria (e.g., *Escherichia coli* and *Legionella pneumophila*), viruses (e.g., adenovirus and norovirus), and protozoa (e.g., *Cryptosporidium* and *Giardia*), are also known as big threats to drinking water safety.¹⁰ Pathogens in drinking water sources usually come from fecal contamination. For example, manure can be a potential source of high levels of bacteria detected in private wells near dairy farms (Figure 2.1). The drinking water treatment plant is the last barrier to prevent waterborne pathogens from being ingested by people. Although disinfection technologies can efficiently remove pathogens and protect drinking water safety, the dramatic increase of pathogen concentrations in drinking water sources can possibly surpass the treatment capacity and result in a public health crisis, such as the 1993 Milwaukee cryptosporidiosis outbreak. For the early detection of organic micropollutant, biotoxin, and pathogen pollution and preventing human exposure, regular monitoring of drinking water quality is urgent and important.

Unfortunately, traditional technologies for waterborne pollutant detection are time consuming and expensive and thus are unsuitable for large-scale and high-frequency drinking water monitoring. For organic micropollutant detection, we are predominantly relying on delicate analytical instruments, such as liquid chromatography–tandem mass spectrometry (LC–MS/MS). The analysis needs to be carried out by well-trained personnel and usually requires laborious sample pre-treatment steps, including filtration, solid-phase extraction, elution, and rotary evaporation. Therefore, the analysis of organic micropollutants, which requires additional efforts for water sample collection and transport, cannot usually be performed in the field. Similarly, the standard analytical methods for waterborne pathogens, such as plate counting, immunoassay, and polymerase chain reaction (PCR), are also time consuming and expensive. Therefore, these methods are unlikely to meet the growing demand for high-frequency drinking water monitoring and detect a pollution incident in a timely manner. It thus becomes an urgent task to develop rapid and inexpensive technologies for waterborne pollutant analysis.

Surface-enhanced Raman spectroscopy (SERS) is an emerging tool for water pollutant detection. SERS was first observed in 1974 from the substantially enhanced Raman intensities of pyridine molecules adsorbed on roughened silver electrodes¹¹ and then explained as the mechanisms that we are familiar with today by Jeanmaire and Van Duyne and Albrecht and Creighton in 1977.^{12,13} Since then and especially after 1997 when single molecule detection was reported, SERS has gradually evolved into an ultrasensitive and versatile analytical tool owing to the advancement of nanotechnology and plasmonics. In addition to its high sensitivity, SERS provides abundant information of bonding vibration, which is known as the “fingerprint” of a molecule and can be used to differentiate chemicals with similar structures. Raman bands are much narrower than fluorescence bands, making SERS a powerful tool for multiplexed analysis. SERS analysis does not require complex sample pre-treatment and well-trained personnel and can be completed within seconds. Because Raman spectrometers are less expensive and smaller than LC–MS/MS instruments, SERS is more promising for onsite pollutant analysis. Because of the above-mentioned advantages, SERS is competitive for the rapid, inexpensive, and onsite analysis of waterborne chemical and pathogenic pollutants.

The objective of this book chapter is to summarize research progress on the applications of SERS for waterborne pollutant analysis from the perspective of an environmental chemist. This chapter is written in a general and qualitative way aiming to serve the broad audience who do not have much knowledge about SERS but would like to apply it for environmental analysis. The focus will be placed on the label-free SERS analytical paradigm, *i.e.*, the Raman spectra collected reflect the chemical structures of the target analytes. For this reason, the targeted pollutants covered herein are organic molecules and pathogens rather than inorganic pollutants (*e.g.*, heavy metal ions) that cannot generate strong Raman scatterings and are usually detected using the indirect labeled SERS paradigm. Following this “introduction” section, we will start to introduce the basic principles of SERS, the differences between labeled and label-free SERS analytical paradigms, and the SERS substrates. Then we will move on to discuss examples of the label-free SERS detection of waterborne

pollutants that are organized based on the type of analyte targeted. Finally, we will talk about the opportunities and challenges that SERS applications are facing for water analysis.

2.2 Principles of SERS

SERS originates from the significantly enhanced local electromagnetic field in the nanoscale proximity from plasmonic nanoparticle (PNP) surfaces upon incident light irradiation.¹⁴ The appropriate dielectric function (high reflection and low absorption) and size (10–100 nm) of gold and silver nanoparticles (AuNPs and AgNPs) endow them with unique interactions with visible light, *i.e.*, their abundant conductive electrons collectively oscillate in response to the changing electric field of the incoming light. At resonant frequency (within the visible range), this unique optical phenomenon, known as localized surface plasmon resonance (LSPR), results in an extraordinarily high light extinction and a substantially enhanced local field. The high visible light extinction of the PNPs gives rise to vivid colors under ambient light, which vary as a function of the metallic identity, size, shape, and aggregation state of the PNPs. The word “localized” indicates that the field is highly localized at the PNP/dielectric interfaces, in contrast to the propagating field in a thin metallic film, which means that SERS signals predominantly come from the regions that are close to PNP surfaces. If two PNPs are very close to each other, the highest electromagnetic field will form within the (sub)nanometer-scale gap between them. These regions give rise to the highest Raman signal enhancement and thus are called SERS hot spots.

As elaboratively explained in many books and literature reports,¹⁵ Raman scattering is described as the loss or gain of energy of the scattered photon compared with the incident one. The energy differences correspond to the transition energy of a molecule from its ground state to excited vibrational modes and are reflected as discrete bands in the Raman spectra. Therefore, Raman spectroscopy is a valuable tool to characterize the chemical structure of a molecule. However, normal Raman spectroscopy cannot be used for the detection of trace organic micropollutants in water because of the low Raman cross sections of common water pollutants. This

disadvantage can be overcome by SERS. When the target analytes are located within nanoscale proximity from PNP surfaces, the excitation and radiation of their Raman dipole are both enhanced by the local field because of LSPR, which gives rise to several orders of magnitude of Raman intensity enhancements. Particularly, when a molecule is located within the SERS hot spot, the enhancement factor (EF, *i.e.*, the ratio of Raman intensities of a molecule with and without PNPs) can be greater than 10^8 and enable single molecule detection. The SERS enhancement mechanism as a result of local field enhancement is called electromagnetic enhancement. In addition, there is a minor mechanism, known as chemical enhancement, that also plays a role in SERS enhancement when there is charge transfer between the target analytes and PNPs. The EF value is an important parameter used to evaluate the performance of a SERS analysis, which can be acquired experimentally by measuring the Raman intensities of target analytes with and without PNPs and estimating the number of molecules that contribute to the Raman intensities in these two scenarios.

2.3 Labeled and Label-free SERS

From the perspectives of an analytical chemist who applies SERS for environmental analysis, SERS can be categorized into two paradigms: labeled and label-free SERS (Figure 2.2). Labeled SERS requires the functionalization of the PNP surfaces with a Raman reporter. The reporter exhibits extremely high Raman cross sections (*e.g.*, dye molecules), which is usually attributed to the resonant effect as a result of the overlap between the incident light energy and its electronic state transition energy. Generally, the Raman reporter-functionalized PNPs are functionalized with recognition elements that can specifically bind to the analytes,¹⁶ which is known as a SERS tag. SERS tags are usually small (< 100 nm) core-shell nanoparticles or nanoparticle aggregates (Figure 2.2a). For a typical sandwich-like assay using a SERS tag, we can quantify the target analytes based on the intensity of the Raman reporter. While in other situations, we quantify the target analytes based on the changes of the Raman reporter spectrum induced by the interactions between them. The labeled SERS analytical paradigm has been used for the detection of pH,¹⁷ biomolecules,¹⁶ protozoa,¹⁸ and so on.

Labeled SERS is an indirect method, *i.e.*, it measures the SERS signals from the Raman reporter instead of the target analyte. Therefore, its selectivity is merely based on the selectivity of the recognition elements.

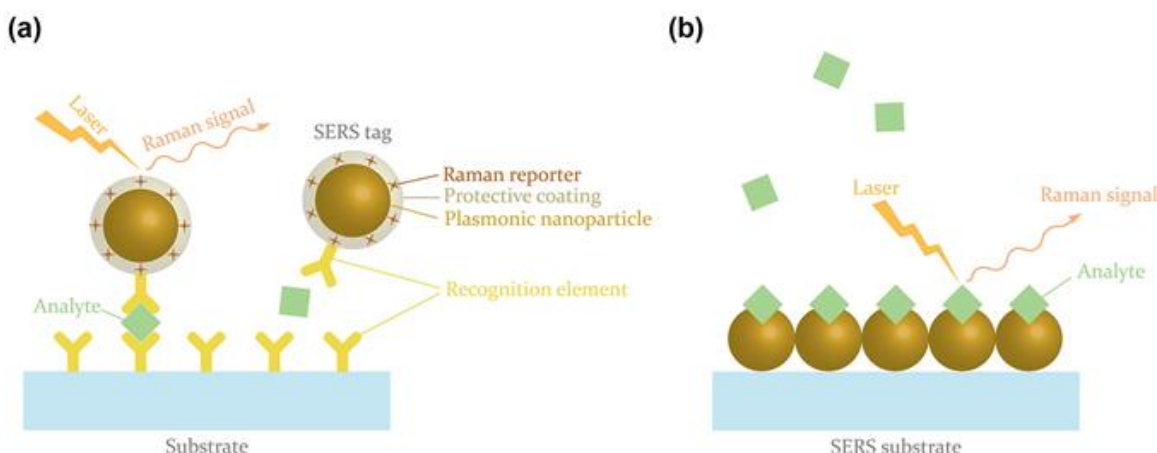


Figure 2.2 Schematic illustration of the working principles of labeled and label-free SERS for target analyte detection.

In this chapter, we will focus on the other analytical paradigm: label-free SERS. Label-free SERS is a direct method, *i.e.*, we directly collect the Raman spectrum of the target analyte that is located on PNP surfaces instead of the Raman reporter (Figure 2.2b). Compared with the SERS tags, label-free SERS analysis will not be limited by the existing recognition elements and can be applied to a broad range of analytes. It is also easier to perform because it does not need the surface functionalization and washing steps. Because the Raman cross sections of common environmental pollutants are much lower than the model Raman reporters, the sensitivity of label-free SERS is usually lower than labeled SERS. However, it can mitigate false positive and negative results that are usually unavoidable in the labeled SERS analytical paradigm as it provides fingerprint Raman spectra of the target analytes. In addition, label-free SERS offers additional details on the orientation of the target analytes on the PNP surfaces and can also be used for real-time monitoring of the chemical structure variation of the target analytes under external stimuli. Furthermore, label-free SERS has the capacity for the simultaneous detection of various target analytes and can even be used to monitor the quality of water with unknown

compositions. Because of the advantages mentioned above, the following sections of this book chapter will be exclusively focused on label-free SERS analysis for water pollutants.

2.4 SERS Substrates

The key for a sensitive label-free SERS analysis is to assemble PNPs into a structure (*i.e.*, SERS substrates) with optimized local electric field enhancement. The schematics of common SERS substrates are shown in [Figure 2.3](#), among which the colloidal AuNPs and AgNPs are the most frequently used SERS substrates because they are easy to synthesize. The aggregation of AuNPs and AgNPs generates SERS hot spots that are sensitive enough for single molecule detection. However, the kinetics of aggregation (*i.e.*, hot spot formation) are very challenging to control, thus making the colloidal substrates unsuitable for quantitative analysis. To overcome this disadvantage, instead of relying on the hot spots formed by PNP aggregation, single nanoparticles carrying a large number of pre-formed hot spots have been synthesized.¹⁹ Etching out the Ag portion from the Ag–Au alloy results in porous AuNPs with a large density of SERS hot spots that are resonant with infrared light. The porous AuNPs can be coated with a thin, porous silica layer to endow them colloidal stability and allow target analytes to diffuse in.¹⁹ This non-aggregating colloidal SERS substrate is expected to show improved quantitative performance but is still difficult to handle and transport because of its large weight and volume.

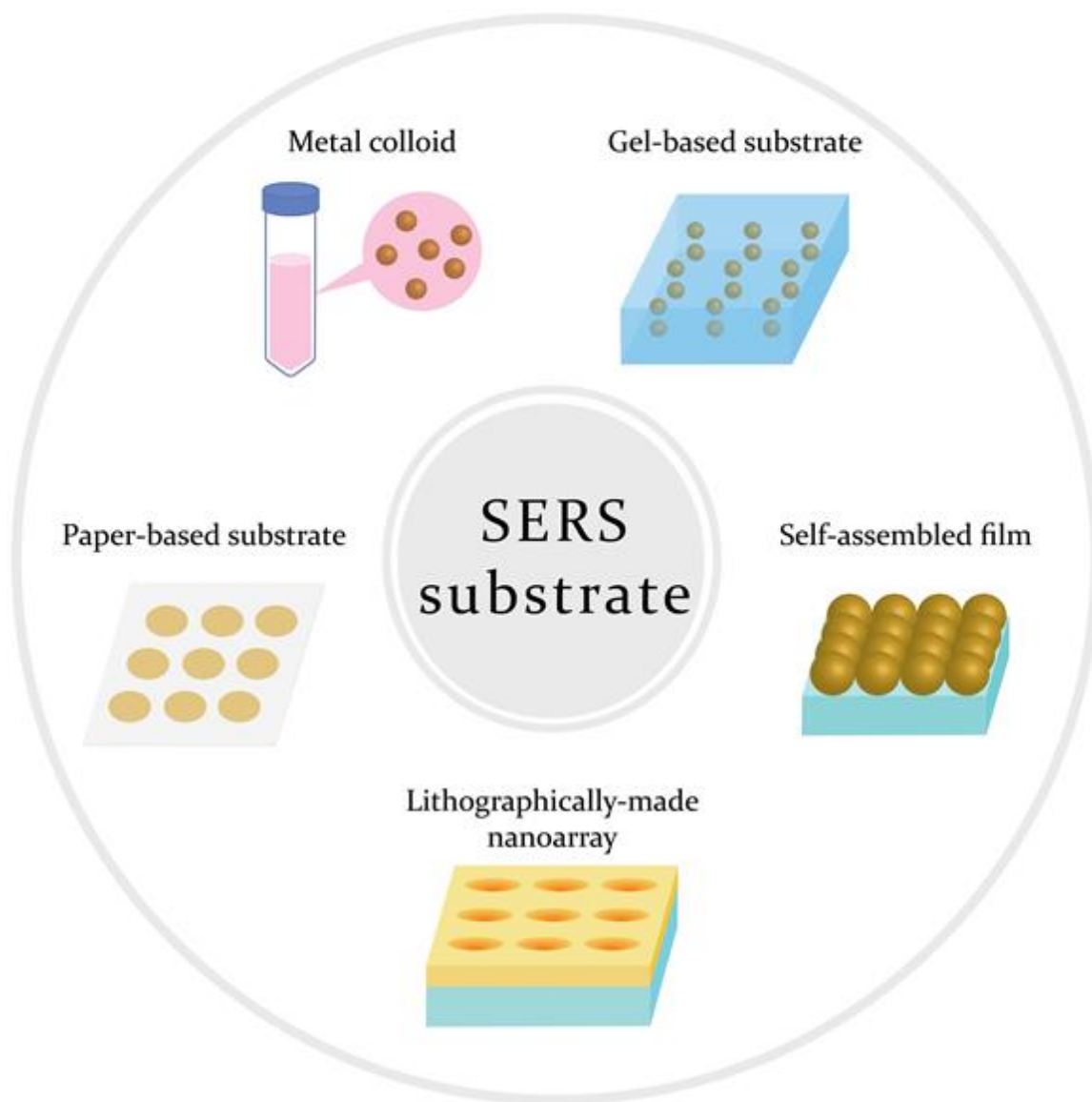


Figure 2.3 A schematic of common SERS substrates.

Compared with colloidal substrates, solid SERS substrates are easier to handle and do not have the problems of uncontrolled aggregation. Highly uniform plasmonic nanoarrays can be synthesized using templating and lithographic approaches,²⁰ which are very expensive and challenging to synthesize on a large scale.^{21–23} These disadvantages limit the applications of the substrates made by the top-down lithographic approaches for regular water monitoring. To avoid the high cost of the top-down synthetic methods, SERS substrates with a large density of hot spots have been

synthesized using bottom-up approaches, *e.g.*, assembling the pre-formed PNPs on a solid support (Figure 2.3). For example, alkanethiolate-functionalized AgNPs and AuNPs can be deposited onto a variety of solid substrates by dip coating.²⁴ By treating the first layer of PNPs with plasma, the second layer can be deposited due to the change of surface hydrophilicity. This process can be repeated to deposit an arbitrary number of layers on the solid surface. The close-packed alkanethiolate-functionalized AgNP superlattice is a highly uniform SERS substrate (the relative standard deviation (RSD) of the crystal violet Raman intensity across a 900 μm^2 area is 4.3%). The reproducibility of the self-assembled PNPs can be further improved by applying the alkanethiols as internal standard and preventing the analytes from entering the hottest spots.²⁵ In addition, polyethylene glycol (PEG)-coated AuNPs can be assembled into a square superlattice on a topographically patterned polydimethylsiloxane (PDMS) mold.²⁶ The superlattice can be subsequently transferred onto a glass slide and used as a SERS substrate. To optimize the SERS performance, the light extinction band of the superlattice substrate can be tuned to match the excitation laser line by changing the lattice parameter.

Similar to pH testing strips, paper-based SERS substrates are easy to synthesize and use and thus have been proposed as an ideal low-cost platform for onsite detection of small molecules.^{27,28} Paper-based SERS substrates can be synthesized by soaking a paper strip in a pre-synthesized nanoparticle colloid or growing PNPs *in situ* onto the paper strip.^{29,30} Inks made of PNP colloids can be written,³¹ or inkjet printed³² onto paper, allowing roll-to-roll synthesis. Similar to coating PNPs onto other solid substrates, it is also challenging to find efficient ways to improve the density of PNPs on paper.²⁸ Citrate-coated AuNPs were first self-assembled at a dimethyl carbonate–water interface using an emulsification method and then transferred to the arrow of a chromatographic paper by dip coating.²⁸ The close-packed AuNPs on the paper arrow enabled an RSD value of bipyridyl Raman intensity of 8.7%. Compared with the cellulosic papers, nanocellulose-based papers/films/membranes are better PNP supports and can achieve higher SERS sensitivities. Recently, gold nanoparticle–bacterial cellulose (AuNP–BC) SERS substrates were synthesized by *in situ* reduction of HAuCl_4 in the presence of BC.³³ Because of the similar

diameters of BC and AuNPs, BC provides nanoscale roughness to host a large number of AuNPs, thus creating densely packed SERS hot spots for ultrasensitive analysis.

With an efficient SERS substrate at hand, choosing appropriate sampling methods will be the next critical step for a successful SERS analysis. For water pollutant analysis, pollutants can be transferred to the SERS substrates by drop coating or immersing the substrates into the pollutant solutions (dip coating). Drop coating usually results in a non-uniform distribution of analytes on the substrate surface induced by the capillary force, which is known as the “coffee ring” effect. While the efficiency of dip coating will depend on the affinity between the pollutants and the substrates. A method that can concentrate the analytes on SERS substrates is highly desired because it is the key for sensitive analyte detection. Capillary forces can be used to direct the analytes to the sensing elements (*e.g.*, AuNPs) at the air–solid interface by simply placing a porous polymeric membrane on the surface of a liquid sample.³⁴ Separation of the target analytes from the co-existing organics (*e.g.*, natural organic matter, NOM) is another important factor to consider for SERS applications using real-world water matrices. Paper substrates can facilitate chemical separation due to the different movement speeds of various chemicals on paper with water as the mobile phase, which is known as paper chromatography. In addition to chromatographic separation, molecular sieves can be coated on PNP surfaces to prevent contact between the interferent molecules and the sensing elements. For example, a zeolite imidazolate framework-8 with a pore size of 0.34 nm excludes adenine and 2,2'-bipyridine with a size of ~ 1 nm from entering the pores and contacting the gold nanorods inside.³⁵ Recently, we used a mesoporous silica shell to coat the gold nanorod aggregates, which minimized the influence of polymer and NOM on the detection of the target analytes.³⁶

2.5 Label-free SERS Detection of Organic Micropollutants

Starting from this section, we will use examples to elucidate how SERS can be used as a label-free tool for the detection of organic micropollutants,

biotoxins, and pathogens in water. We will highlight the adaptations that are required to make SERS work for different target analytes.

2.5.1 Drugs

In this section, we will discuss the examples of SERS applications for pharmaceutical and illegal drug analysis. Drop coating the drug-containing water onto a solid substrate is the most common method of SERS detection. Methamphetamine with a limit of detection (LOD) of 160 ppb was detected by drop coating a 2 μ L liquid sample onto the hemispherical microcavity array within a glass slide.³⁷ Core-shell nanopeanuts that carried crystal violet acetate as the internal standard were embedded in the microcavity and used as the sensing elements. When pre-concentrated using a syringe column needle containing a poly (methacrylic acid-ethylene glycol dimethacrylate) sorbent, the LOD of methamphetamine in urine/serum samples can be further reduced to 10 ppb. Five representative illegal drugs, including 2C-B, cocaine, fentanyl, hydrocodone, and JWH-018, were detected using a paper-based SERS substrate synthesized by dip coating.³⁸ LODs for these compounds within the range 0.6–26 ng (0.08–3.7 ng mm⁻²) were achieved by drop coating their aqueous solutions onto the paper substrate and performing SERS analysis after air drying.

Direct drop coating results in a non-uniform distribution of the analytes over the substrate, leading to highly heterogeneous SERS intensities. Regulating the electrostatic forces between the SERS substrate and the target analytes is a feasible approach to enhance their affinity.^{39,40} Intravenous drugs, such as gentamicin and dobutamine, were detected using normal Raman and SERS at clinically-relevant concentrations, respectively.⁴⁰ Compared with gentamicin, dobutamine at a concentration clinically-relevant for intravenous therapy does not generate a detectable Raman signal. Therefore, an Au film over nanosphere (Au FON) substrate was used to enhance its Raman intensity. Due to the weak affinity of dobutamine toward Au FON, an electric potential was applied to the Au FON to drive dobutamine toward the substrate surface. In this way, a LOD of 3×10^{-7} M was achieved, which is four orders of magnitude lower than the clinically relevant concentration. The adsorption of amine-containing compounds toward SERS substrate can also be enhanced by adjusting the

solution pH.³⁹ Carbamazepine—a neural pharmaceutical drug, cannot be detected using citrate-coated AuNPs at circumneutral pH because of its weak association with AuNP surfaces. However, when the solution pH was lowered to a value below its pK_a , the SERS signals of carbamazepine were reproducibly detected across the substrate because of the electrostatic attraction between the protonated amine group of carbamazepine and the negatively charged carboxylate group of citrate.

2.5.2 Pesticides

Pesticides are used in tremendously large amounts, *e.g.*, the use of pesticides in the agricultural sector in the United States reached 387.4 thousand metric tons in 2012.⁴¹ A variety of pesticides have been frequently detected in natural and engineered water systems and pose risks to human health. For the detection of remaining pesticides in food products, PNP colloids can be directly applied on the surface of a fruit or vegetables followed by Raman spectrum collection.^{41,42} For label-free SERS detection of trace pesticides in water, sensitivity and reproducibility remain the two greatest challenges to overcome. As an effort to improve the sensitivity of pesticide detection using SERS, paper-based substrates were treated with an alkyl ketene dimer to convert the hydrophilic hydroxyl groups of cellulose to hydrophobic alkyl groups.⁴³ In this way, the contact angle of the aqueous droplet containing AgNPs on the filter paper increased, resulting in a higher areal density of the deposited AgNPs and thus greater SERS sensitivity and reproducibility. This hydrophobic paper SERS substrate achieved ultrasensitive detection of ferbam and thiram with LODs of 0.46 and 0.49 nM, respectively.

The two pesticides mentioned above (*i.e.*, ferbam and thiram) both exhibit high affinity to AgNP surfaces. For the pesticides that are weakly associated with PNP surfaces, measures need to be taken to improve the affinity between them. For example, trace atrazine in water (below its maximum contaminant level in drinking water, *i.e.*, 3 ppb) was reproducibly detected using the AuNP–BC substrate at a solution pH value lower than its pK_a , which was attributed to the enhanced electrostatic attraction between the protonated secondary amines of atrazine and the negatively charged

citrate on AuNP surfaces.³⁹ Some hydrophobic pesticides do not have specific functional groups that are electrostatically attractive toward PNP surfaces. To enable their SERS detection, people can take advantage of the hydrophobic–hydrophobic interactions between the pesticides and the SERS substrates. Alkyl dithiols were functionalized on the surfaces of colloidal AuNPs and AgNPs to make them hydrophobic and induce their aggregation for SERS hot spot generation.⁴⁴ The chain length of the alkyl dithiols was optimized to maximize electromagnetic enhancement and target analyte enrichment. Organochlorine pesticides, including aldrin, dieldrin, lindane, and α -endosulfan, are highly persistent and toxic pollutants, which cannot be detected using conventional SERS substrates. After the functionalization of AuNP surfaces with alkyl dithiols, the pesticides can be enriched to the hot spots that contain alkyl groups *via* hydrophobic–hydrophobic interactions and subsequently detected at LOD values of 10^{-8} M.

2.5.3 Explosives

Similar to drugs and pesticides, drop coating of aqueous solutions containing explosives onto a SERS substrate is a rapid and facile method for their detection. Aliquots of solutions of three representative explosives, *i.e.*, trinitrotoluene (TNT), nitroglycerine, and triacetone triperoxide, were drop coated onto a commercial SERS substrate—Klarite. Following air drying, the minuscule amounts of explosive solids left on the Klarite were analyzed using SERS.⁴⁵ Clear Raman spectra of the explosives down to several hundred picograms were readily collected within seconds. Similarly, aqueous solutions containing 5 μ M picric acid, 1 μ M 2,4-dinitrotoluene, and 10 μ M 1,2,4-triazol-5-one were drop coated onto a Ag/AuNP aggregate-loaded filter paper and detected in the same way as described above.⁴⁶

As discussed earlier, it is challenging to achieve reproducible SERS detection using the drop coating method because of the random orientations and distances of the explosive molecules toward the SERS substrates. To overcome this disadvantage, strategies to promote the host–guest complexation between PNP surface coatings and the explosives have been explored.^{47,48} One example is the SERS detection of TNT by taking

advantage of the formation of the Meisenheimer complex.⁴⁷ The citrate-coated AuNPs were first functionalized with cysteine, which underwent aggregation upon the addition of TNT because of the formation of the covalent bond between the nucleophilic amine group of cysteine and the electron-deficient aromatic ring of TNT (*i.e.*, the Meisenheimer complex). The aggregation of cysteine-coated AuNPs also resulted in a large number of SERS hot spots with an EF up to 10^9 . Ultrasensitive detection of TNT in water with a LOD of 2 pM was achieved using this strategy. A similar strategy for explosive detection was recently reported by Faulds *et al.*,⁴⁸ where explosive molecules formed Janowsky complexes with the enolate ion of the 3-mercapto-2-butanone on the AuNP surfaces. With this method, TNT, hexanitrostilbene, and 2,4,6-trinitrophenylmethylnitramine were detected with LODs of 6.81, 17.2, and 135.1 $\mu\text{g L}^{-1}$, respectively.

2.5.4 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are hydrophobic organic pollutants with weak affinity toward the hydrophilic AuNP or AgNP surfaces. To enable the label-free SERS detection of PAHs, “molecular traps” are usually required to capture the PAH molecules on PNP surfaces. A macrocycle—calix[4]arene was used as the molecular trap to capture trace PAHs from water.⁴⁹ After being functionalized onto AgNP surfaces, the calix[4]arene can form host–guest complexes with guest PAH molecules *via* π – π stacking forces. The size and functional groups on the upper rim (away from the AgNP surfaces) of the calix[4]arene cavity acted as the molecular screens for the selective detection of pyrene and benzo[*c*]phenanthrene among other PAHs, including anthracene, triphenylene, coronene, dibenzanthracene, chrysene, and rubicene. Another macrocyclic molecule— β -cyclodextrin (β -CD) was also used as the molecular trap for the SERS detection of PAHs.⁵⁰ However, this study used Rhodamine 6G as the SERS reporter and thus falls outside of the focus of this chapter.

In addition to macrocycles, porous polymers with abundant micropores were also used for PAH capture and subsequent SERS detection.^{51,52} AuNPs were loaded on a covalent organic framework (COF) support *via* anchoring at the nitrogen atom sites in the COF skeleton.⁵¹ A significant

enhancement of PAH Raman intensities was observed from the AuNP–COF nanocomposite compared with its individual components. This enhancement can be attributed to both the high hot spot density induced by the COF support and the high affinity between COF and PAHs. Although this SERS substrate demonstrated great performance for PAH analysis, the exact sites for efficient PAH adsorption and electromagnetic enhancement were not clearly identified. Compared with non-selective adsorbents like COFs, molecularly imprinted polymers (MIPs) can be used for selective capture and SERS detection of PAHs.⁵² Following layer-by-layer deposition of AuNPs on a glass slide, a thin film of MIPs that were synthesized with pyrene and fluoranthene as the templates was spin coated onto the AuNP layers. After the removal of the templates, the cavities left within the MIPs enabled the templated PAHs to enrich onto the SERS substrate. Using the AuNP–MIPs, pyrene and fluoranthene were detected with a LOD of ~1 nM. The pyrene templated AuNP–MIP only showed the Raman spectrum from pyrene in a mixture of three PAHs (pyrene, fluoranthene, and benzo[*a*]pyrene) with equal concentrations, demonstrating its excellent selectivity.

2.6 Label-free SERS Detection of Biotoxins

Unlike small synthetic chemicals, biotoxins are usually large molecules that have difficulty entering SERS hot spots. Therefore, the volume of literature reports on label-free SERS detection of biotoxins is much smaller than that on synthetic chemicals. In this chapter, we will take microcystin as an example to elucidate the progress and challenges of label-free SERS for biotoxin detection. Microcystins are cyclic heptapeptides that are produced by cyanobacteria and known for their strong hepatotoxicity. Standard methods for microcystin analysis are LC–MS/MS and enzyme-linked immunosorbent assay (ELISA), which are very expensive and time consuming. Recently, SERS tags functionalized with anti-microcystin antibodies and aptamers were developed for fast microcystin analysis.⁵³ Direct analysis of microcystin-LR down to 2 ng using drop coating deposition Raman (DCDR) has also been reported.⁵⁴ However, solid-phase

extraction is required when the microcystin-LR concentration is low due to the low sensitivity of normal Raman spectroscopy.

Label-free SERS detection of microcystins at environmentally relevant levels usually requires a pre-concentration step. In a latest research, the Fab's fragments of a monoclonal anti-microcystin antibody were functionalized onto the gold coated magnetic nanoparticles to extract microcystin-LR from water and blood plasma media.⁵⁵ Subsequently, the microcystin-LR was eluted from the adsorbents and further purified using a size exclusion column. Finally, the pre-concentrated microcystin solution was drop coated onto a gold-coated silicon nanopillar and paper-based SERS substrates ($EF = 2.5 \times 10^6$ and 3×10^5) for Raman analysis. The limit of quantification (LOQ) for microcystin-LR achieved using this label-free SERS method was 10 fM, which is below the drinking water limit set by the World Health Organization (*i.e.*, 1 ppb). This study highlights the feasibility of label-free SERS for microcystin analysis and the important role of sample purification and pre-concentration. Recently, a study reported the label-free SERS detection of microcystin-LR by drop coating its aqueous solution onto a commercial SERS substrate (AgNPs deposited on a filter membrane substrate, or SERS-AG).⁵⁶ This simple method for microcystin-LR analysis achieved a surprisingly low LOD of 1 ppt without sample pre-treatment, which is 1000 times lower than the WHO standard. However, the LOD dramatically increased to 1 ppm and 1 ppb for microcystin-LR spiked tap water before and after 0.22 μm filter filtration, indicating the strong interference from the tap water matrix.

2.7 Label-free SERS Detection of Waterborne Pathogens

Waterborne pathogens, including protozoa, bacteria, and viruses, are too big to enter the nanogaps between PNPs (*i.e.*, typical SERS hot spots). However, they can be probed by atypical SERS hot spots, such as tips of nanorods, sharp corners of nanocubes, and nanowell arrays. Because the Raman intensity of the whole pathogen cell is not homogenously enhanced by the SERS substrate, the reproducibility of the collected Raman spectra can be a big problem for label-free SERS detection of waterborne

pathogens. In this section, we will discuss the applications of label-free SERS for the detection of bacteria and viruses and the accompanying reproducibility problem.

2.7.1 Bacteria

Bacteria are a common type of pathogen and are responsible for many waterborne diseases, such as cholera, typhoid fever, and bacillary dysentery.⁵⁷ Due to the large size of a bacterial cell, it is visible under an optical microscope. By coupling a confocal microscope with Raman spectroscopy, three-dimensional chemical information of a single cell can be acquired. For their label-free SERS detection, bacteria can be filtered out from water onto a plasmonic membrane for Raman analysis. Electrospun filters made of poly(vinylene fluoride), poly(L-lactide acid), and nylon were sputter coated with a 90 nm gold film and used as SERS substrates for bacterium detection.⁵⁸ Two types of bacteria—*Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) suspended in water were immobilized onto the filter SERS substrates by drop coating coupled with vacuum filtration. The average SERS spectra of both bacteria were thus acquired and used for their differentiation and quantitation. Because of the complex compositions of the bacteria, proteins, phospholipids, and polysaccharides all contribute to the observed Raman bands, making accurate band assignment very challenging.

Unfortunately, the drop coating method results in random orientation of bacteria toward the SERS substrates and non-uniform enhancement at different locations of the cell wall. This heterogeneous SERS enhancement will lead to significant variation of the Raman intensity as well as the spectral pattern from spot to spot, making quantitative analysis challenging. To improve the reproducibility and sensitivity for bacterium detection, a AgNP shell was grown onto the bacterial cell wall by *in situ* reduction (Figure 2.4).⁵⁹ The aqueous suspension of AgNP-coated bacteria was drop coated onto a hydrophobic glass slide followed by real-time SERS spectrum collection as the droplet was drying. The *in situ* AgNP growth on the cell wall resulted in higher surface coverage and $30 \times$ higher SERS intensity compared with simply mixing AgNPs and the bacteria, which enabled a LOD of 2.5×10^2 cells per mL. Using this approach, three strains of *E. coli*

and one strain of *Staphylococcus epidermidis* (*S. epidermidis*) were easily discriminated with the assistance of multivariate analysis. Without adding any chemical reducing agents, Au^{3+} and Ag^{+} can be directly reduced to metallic nanoparticles by *Geobacter*.⁶⁰ The *in situ* formed NPs gave the chemical information both outside and inside the bacterial cell wall. However, the abundant information provided by SERS has not been sufficiently interpreted due to a lack of a database for bacterial SERS spectra.

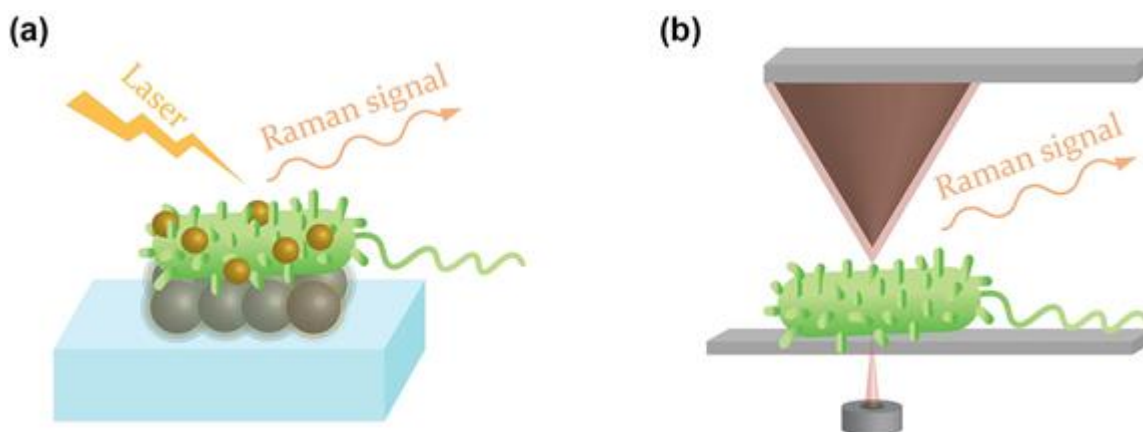


Figure 2.4 Schematic illustration of (a) SERS and (b) TERS detection of a single bacterium.

In addition to SERS whose spatial resolution is limited by the diffraction limit of light, tip-enhanced Raman spectroscopy (TERS) can also be used for single bacterium detection but provides a much higher spatial resolution (Figure 2.4b). TERS has been used for single *S. epidermidis* cell analysis.⁶¹ Because of the 50 nm spatial resolution achieved by TERS, variations of chemical information across the cell surface were identified, which is important for many biological processes.⁶¹

2.7.2 Viruses

Regarding SERS analysis, viruses share many similarities with bacteria. SERS tag-based immunoassay is also the most commonly adopted paradigm for SERS detection of viruses as they are larger in size than the typical volume of hot spots.⁶² The fact that viruses cannot enter the

nanogaps indicates that the label-free virus detection will predominantly rely on the “open-ended” hot spots, such as the sharp tips and nanowells. For example, rotavirus was detected using the SERS substrate made of a silver nanorod array.⁶³ This substrate was synthesized using oblique angle vapor deposition and demonstrated excellent reproducibility for Raman intensity ($EF > 10^8$) and spectral pattern. An aliquot of a virus aqueous suspension was drop coated onto the SERS substrate and air dried before Raman analysis. Different strains and genotypes of viruses were discriminated and quantified with the assistance of partial least squares-discriminant analysis. The same type of SERS substrate was also used to detect adenovirus, rhinovirus, human immunodeficiency virus, influenza virus, respiratory syncytial virus (RSV), and Dengue.^{64,65} It was recently discovered that the antinflaviviral antibody-conjugated AuNPs that were attached onto the virus surfaces enabled the direct collection of the SERS spectra of Dengue viruses (characterized by the amide I Raman band and $-CH_2$ deformation) and West Nile virus (characterized by the skeleton Raman mode and $-CH_3$ rocking).⁶⁶ Because of the presence of antibodies between the viruses and the AuNPs, further clarification is needed on the exact locations of viruses that undergo the highest SERS enhancement. Although most research into the SERS detection of viruses is focused on diagnostic applications, the embodied insights and methodologies can be easily translated to water monitoring.

2.8 Conclusion and Perspectives

This book chapter aims to give the readers an introductory level of knowledge of SERS application as a label-free tool for water pollutant analysis. A SERS substrate with high EF is necessary but insufficient for sensitive analysis. Although tremendous progress has been made toward developing efficient SERS substrates, most of them have only been challenged by model Raman compounds. For environmental pollutant detection, the substrate EF, their Raman cross sections, and affinity toward the substrate surface should be taken into consideration simultaneously. For large analytes like biotoxins and pathogens, the EF values probed using small chemical molecules cannot be directly used to predict their SERS

detection. In addition, the SERS spectra collected from bacteria and viruses should be further interpreted while the locations that contribute to the SERS intensities need to be unambiguously pinpointed. The results of the SERS analysis of water pollutants should be validated in real-world water matrices and using well-established analytical tools, such as LC–MS/MS and PCR.

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Chapter 3

Merging of MOFs and Graphene Analogous: Strategies for Enhanced Sensing Properties

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3.1 Introduction

Environmental pollution has increasingly occurred due to excessive human activities and industrial manufacture, resulting in a series of environmental issues including imbalanced ecosystems, aggravated climate change, global warming and air, soil and water pollution, which have posed huge threats to human life and health. The large amount of industrial waste gas and the burning of fuel lead to an obvious increase in the concentration of harmful gases and greenhouse gases in the air, such as H₂S, SO₂, NH₃, CO₂ and CH₄, which have caused many diseases to human beings, such as asthma, respiratory diseases, cardiovascular diseases and even cancer.¹ Meanwhile, contaminants in water have come from the discharge of industrial wastewater, the settling of air pollution, and the leaching of soil pollution. More than 650 million people around the world have no access to safe drinking water, and one child under the age of five dies from diarrheal disease caused by dirty water every two minutes, which could have been prevented.² Moreover, emerging contaminants (ECs) and persistent organic pollutants (POPs) at trace concentrations have also been detected in water and soil, and their harm shouldn't be underestimated. ECs have been in the environment for a long time, but their existence and potential harm have only been discovered recently due to their low concentrations and difficulties in detection.³ Many ECs, such as endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) and some other medicines, are closely related to human daily life, which poses a great challenge for pollution control. POPs persist in the environment with high toxicity, durability and long-distance migration, and are easily accumulated through biological food chains, thus they are more toxic to humans at the top of the chain.^{4,5} Both ECs and POPs are chemically stable and easily bio-accumulated, causing great harm even at low concentrations. After bioaccumulation, the toxicity of ECs and POPs can increase thousands of times, posing a potential threat to ecological systems and the health of people.⁵ Thus far, many effective sensing technologies have been developed to identify and monitor environmental contaminants.⁶ However, conventional contaminant monitoring technologies are challenged by the variability and complexity of the environmental matrix and the low concentration of target

contaminants.^{7,8} Therefore, it is of great significance to find advanced materials with excellent properties to establish innovative sensing strategies and technologies.

Over the past decade, many efforts have been made to build up the sensing platforms for effective sensing of the environmental pollutants mentioned above. In addition, nanotechnologies have developed markedly with applications in many environmental fields due to their unique characteristics. According to our research, the requirements for materials with outstanding features and advanced surfaces and interfaces have been provided as follows. First, an active and unique material surface and interface are needed to achieve selective and sensitive detection reactions. Second, the structure should be stable and durable enough when exposed to pollutants in different media. Third, environmentally friendly and sustainable materials are particularly crucial when applied in the environment to avoid secondary pollution. Therefore, MOF and GA are emerging as popular candidates to build interfacial structures, which provide fascinating properties for enhanced sensing strategies with high sensitivity and selectivity.

Known as three-dimensional (3D) porous coordination polymers, MOFs are formed by connecting metal ions or their clusters with linked organic ligands through coordination bonds^{9,10} and exhibit many extraordinary properties including great flexibility, ease of synthesis, tunable pores, selective functional groups and tailorable chemical affinities toward specific tasks.¹¹ The large specific surface area with huge porosity endow MOFs with strong adsorption abilities, which enable MOFs to enrich and detect the trace concentration contaminants.¹⁰ Many good and sensitive sensing platforms were built based on the catalytic activity and sensing ability of MOFs due to their unsaturated metal centers and metal clusters. For example, Wang *et al.* proposed a label-free sensing strategy based on the enzyme-mimicking activity of MOFs and applied it to colorimetric detection of biomolecules.¹¹ In addition, some fluorescent MOFs were developed recently, which provide the possibility of building fluorescent sensing platforms. For example, NH₂-MIL-53(Al) is a novel highly fluorescent MOF fabricated by Lu *et al.* via a hydrothermal method, which was applied in the sensing of free chlorine.¹² Li *et al.* fabricated a material that deposited MOF on natural fibroin fibers and demonstrated its application in the fluorescent/colorimetric sensing of copper ions.¹³ However, non-conductivity or poor conductivity with slow electronic transfer rates are common defects in most MOF materials, which are attributed to the non-conductivity of the organic framework, thus limiting the application of MOFs in the scope and efficiency of detection. For instance, UiO-66 (Zr₆O₄(OH)₄(BDC)₁₂) with a crystal structure constituted by Zr₆O₃₂ units possessed high thermal and chemical stabilities, but its efficiency for electron and charge transfer was very low.¹⁴ Some porous MOFs, such as HKUST-1, suffered from significant stability problems, especially in view of their interaction with water, which severely limited their practical application in detection.¹⁵ In order to break through the limitations of MOFs and improve their performance, one way out is to form MOFs composites or derivatives by compounding with other materials.

Graphene, as a well-known two-dimensional (2D) material, has attracted great interest since its discovery in 2004, leading to a rapid development of 2D nanotechnology. Graphene analogs (GA), including graphene, graphene oxide (GO), reduced graphene oxides (rGO) and graphene quantum dots (GQDs) present a great many outstanding features, such as quantum hall effects (QHE), high carrier mobility, large specific surface area, excellent electron migration ability, thermal conductivity, and great mechanical strength.^{10,14,16} Meanwhile, GA's unique, harmonious plane structure with oxygen-containing functional groups anchored on the surface and edges provide many active sites for further functionalization and turning properties.^{16,17} Thus, the coupling of MOFs with GA materials has emerged in recent years. MOF-GA materials include MOF-GA composites and MOF-GA derivatives, which combine the excellent characteristics of high porosity and catalytic activity of

MOFs as well as the 3D structure, high mechanical and elastic strength, high conductivity, and easy functionalization of GA materials with the weakness of modified MOF materials. Many effective and advanced MOF–GA materials have been developed to be applied in electrochemical and luminescence sensing due to their high electron transmission rate, good electrical conductivity and easy functionalization characteristics.

In this chapter, we will first discuss the latest developments in the preparation strategies of MOF–GA materials. The integration of 3D MOFs and 2D GA improves the mechanical properties and stability of MOF, and it endows the composites with excellent properties, including accelerated electron transfer rates and a prominently enhanced stability with unique hierarchical structure ascribed to the graphene-based materials, as well as high adsorption capacities and catalysis activities and remarkably promoted surface chemical properties obtained from the MOFs. Sequentially, as shown in Figure 3.1, the applications of MOF–GA materials in environmental contaminant sensing will be discussed mainly from the perspective of the detection of gaseous contaminants, organic contaminants and inorganic ions. Furthermore, prospects and further developments in this exciting field of MOF–GA-based sensing platforms are suggested.

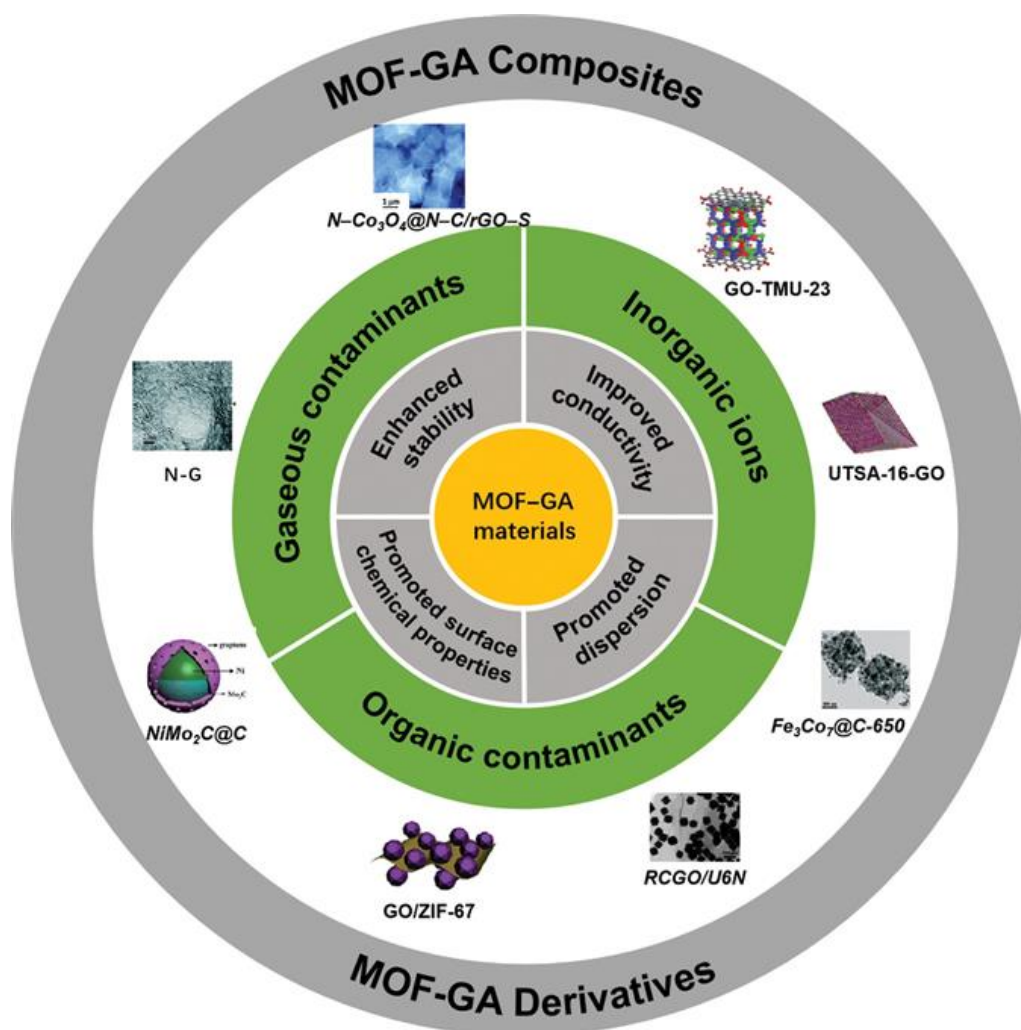


Figure 3.1 Schematic illustration of MOF and GA merging strategies.

3.2 Preparation and Properties of MOF–GA Materials

In this section, we will focus on the preparation methods of MOF–GA composites and MOF–GA derivatives. This discussion shall provide clues for optimal selection of a MOF–GA for a particular sensor and help in understanding the advantages and disadvantages of the chosen method.

3.2.1 Preparation of MOF–GA Composites

MOF–GA composites are a complex of MOFs and GA materials (Figure 3.2), which effectively combines 2D GA and 3D MOF materials to form a composite, resulting in a fusion of 2D and 3D structures. MOF–GA composites possess new physical and chemical properties and enhanced performance that cannot be possessed by a single component. Commonly used methods for preparing MOF–GA composites include self-assembly, *in situ* growth and layer-by-layer deposition.

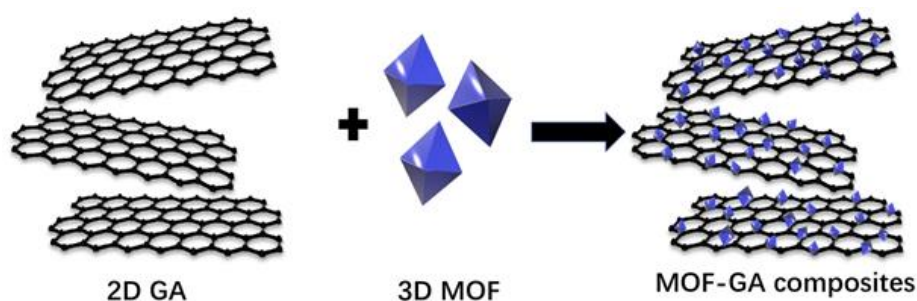


Figure 3.2 Schematic of MOF–GA composite preparation.

3.2.1.1 Self-assembly

Self-assembly is a preparation method driven by electrostatic interaction, π – π stacking, hydrogen bonding and other forces.¹⁷ The functional groups of GA materials, including hydroxyl and epoxide groups on the basal plane, carboxylate groups located at the edges of the layers, and aromatic sp^2 domains, allow GO to participate in the bonding interactions in MOFs as structural nodes and guide the growth of MOFs.¹⁰ Using the self-assembly process, many MOF–GA composites were synthesized *via* the integration of pre-synthesized MOFs and GA materials, which retained the original form and function of MOFs and GA. For example, Wang *et al.* constructed stable Cu-based MOF–GA composites *via* an ultrasonication method with dispersible MOFs and GO, and then the composites were coated on the surface of a glassy carbon electrode (GCE) by an electro-reduction process.¹⁸ Li *et al.* employed the self-assembly method to fabricate MOF–GA by mixing $M^{n+}@Y$ -1,4-NDC-MOF and GO followed by electrochemical reduction; and before that, the anionic MOFs were pre-synthesized through a cationic exchange strategy between metal cations and MOFs.¹⁹ Wang *et al.* reported a GA well-trapped MOF (Figure 3.3c and f) *via* self-assembly with the assistance of hydrochloric acid.²⁰ Three kinds of materials were prepared for comparison, including RCGO/U6N synthesized using *in situ* growth method (Figure 3.3a and d), RDGO/U6N synthesized by random mixture of UiO-66–NH₂ and GO (Figure 3.3b and e) and the graphene well-trapped UiO-66–NH₂ (RGOWU6N) (Figure 3.3c and f). The existence between UiO-66–NH₂ crystals was shown exactly for all materials, but the contact routes of UiO-66–NH₂ octahedrons and graphene were different. The interaction between the MOF and GA was random for RCGO/U6N (Figure 3.3b and e), and

single-face for RDGO/U6N (Figure 3.3a and d). For well-trapped UiO-66-NH₂ (RGOWUN), the UiO-66-NH₂ octahedrons were wrapped by graphene layers on every face of the octahedrons, which can be clearly seen in the SEM images. The self-assembly method provided random interaction between MOF and GA. However, this could be adjusted in acid conditions *via* electrostatic attraction. Well-trapped GA preferentially inhibited the recombination of photo-generated electrons and holes and accelerated the electron transfer rate, thereby improving the photocatalytic properties.²⁰

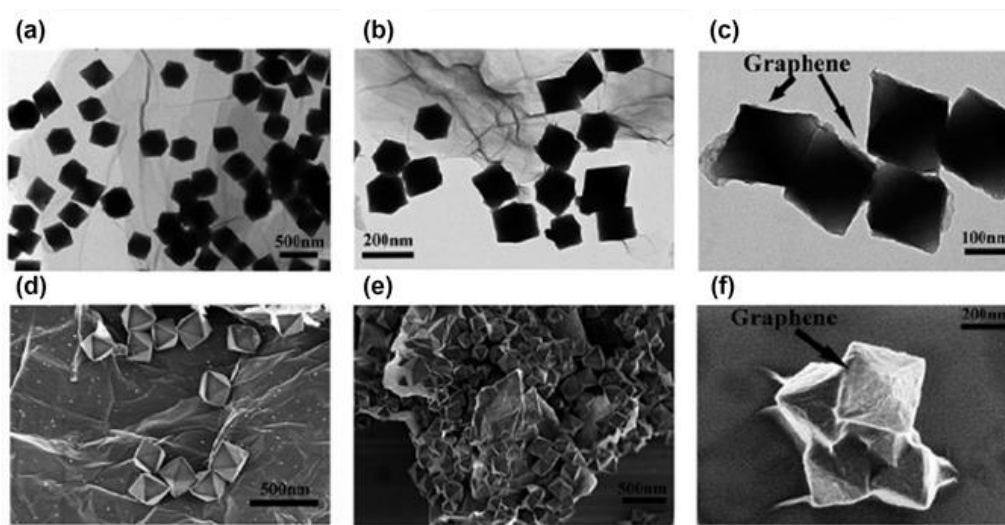


Figure 3.3 TEM and SEM images of (a) and (d) RCGO/U6N, (b) and (e) RDGO/U6N, and (c) and (f) RGOWU6N. Reproduced from ref. ²⁰ with permission from the Royal Society of Chemistry.

3.2.1.2 *In Situ Growth*

The *in situ* growth method is a feasible way to synthesize MOF-GA composites using MOF precursors and GA materials as raw materials. Specifically, the well-dispersed mixture of GA materials and MOF precursors can be treated using a few methods, such as hydrothermal, solvothermal, microwave and so on.^{16,21} Through the *in situ* growth method, MOFs are synthesized and strongly embedded on the surface of GA materials. Since the growth of MOF crystals is limited by graphene, the size of MOF in MOF-GA is smaller than the original MOF. During the *in situ* growth process, GA materials also work as templates to control the morphologies and structures of the composites. For example, Wu *et al.* prepared a Zn-BTC MOF-GA composite by *in situ* growth of ZnO nanoparticles coated with nanoporous graphene.²² Bhoria *et al.* employed functionalized GO as support for the *in situ* growth of HKUST-1 to synthesize MOF-GA composite.²³

There are many studies on the preparation of MOF-GA composites using *in situ* growth methods. Shen *et al.* first synthesized a core-shell Co-based MOF (UTSA-16) wrapped with GA *via* hydrothermal reaction of the mixture of graphene-based materials, cobalt and citrate. Prior to being wrapped by GA, the formation of MOF cores was promoted by the chelation of the Co ions, K ions and citrate due to the chemical interaction of hydroxyl and carboxyl groups and the conformational flexibility of citrate (Figure 3.4).²⁴ Likewise, Zn-based MOF-GA composites were synthesized using an *in situ* hydrothermal method with the addition of GO and a mixture of well-dispersed

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-aminoterephthalic acid.²⁵ Xu *et al.* developed a superfast method to synthesize Cu-based MOF–GA composites at room temperature within one minute *via* the addition of ZnO nano-slurries into a mixed solution of MOF precursors and GO. During the process, Cu(II) reacted with ZnO to form a Zn–Cu hydroxy double salt, which exhibited a high anion exchange capacity and rate, accelerating the synthesis of HKUST-1@GO. The formed HKUST-1 was uniformly embedded on the surface of GO with a small size of about 0.8 μm .²⁶ Cr-based MOF–GA composites were fabricated through *in situ* solvothermal synthesis method with the addition of 5 wt% amounts of GO and exhibited a large BET surface area of 3502.2 $\text{m}^2 \text{g}^{-1}$.²⁷ A microwave-assisted ball-milling method was firstly used in the *in situ* synthesis of Ni-based MOF–GA composites.²⁸ MOF–GA composites with smaller sizes were obtained successfully using the ball-milling process due to its ability to restrain the growth of MOF seeds without the requirement of a solvent. However, the process also inhibited the formation of MOF crystallites, which was solved by the assistance of a microwave to form a Ni-based MOF of regular cuboids.

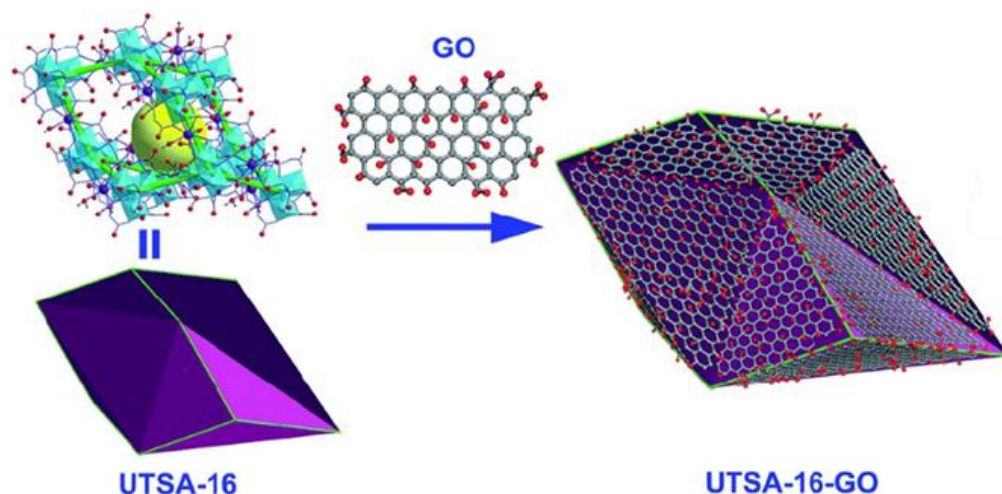


Figure 3.4 Schematic diagram showing the formation of the MOF–GA composites. Reproduced from ref. ²⁴ with permission from the Royal Society of Chemistry.

In addition to 2D GA materials, various GA materials with different structures were also applied in the formation of MOF–GA composites with unique structures, endowing the composites with better properties, such as higher adsorption capacity and accelerated electron transfer rate as well as better inhibition of the recombination of photo-generated electrons. For example, Yang *et al.* applied 3D GA as templates *via* an *in situ* synthesis method to generate MOF–GA composites with 3D structures. 3D GA was reduced from GO *via* a hydrothermal method at 180 °C with the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$. Graphene nanoribbons, derived from the oxidation of multiwalled carbon nanotubes, were used as structure-directing templates to form Fe-based MOF–GA composites *via* an *in situ* solvothermal method and allowed graphene to diffuse intensively on the surface of the MOF.²⁹ In another study, GA coated with MOF composites were fabricated *in situ* *via* mixing GQD and ZIF-8 precursors using the GQDs as templates and standing for 24 hours.³⁰

3.2.1.3 Layer-by-layer Deposition

The layer-by-layer deposition method involves either coating metal clusters and organic ligands on the GA-based materials alternately for many cycles or the deposition of various layers of GA on the MOF. Through this method, various thicknesses and layers of MOF–GA composites could be prepared by changing the growth cycles during the synthesis process.

Huang *et al.* synthesized MOF–GA membranes *via* layer-by-layer deposition of a GO suspension on a semi continuous ZIF-8 layer to achieve the hydrogen selectivity using the gaps between the ZIF-8 crystals blocked by GO layers with capillary forces and covalent bonds.³¹ Wei *et al.* fabricated core-shell structured MOF–GA composites *via* a layer-by-layer assembly synthesis method. ZIF-8 nanomaterials were first coated on the surface of GO using an *in situ* synthesis approach, and the composites acted as seeds for the following growth of ZIF-67 to form ZIF-8@ZIF-67 core-shell nanoparticles embedded on the GO surface. As ZIF-8 seeds avoided the overgrowth of ZIF-67, the overall crystal sizes of ZIF-8@ZIF-67 were significantly reduced compared with that of ZIF-67 grown directly on GO chips. The composites were successfully applied as precursors for the synthesis of Co/N-doped carbon catalysts (Figure 3.5).³²

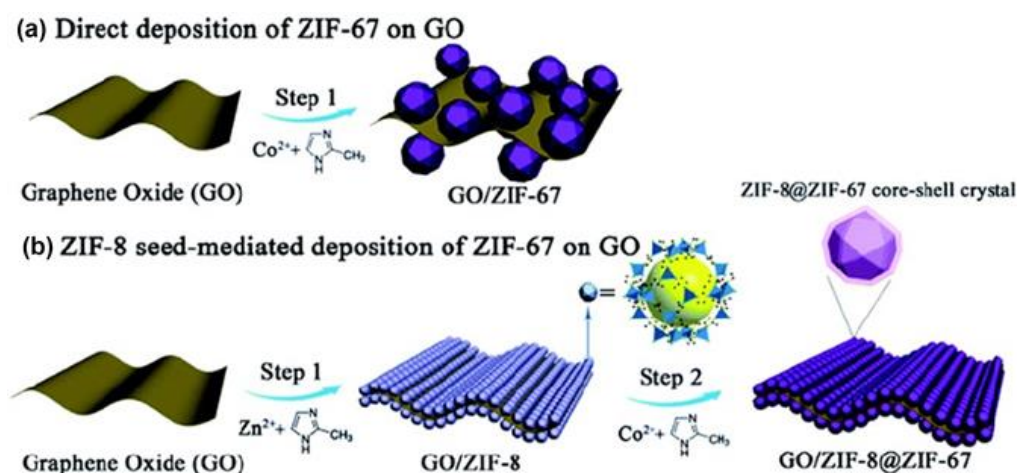


Figure 3.5 Comparison of different methods for the synthesis of MOF–GA composites (a) direct deposition of ZIF-67 on the GO sheet, (b) ZIF-8 seed-mediated deposition of ZIF-67 on the GO sheet. Reproduced from ref. ³² with permission from the Royal Society of Chemistry.

3.2.2 Preparation of MOF–GA Derivatives

MOF–GA derivatives are the products of MOF–GA composites calcined at high temperature, including metal or metal oxide nanoparticles, porous graphene materials, and metal oxide–graphene nanocomposites, *etc.* During the calcination process, the organic components in MOFs will be transformed into carbon materials, while the metal components in MOFs will be transformed into the corresponding metal nanoparticles (or evaporate at too high a temperature). The obtained metal nanoparticles would be wrapped with a firm and uniform graphene-based nesting, which helps these uniformly dispersed metal nanoparticles avoid aggregation (Figure 3.6).¹⁶ In addition, the structure and composition of MOF–GA derivatives could be controlled by tuning the calcination conditions. For example, porous metal oxide nanoparticles can be synthesized when MOFs are calcined in air, while metal nanoparticles are formed by calcination of MOFs in an N_2 atmosphere at high temperature, and their coated graphene nanosheet layers are formed *via* the calcination of organic ligands. Generally, MOF–GA derivatives can be obtained using single-metal MOF–GA composite

calcination, bimetallic MOF–GA composite calcination or heteroatom doping of MOF–GA derivatives.

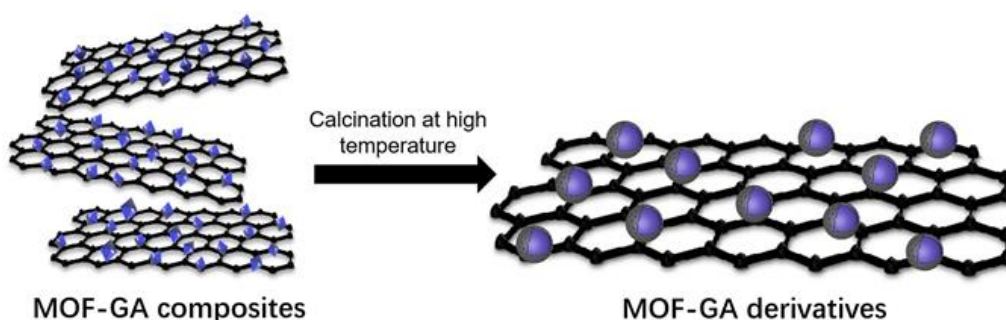


Figure 3.6 Schematic of MOF–GA derivative preparation.

3.2.2.1 Single-metal MOF–GA Derivatives

Metal clusters of MOFs were oxidized to metal oxides by calcination, homogeneously dispersed and strongly anchored on the surface of the formed GA,¹⁶ which preserved the activity of the metal catalysts well. Peng *et al.* prepared a $\text{CeO}_2 - x\text{-C-rGO}$ material *via* the pyrolysis of a MOF–GA composite at 450 °C in air for two hours and then at 600 °C in Ar. After calcination, polycrystalline CeO_2 nanoparticles were distributed randomly on the surface of the rGO nanosheets.³³

Similarly, transition metals are promising catalytic materials. MOFs prepared from transition metals were used as precursors or templates, which were calcined to embed transition metal nanoparticles into GA materials to obtain MOF–GA derivatives.¹⁶ For example, a kind of MOF–GA derivative, 3DGN– Mn_2O_3 , was synthesized by calcining MOF–GA precursors at 450 °C in air (Figure 3.7a).³⁴ In other research, Yan *et al.* implanted a Ni-based MOF into GO to synthesize MOF–GA composites. After further calcination of the composites, ultrafine Ni_2P nanoparticles were uniformly anchored on the surface of rGO, with an average size of 2.6 nm (Figure 3.7b).³⁵ As a common catalytic metal, cobalt is also frequently used to prepare MOF materials, and many studies on MOF–GA derivatives of Co-based MOFs have been reported. For instance, Song *et al.* immersed functionalized GA in a Co^{2+} solution to form MOF–GA composites, after pyrolyzation at 500 °C in N_2 , the formed Co nanoparticles were well dispersed on the GA surface.³⁶

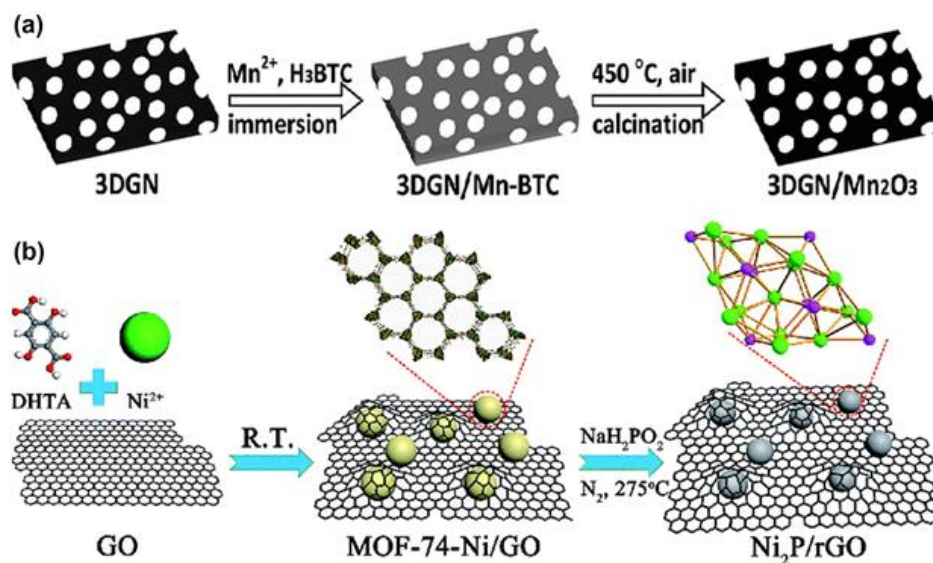


Figure 3.7 (a) Schematic illustration of the fabrication of 3DGN-Mn₂O₃. Reproduced from ref. ³⁴ with permission from the Royal Society of Chemistry. (b) Illustration of the synthesis procedure for Ni₂P-rGO. Reproduced from ref. ³⁵ with permission from the Royal Society of Chemistry.

Structural engineering is an effective strategy to prepare high-performance MOF-GA derivatives. By integrating different components, giving full use of each components' advantages to form different structures such as core-shell structures, sandwich structures and layered structures. Yang *et al.* designed a Cu-based MOF-GA derivative with a core-shell structure. During the calcination, Cu is coated by a carbon shell formed from organic ligands in the MOF, the size distribution of the Cu@C nanoparticles with core-shell structure was in the range 90–100 nm, and they were uniformly dispersed on the surface of the GA layers.³⁷

3.2.2.2 Bimetallic MOF-GA Derivatives

Due to the synergetic effect of bimetallic, the catalytic properties of bimetallic MOF-GA derivatives are enhanced compared to their monometallic counterparts.³⁸ Among them, bimetallic MOF results from the reaction of organic ligands with two metal ions with a similar charge density and electronic configuration to form a single-phase mixed bimetallic MOF, rather than a simple combination of two single-metal MOF materials.³⁹ For example, Yang *et al.* first mixed Cu and Co to prepare a Cu-Co bimetallic MOF, and then mixed it with GA to prepare bimetallic MOF-GA composites, which were further calcined to produce MOF-GA derivatives.⁴⁰ Li *et al.* synthesized GA coated Ni-Mo nanoparticles by heating the prepared Ni-Mo bimetallic MOF crystal at 700 °C for two hours in a N₂ stream (Figure 3.8a).⁴¹ In the same way, Zn and Co ions were uniformly dispersed in the mixed solution of rGO and 2-methylimidazole to prepare Zn-Co bimetallic MOF-GA composites (Figure 3.8b). After calcination, the homogeneous dispersion of Zn and Co on the surface of GA was observed using TEM.⁴²

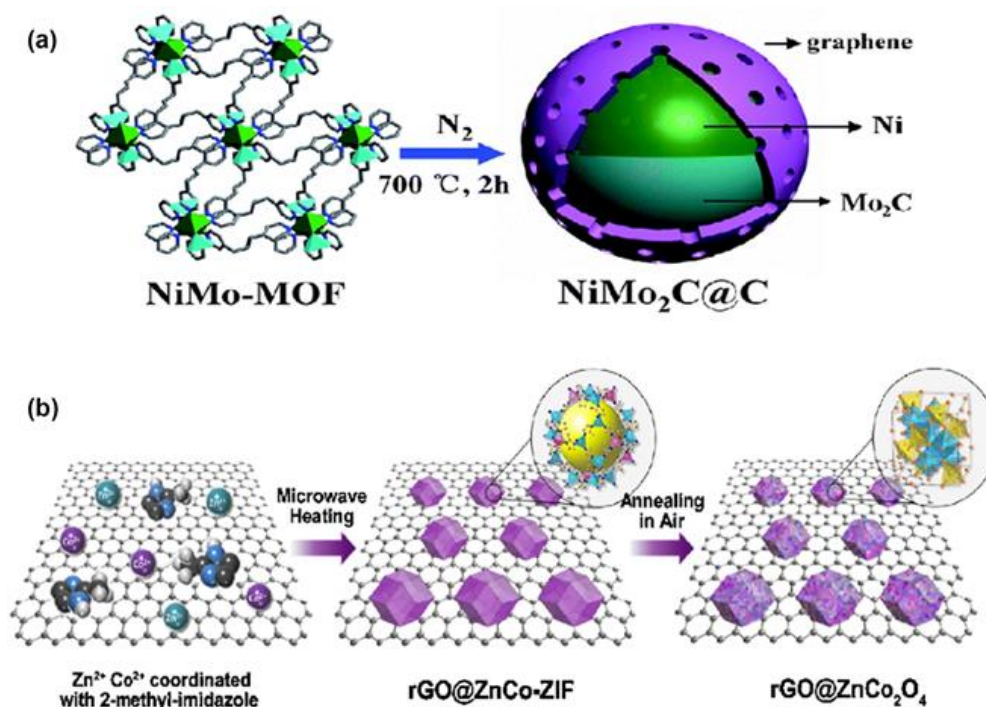


Figure 3.8 (a) Synthesis of the $\text{NiMo}_2\text{C}@\text{C}$ catalyst derived from NiMo-MOF . Reproduced from ref. ⁴¹ with permission from the Royal Society of Chemistry. (b) Schematic illustration of the formation of the Zn–Co bimetallic MOF–GA with hierarchical structure. Reproduced from ref. ⁴² with permission from Elsevier, Copyright 2018.

In addition, the temperature control of MOF–GA composites during the calcination process has a great influence on the size and structure of the material. In the synthesis of MOF–GA derivatives, different temperatures in the calcination process were investigated. As shown in Figure 3.9, graphene-encapsulated Fe_xCo_y bimetallic ($\text{Fe}_x\text{Co}_y@\text{C}$) nanocages were fabricated *via* thermal decomposition of Prussian blue analog (PBA) $\text{Fe}_y\text{Co}_{1-y}[\text{Co}(\text{CN})_6]_{0.67} \cdot n\text{H}_2\text{O}$ nanospheres at different temperatures (500, 650 and 800 $^\circ\text{C}$) in N_2 . The crystal sizes of the Fe_xCo_y nanoparticles became larger with an increased heating temperature from 500 $^\circ\text{C}$ to 800 $^\circ\text{C}$. Meanwhile, the Fe_3Co_7 nanocrystals were completely coated with GA shells (5–20 layers) with an interlayer distance of 0.34 nm, which was proved using HR-TEM images of single nanocrystals.⁴³

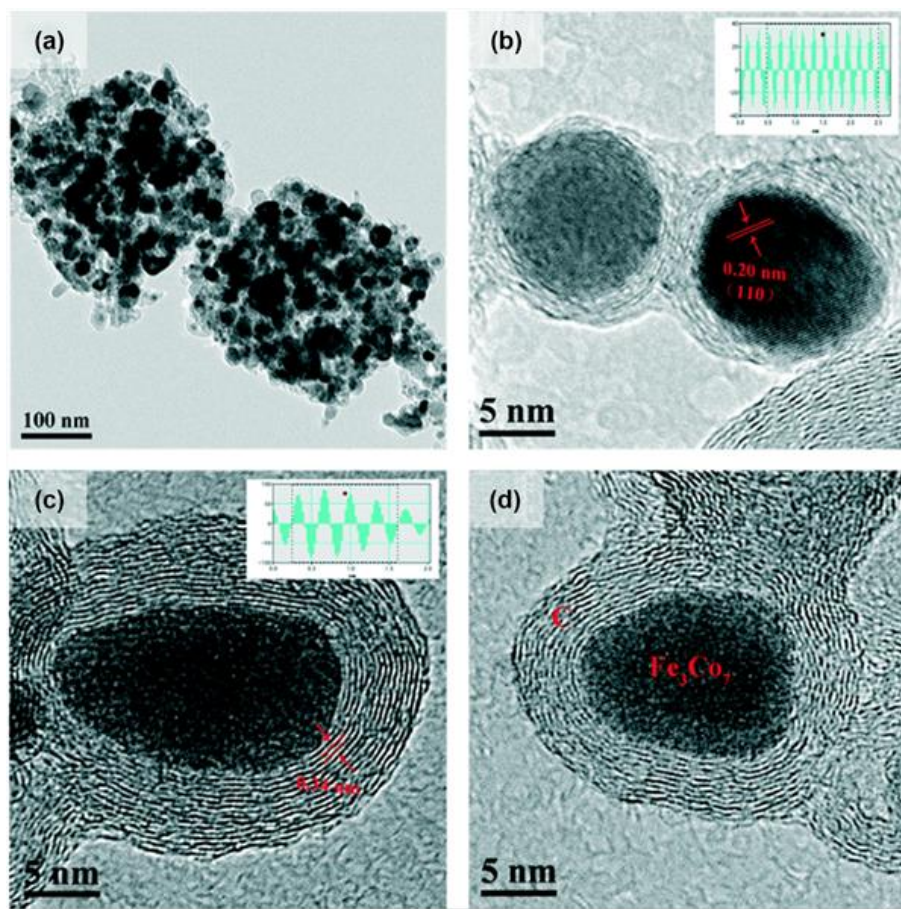


Figure 3.9 TEM image (a) and HR-TEM images (b, c, d) of $\text{Fe}_3\text{Co}_7@\text{C}-650$. Reproduced from ref. ⁴³ with permission from the Royal Society of Chemistry.

3.2.2.3 Nitrogen-doped MOF–GA Derivatives

Another effective strategy to enhance the performance of single-metal MOF–GA materials is to synthesize MOF–GA derivatives with a nitrogen-doped structure. By adding a nitrogen source to the MOF–GA precursor and calcining, a graphene carrier containing a nitrogen-doped structure is formed to improve the catalytic activity and stability of the material. These metal nanoparticles with special nitrogen coordination are embedded in GA after high-temperature calcination, which not only increases electronic conductivity, but also improves stability.¹⁶ A series of graphene-encapsulated transition metal nitrides (TMN) were prepared *via* thermal decomposition of MOF precursors at 650 °C in a N_2 atmosphere, and nitrogen-doped GA layers were derived from the $-\text{CN}$ groups of PBAs, which served as both a nitrogen and carbon source.⁴⁴ Likewise, multilayer core–shell nitrogen-doped composites $\text{Co}@\text{CoO}_x@\text{N-carbon-GA}$ were developed by Xing *et al.* *via* pyrolysis followed by controllable oxidation (Figure 3.10a).⁴⁵ With the addition of polyvinylpyrrolidone (PVP), nitrogen-doped composites ($\text{Co}@\text{N-carbon-GA}$) were obtained using Co-MOF-GA-PVP as the precursor to be calcined at 700 °C in N_2 . Then, CoO_x shells were generated through controllable oxidation of the composites at 200 °C in air and exhibited higher catalytic activity than their single-layer counterparts

in terms of hydrogen generation.⁴⁵ Porous N-Co₃O₄@N-C materials were synthesized *via* the pyrolysis of MOFs in N₂ at 550 °C and in air at 350 °C; then the materials were wrapped with GA through electrostatic interactions, followed by heating in N₂ to form the N-Co₃O₄@N-C-GA nanocomposites⁴⁶ (Figure 3.10b).

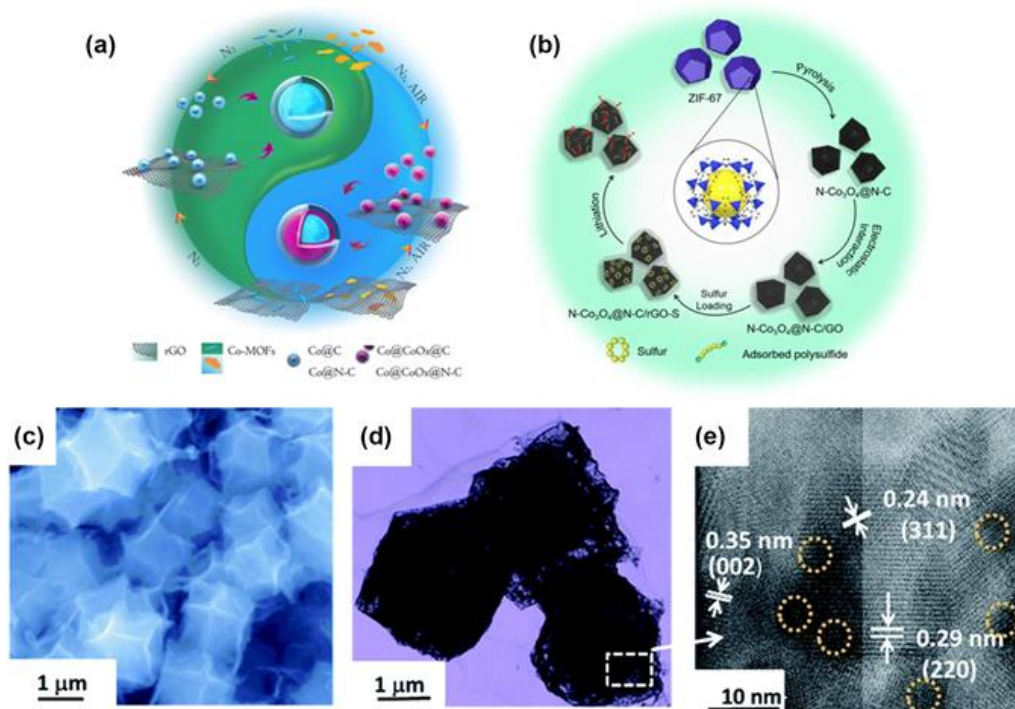


Figure 3.10 (a) Illustration of the stepwise structure evolution from Co-MOFs composites to Co@N-carbon-GA. Reproduced from ref. ⁴⁵ with permission from American Chemical Society, Copyright 2016. (b) Schematic illustration of the formation of N-Co₃O₄@N-C-GA. (c) FESEM, (d) TEM and (e) HRTEM images of N-Co₃O₄@N-C-GA. Reproduced from ref. ⁴⁶ with permission from the Royal Society of Chemistry, Copyright 2018.

In other reports, nitrogen-doped MOF-derived GA materials were prepared by pyrolysis of a mixture of additional nitrogen precursors (including dicyandiamide, melamine and urea) and MOF at 800 °C in a N₂ atmosphere.⁴⁷ In addition, bimetal oxide-GA nanocomposites were developed by Hao *et al.* Ni was introduced into the MOF-GA composites, followed by thermal treatment to form Ni-Co oxides supported on Co-N decorated GA (Ni_xCo_yO₄-Co-NG).⁴⁸ Moreover, porous metal-free graphene materials with hollow structures were obtained by acid leaching of MOF-GA derivatives. Carbon-GA materials with hollow structures were formed by pyrolysis of Co-MOF-GA at 750 °C in an Ar atmosphere, followed by leaching in hydrochloric acid at 80 °C.⁴⁹ Liang *et al.* heated a mixture of MOF and dicyandiamide at 800 °C under a N₂ atmosphere; then the unstable iron species were removed by H₂SO₄ at 80 °C to generate nitrogen-doped GA for the application of PMS activation (Figure 3.11).⁵⁰

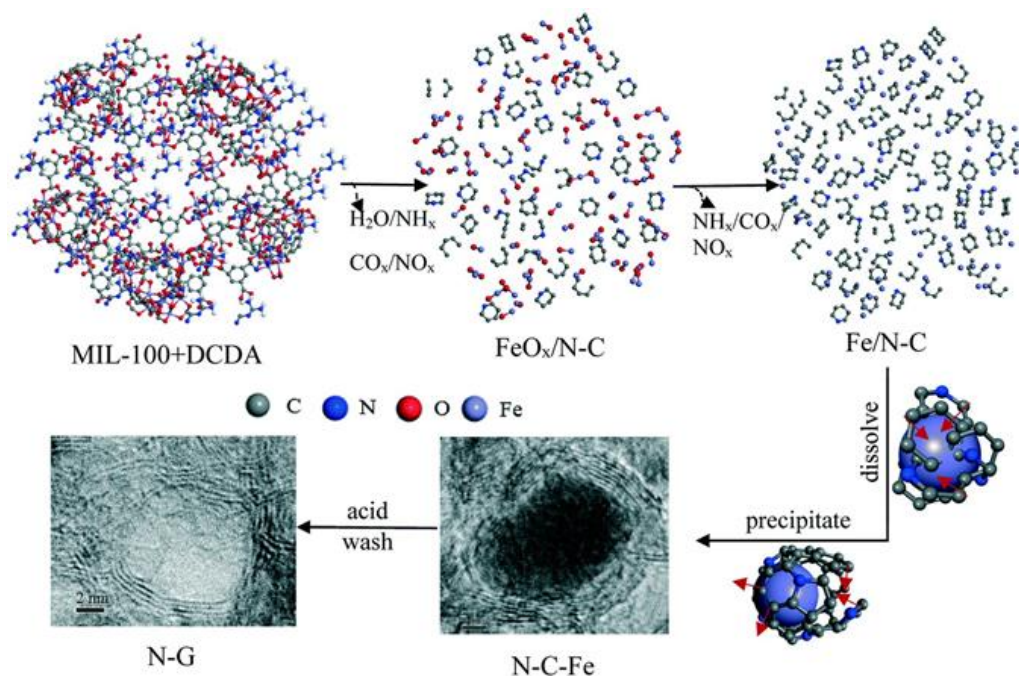


Figure 3.11 The formation mechanism of nitrogen-doped GA. Reproduced from ref. ⁵⁰ with permission from the Royal Society of Chemistry.

3.2.3 Enhanced Properties of MOF–GA Materials

It is well known that MOFs exhibit poor electrical conductivity, which limits their potential applications in the electrochemical field. The introduction of GA materials with good conductivity perfectly alleviates the defects of low conductivity of MOFs, and acts as an electronic bridge connecting the dispersed MOF and the GA materials to accelerate electron transfer between the MOFs and that between GA and the MOF.^{16,20} The improvement of MOF–GA material conductivity makes photochemical and electrochemical applications possible. In addition to poor electrical conductivity, structural instability is another challenge for MOF materials, which is caused by the weak coordination bond between the metal node and the organic ligand.¹⁶ The interaction between the MOFs and GA enhances the stability of materials ascribed to the formed unique hierarchical structures, which also act as the protection for MOFs to resist the complicated environmental medium during practical applications.⁴² In addition, the oxygen-containing functional groups on GA can bond with the metal center of the MOF to further enhance the stability of the material.¹⁰ From another perspective, GA with a large specific surface area is used as a mechanical carrier for MOF, allowing MOF crystals to be evenly dispersed on its surface, effectively preventing agglomeration. The promoted adsorption abilities of MOF–GA materials help to increase the detection sensitivity, reducing the detection limits. With functional ligands in MOFs and abundant oxygen-containing groups in GA materials, the materials are endowed with abundant surface chemical properties, providing the possibility to build selective and sensitive detection platforms based on different mechanisms, including colorimetry, fluorescence, electrochemistry, *etc.*

3.3 Sensing of Environmental Contaminants

As mentioned above, MOF–GA materials integrate the advantages of both MOFs and GA, which are embodied in the following aspects.^{51,52} (1) MOFs with high porosity and large specific surface area are conducive to the effective enrichment of analytes, amplification of response signal and improvement of detection sensitivity. (2) The cavities and available channels with special structure of MOFs can be selective to specific analyte by size repulsion effect. (3) The introduction of GA in MOFs not only improves the conductivity, but also can be used as the support of MOFs nanoparticles to prevent their agglomeration, which alleviates the problems of low conductivity and poor structural stability of MOFs. Therefore, MOF–GA materials have become an ideal sensor for sensing platforms for environmental contaminants.

In general, the detection of environmental contaminants by MOF–GA materials is mainly achieved through two mechanisms, namely optical and electrochemical. First, the florescence and luminescence performance of some MOF–GA materials make them the core for fabricating sensitive sensing platforms. Moreover, their high porosities and adsorption abilities make MOFs good hosts to adsorb and accumulate analytes for sensing. The luminescence occurs when electrons in excited singlet states return to the ground state *via* photon emission but the signal is attenuated or quenched upon the absorption of the analyte, which is known as the ‘turn-off’ mechanism.⁵³ Second, due to their high electrical conductivity, MOF–GA materials have been successfully applied in electrochemical sensing platforms. For electrochemical sensors, the accumulation of analytes affects the sensitivity of signals, which makes the mechanism sense environmental contaminants efficiently.^{54,55}

There are many kinds of contaminants in the environment, which can be divided into gaseous, organic compounds and inorganic ions. The reported use of MOF–GA materials as sensing platforms for multiple contaminants in the environment is summarized in Table 3.1.

Table 3.1 Summary of the sensing applications of MOF–GA composites and derivatives and of the methods applied for composite preparation.

Sample	Components		Preparation method	Contaminants	Detection method	Limit of detection	Ref.
GA	MOF						
Cu–BTC	Graphene	Cu–BTC	Self-assembly	Ammonia	Electrochemical	6.0×10^{-6} mM	⁵⁶
MOF–graphene hybrids							
Co ₃ O ₄ –FGH	GO hydrogels	ZIF-67	Self-assembly	Acetone gas	Electrochemical	1.0×10^3 ppb	⁵⁷
A-GO–L–Zn ²⁺	GO	Single crystal of L complex with Zn ²⁺	Self-assembly	TNT DNT	Fluorescence	TNT: 0.2×10^3 ppb DNT: 0.2×10^3 ppb	⁵⁹
Cu–BTC–ERGO–GCE	GO	Cu–BTC	<i>In situ</i> growth	2,4,6-trinitrophenol	Electrochemical	0.1×10^{-3} mM	⁶⁰
NH ₂ –MIL-	GO	NH ₂ –	<i>In situ</i>		Electrochemical	UA: $0.8 \times$	⁶¹

101(Fe)-GO		MIL-101(Fe)	growth		UA, XA, HX		10^{-5} mMXA: 0.4×10^{-5} mMHX: 0.3×10^{-4} mM	
NH ₂ -UiO-66-RGO	rGO	NH ₂ -UiO-66	Self-assembly	Cip		Electrochemical	6.67×10^{-6} mM	63
Cu-BTC@GS	Graphene	Cu-BTC	<i>In situ</i> growth		XA, HXA, BPA, CP	Electrochemical	XA: 1.1 ppb HXA: 7.3 ppb BPA: 1.2 ppb CP: 1.9 ppb	64
GA-UiO-66-NH ₂	Graphene aerogel	UiO-66-NH ₂	<i>In situ</i> growth		Cd ²⁺ , Pb ²⁺ , Cu ²⁺ , Hg ²⁺	Electrochemical	Cd ²⁺ : 9×10^{-6} mM Pb ²⁺ : 1×10^{-6} mM Cu ²⁺ : 8×10^{-6} mM Hg ²⁺ : 0.9×10^{-6} mM	66
GQDs: Eu-ZIF-8	GQDs: Eu	ZIF-8	<i>In situ</i> growth	S ²⁻		Fluorescence	0.12×10^3 ppb	70

3.3.1 Detecting Gaseous Contaminants

Gaseous contaminants are caused by a large amount of waste gas being discharged into the atmosphere, such as ammonia (NH₃), acetone, formaldehyde, *etc.*, which seriously affects the quality of the atmospheric environment. The special pore structure of MOF-GA materials can absorb a large number of gas molecules, which makes it very suitable for gas detection. Thereby, many studies have been devoted to the use of MOF-GA materials for the detection of gaseous pollutants. For example, Cu-MOF-GA materials were prepared by Bandosz's group with Cu-based MOFs and graphene, and the materials were applied to detect NH₃ at low concentrations in dry air (Figure 3.12a).⁵⁶ The synergistic effects of MOF and GA improved the conductivity, porosity and chemistry of the materials with good charge carrier mobility. When exposed to NH₃, the structures of materials consisting of MOF crystals with embedded GA layers were destroyed due to the adsorption reaction, resulting in the collapse of the MOF units, which lead to electrochemical signals due to the increased

material resistivity.⁵⁶ The reliability of Cu-MOF-GA materials for detecting NH_3 was therefore first validated.

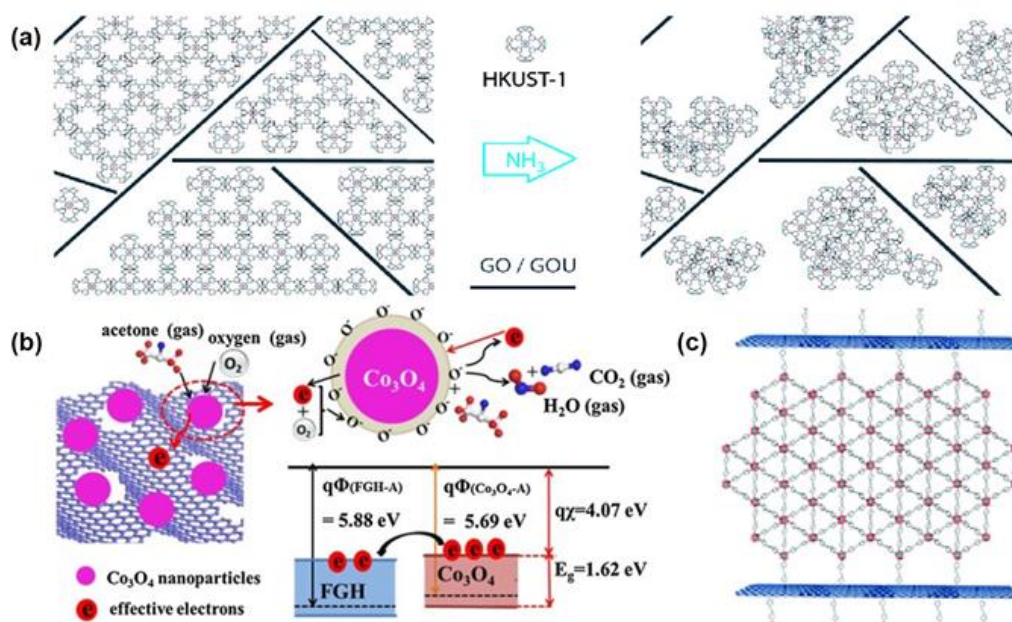


Figure 3.12 (a) Crystal structure of Cu-MOF-GA and changes in the texture of the hybrid materials upon exposure to NH_3 . Reproduced from ref. ⁵⁶ with permission from the Royal Society of Chemistry. (b) Schematic illustration of the acetone sensing mechanism for Co_3O_4 -GA. Reproduced from ref. ⁵⁷ with permission from Elsevier, Copyright 2018. (c) Schematic of the proposed bonding of MOF-GA. Reproduced from ref. ⁵⁹ with permission from the Royal Society of Chemistry.

Acetone, one of the volatile organic compounds (VOCs), is the most commonly used chemical reagents in industry and laboratories and is usually regarded as a breath biomarker of diabetes patients.⁵⁷ Therefore, the detection of acetone is important for environmental monitoring and personal safety protection. Ding *et al.* fabricated functionalized GA that were decorated with MOF-derived Co_3O_4 nanostructures (Co_3O_4 -GA) to detect acetone in air with a detection limit as low as 1.0×10^3 ppb. In addition, the Co_3O_4 -GA material showed an excellent selectivity in the presence of other interfering gases (ethanol, carbon dioxide, oxygen, ammonia, methane). The good sensing property of the Co_3O_4 -GA material was attributed to the unique porous structure allowing the easy access of acetone gas to Co_3O_4 and the interaction area between Co_3O_4 and acetone was increased.⁵⁷ (Figure 3.12b). Moreover, the detection limit of Co_3O_4 -GA synthesized by Xiong *et al.* for acetone can be as low as 50 ppb, which can be attributed to the high-speed gas transfer pathways provided by the special pore structure of MOF-GA.⁵⁸

Similarly, the fluorescence and luminescence characteristics of MOF-GA materials can also effectively detect gaseous contaminants. Lee *et al.*⁵⁹ fabricated a luminescent MOF functionalized GA nanocomposite to detect explosive gas (dinitrotoluene (DNT) and trinitrotoluene (TNT)) (Figure 3.12c). The nanocomposites were obtained by assembling azobenzoic acid-functionalized GA, *trans*-4,4'-stilbene dicarboxylic acid (H_2L) and Zn^{2+} , combined with a structure of alternating GA layers

and MOFs layers. Ascribed to the high photoluminescence quantum yield, the H₂L materials were chosen as linkers. In the complex, the low density and regularity of the MOFs enhanced the interaction between linkers and DNT or TNT. The photoluminescence quantum yield of the stilbenes decreased significantly during light-induced *trans-cis* isomerization. When this isomerization mechanism was suppressed, and the quantum yield theoretically approached 100%. In the nanocomposites, the H₂L linkers on the MOF structure were much more stabilized with the addition of GA layers compared to pure L with Zn²⁺, which suppressed the isomerization mechanism, broadening the quantum yield greatly. After the MOF–GA nanocomposites were exposed to explosive vapors, fluorescence of the nanocomposites was quenched due to charge-transfer interactions between the electron-deficient aromatic rings of DNT and the electron-rich aromatic groups of L.

3.3.2 Detecting Organic Contaminants

Organic contaminants have become one of the most critical environmental problems due to their recalcitrance and persistence in the environment. Organic dyes, medical drugs, and industrial organic chemicals are all typical organic contaminants. Therefore, the detection of organic contaminants is vital for environmental monitoring and chemical control in industrial fields. Recently, MOF–GA derivatives have gained great attention in the sensing field due to their excellent high conductivity. For example, an effective electrochemical sensing platform was fabricated to detect 2,4,6-trinitrophenol (TNP) *via* electrodepositing the Cu-MOF and the GA on a GCE, with a wide linear range from 0.2 to 10×10^{-3} mM and a detection limit of 0.1×10^{-3} mM.⁶⁰

PPCPs are an emerging class of organic contaminants that can have harmful effects on organisms even at low doses. Therefore, many sensors based on MOF–GA have been reported for the detection of PPCPs in water. Fu *et al.* pre-synthesized MOF NH₂–MIL(101)–Fe covalently connected with GA using ultrasonication treatment. The nanohybrids were electrochemically reduced on the surface of GCE to detect three purine metabolic derivatives successfully with ultra-stable and sensitive performance, including uric acid (UA), xanthine (XA), and hypoxanthine (HX).⁶¹ Similarly, an electrochemical sensor was fabricated on a GCE with GA nanoribbons and *in situ* growth of the MOF. The modified electrode was applied in the sensing of Imatinib (an anticancer drug) with a limit of detection of 6 nM and exhibited a good linear electrochemical relationship.⁶² In addition, an electrochemical sensing platform was fabricated with a Zr-based MOF NH₂–UiO-66 and GA composite as working electrodes to determine ciprofloxacin (Cip) *via* an anodic stripping voltammetry method with the assistance of Cu²⁺ (Figure 3.13). Cip can complex with Cu²⁺, thus the oxidization current of Cu²⁺ would decrease in the presence of Cip. The detection limit was 6.67×10^{-6} mM, and the linear working range was 0.02 to 1×10^{-3} .⁶³

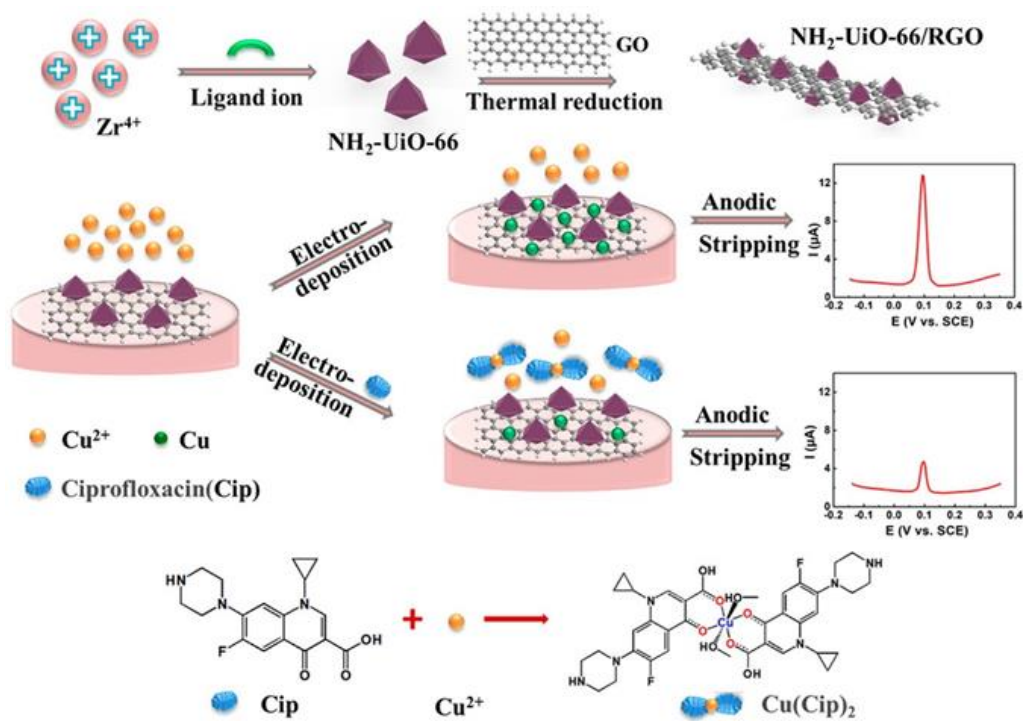


Figure 3.13 Schematics of the $\text{NH}_2\text{-UiO-66-RGO}$ synthesis procedure and the electrochemical detection of ciprofloxacin with the aid of Cu^{2+} . Reproduced from ref. ⁶³ with permission from American Chemical Society, Copyright 2019.

MOF-GA materials also play an important role in the sensing of industrial organic chemicals. For example, MOF-GA composites were synthesized through thermal annealing of Ni-BTC MOFs.⁶⁴ An electrochemical sensing platform was fabricated based on Ni@graphene composites with magnetic GCE (C-SNi@G-MGCE) to detect hydroquinone and catechol, showing the advantages of binder-free and easy preparation routes.⁶⁴ Compared to the bare MGCE, the better electrocatalytic activities toward the oxidation and reduction of hydroquinone and catechol were observed due to the larger active areas and faster electron transfer abilities of the C-SNi@G-MGCE. In another work, ball-milled exfoliated GA with high conductivity was integrated with an *in situ* synthesized Cu-based MOF on the surface of the GCE to build a sensitive electrochemical sensing platform. The sensing platform was applied to detect biomolecules (XA and HX) and phenolic pollutants (bisphenol A (BPA) and *p*-chlorophenol (CP)) with enhanced sensitivity and increased response signals.⁶⁵

3.3.3 Detecting Inorganic Ion Contaminants

Inorganic ions in the water environment can be divided into cations and anions. Among them, inorganic cations mainly refer to heavy metal ions, such as Pb^{2+} , Cd^{2+} , Cu^{2+} and so on. While, the inorganic anions mainly refer to NO_2^- , NO_3^- , S^{2-} , PO_4^{4-} , etc. The following sections will discuss the application of MOF-GA materials in inorganic ion detection from two aspects: cations and anions.

3.3.3.1 Inorganic Cationic Contaminants

Heavy metal ions are the most widely distributed and harmful and non-biodegradable contaminants in the water environment. These heavy metal pollutants, even at trace levels, are considered highly

toxic and endanger human health. However, according to the current research literature, few studies are devoted to the application of MOF–GA materials to heavy metal detection in water environments. Lu *et al.* developed an electrochemical method based on GA and MOF composites for the simultaneous detection of multiple heavy metal ions (Cd^{2+} , Pb^{2+} , Cu^{2+} and Hg^{2+}) in aqueous solutions.⁶⁶ The introduction of GA enhances the electron transfer in the MOF–GA composite, while the hydrophilic group of MOF promotes the interaction with the heavy metal cation, which improves the selectivity and sensitivity of the MOF–GA composite to allow heavy metal ion detection. The research results show that the detection limit of MOF–GA materials for heavy metal ions can reach 9×10^{-6} mM for Cd^{2+} , 1×10^{-6} mM for Pb^{2+} , 8×10^{-6} mM for Cu^{2+} , and 0.9×10^{-6} mM for Hg^{2+} . In addition, in another study Wang *et al.* established a ratiometric electrochemical sensing method for a ferrocenecarboxylic acid (Fc)-functionalized MOF and GA composite to simultaneously detect Cd^{2+} , Pb^{2+} and Cu^{2+} .⁶⁷ Among them, the introduction of Fc can be used as an internal reference for ratiometric detection, which improves the reproducibility and reliability of electrochemical detection. Thus, it can be seen that the MOF–GA material has application potential and broad prospects for the detection of multiple heavy metal pollutants in the water environment.

3.3.3.2 Inorganic Anion Contaminants

As we all know, nitrite has become a ubiquitous anionic contaminant in the water environment and causes a variety of human health problems.⁶⁸ According to their report, Saraf's group synthesized a multifunctional Cu-MOF–GA composite by ultra-sonication of slow diffusion-driven Cu-MOF crystals and GA, achieving the electrochemical sensing of nitrite. The MOF–GA composite showed higher sensitivity with the faster electron transfer rate in the electro-oxidation of nitrite, which was attributed to the synergistic effects between the pseudocapacitive Cu-MOF and the electric double layer capacitive GA (Figure 3.13a). A wide linear relationship ranging of 3–40 000 μM was observed with a detection limit of 33×10^{-6} mM.⁶⁸ Chen *et al.* incorporated GA with an average size of 3.1 nm into a mesoporous porphyrinic Zr-MOF *via* direct impregnation. After incorporation, the donor–acceptor charge was transferred from GA to the porphyrinic linkers, which increased the electrical conductivity of the material compared to that of the pristine MOF and GA; nitrite in aqueous solutions was electrochemically detected selectively and sensitively by the MOF–GA material.⁶⁹

On the other hand, the fluorescence characteristics of MOF–GA can also be effectively used to detect anionic contaminants. For example, a fluorescence turn-on sensor for sulfide ions (S^{2-}) was developed using europium-doped GA with a MOF.⁷⁰ The GA was prepared by a solvothermal approach (< 10 nm in diameter). The MOF–GA composites showed better fluorescence signals compared to the GA due to a better separation and dispersion of GA nanocomposites, owing to the host guest interaction caused by the matrix structure of MOF nanocomposites. When the concentration of MOF nanocomposites exceeded the saturation level, the fluorescence intensity decreased with the scattering of light; but, the addition of S^{2-} counteracted agitation and light scattering, restored and enhanced the fluorescence signal and further promoted the separation of GA. Accordingly, a fluorescence turn-on sensor for S^{2-} was successfully constructed with a detection limit of 0.12×10^3 ppb (Figure 3.14b).

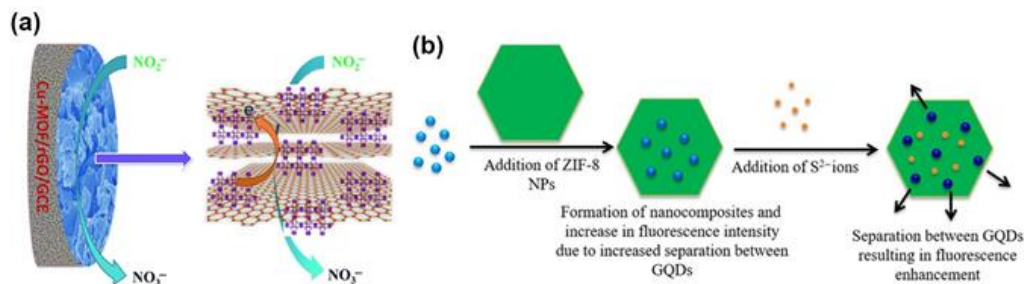


Figure 3.14 (a) Schematic of the nitrite sensor. Reproduced from ref. ⁶⁸ with permission from the Royal Society of Chemistry. (b) Schematic of S^{2-} sensing by GA based on an indirect approach involving FL enhancement through the separation of GA in the MOF matrix. The addition of S^{2-} ions to MOF–GA solution resulted in further enhancement of the GA FL intensity. Reproduced from ref. ⁷⁰ with permission from the Royal Society of Chemistry.

3.4 Conclusions and Perspectives

Environmental pollution seriously threatens the ecosystem and the health of human beings. Therefore, the establishment of sensitive and selective sensing platforms is of great significance for monitoring and controlling contaminants, and the primary goal is to develop advanced and suitable materials to fabricate sensors with high response signals and sensitivity. As noted above, MOF–GA materials synthesized by self-assembly, *in situ* growth, and layer-by-layer deposition and further modified by various calcination strategies are considered to be promising materials, exhibiting unique structures and superior chemical and mechanical properties, including enhanced stability, accelerated electron transport, increased charge carrier and promoted surface chemical properties. Moreover, these materials have been applied successfully in the application of sensing for environmental contaminants, such as gaseous contaminants, organic compounds, inorganic ions and biochemical molecules, with high response signals and selective and sensitive behaviors.

However, there are still several key aspects that need further study. First of all, due to the possibility of leaching, the potential toxicity of the material is one of the key issues that must be considered. Even though these nanomaterials exhibit excellent performance in pollutant monitoring and sensing, the leached materials may be released into the environment and affect human health. While monitoring pollutants in the environment, we should also pay attention to whether these materials will cause secondary environmental pollution. Another significant challenge regarding the MOF–GA is how to maintain the long-term effectiveness of materials in complex environmental media. Compared with the simple media commonly used in laboratory research, the complex media in the environment may cause interference and affect the monitoring sensitivity of materials, which puts forward high requirements for the stability of materials in complex environmental media. Therefore, in order to design and manufacture composite nanosensors with specific functions and more stability, it is necessary to deeply understand and consider the synthesis mechanism of MOF–GA. Last but not least, many new scientific advances have raised inflated expectations, but most of the current research is conceptual and not commercially available. Future research must focus on addressing industrial needs and practical problems, realizing the transformation of scientific research to technological and commercialization, which would benefit the entire society.

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Chapter 4

Nano Meets Membrane: Toward Enhancing the Performance of Water Treatment

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4.1 Introduction

Water shortage has become a global crisis nowadays.¹ The United Nations claimed “clean water and sanitation” as one of seventeen global development goals² (also see <https://www.un.org/sustainabledevelopment/>). A countermeasure for remitting such a crisis is to recover as much as clean water from sewage *via* water treatment. Among lots of approaches, nanotechnology and membrane technology are emerging rapidly. Nanomaterials (NMs) can act as adsorbents (*e.g.* activated carbon for adsorption) or catalysts (*e.g.* ferric NMs for Fenton-like catalysis) for

contaminant removal, and membranes can reject pollutants and let only water pass through.

Membrane technology can be roughly divided into two parts, pressure-driven processes and non-pressure-driven processes. The pressure-driven processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). According to this order, the pores on the corresponding membrane are smaller and smaller, resulting in lower and lower flux (see Figure 4.1). The non-pressure-driven processes usually refer to membrane distillation (MD), pervaporation (PV) and forward osmosis (FO).

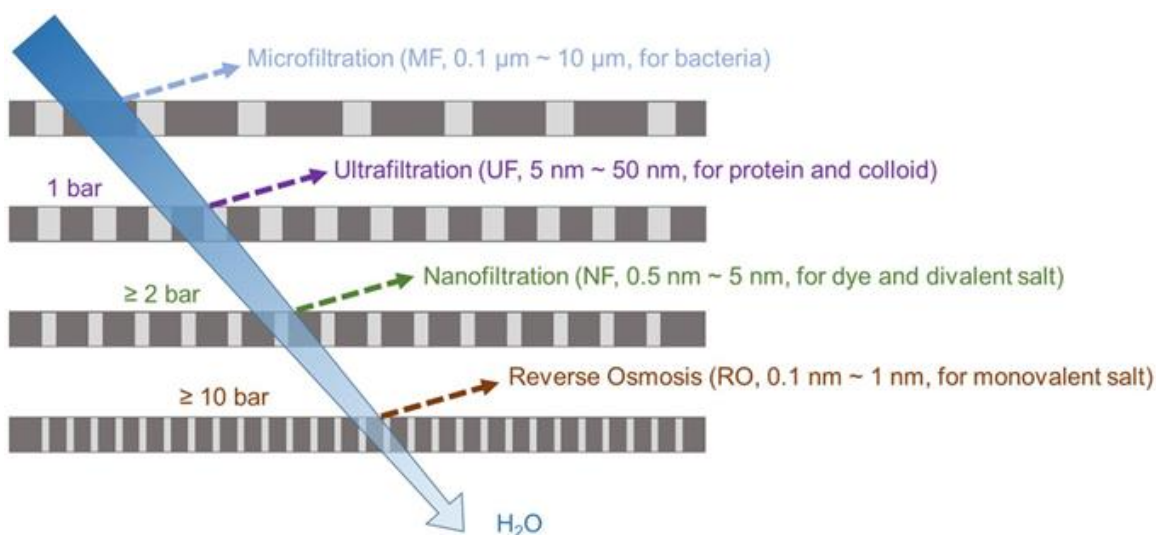


Figure 4.1 Schematic illustration of MF, UF, NF and RO technologies.

However, membranes always suffer a trade-off between the membrane permeability and selectivity. Promoting solute rejection seems to inevitably cause permeability decline. Membrane researchers have been working on breaking such a trade-off for a long time. Enhancing permeability and selectivity simultaneously is always very attractive but hard to achieve. Li's team added poly (ethylene imine) (PEI) into dope solutions to tailor the thermodynamic properties and kinetics during a non-solvent induced phase separation (NIPS) process.³ At an appropriate PEI dose, the resulting poly (ether sulfone) (PES) UF membrane can showcase synchronous elevation in permeability and selectivity compared with the non-PEI counterpart.

Seeing the potential of NMs in water treatment, scientists have tried combining NMs with membranes to enhance the water treatment efficiency. In membrane production, NMs can be involved in the fabrication process such as the dopant solution and crosslinking system. In water treatment process, NMs are also applied, *e.g.* as the draw agent in FO process. This chapter will focus on the marriage between NMs and polymeric membranes and try to illustrate this from multiple angles. We will illuminate how NMs enhance pressure-driven processes (including UF, NF and RO process), then have a brief review on NMs assisted non-pressure-driven processes (including MD, PV and FO process) and finally give our summary and perspectives.

4.2 NM-enhanced UF Performance

As a most common methodology, NIPS has been extensively used for polymeric UF membrane preparation. Briefly, polymeric materials, together with additives (sometimes not), are dissolved into polar organic solvents to prepare a dope solution. Such a dope solution is cast into a thin film with a thickness of hundreds of microns on a clean flat platform subsequently (immediately or after the point of solvent evaporation), the thin film-loaded flat is immersed into a coagulation bath to trigger the phase separation process, and finally a piece of polymeric membrane is solidified. There is flexibility for researchers in choosing the timing of NM introduction into the UF membrane, *i.e.* before or after the manufacture of membranes. The three most popular approaches are stated here and all of them are aimed at enhancing UF performance.

4.2.1 Binding NMs Upon Membrane Surfaces

The binding method requires a substrate, NMs and binding agent owing to the usually weak interactions between NMs and polymeric UF membranes. Binding NMs with membranes has proven useful in tailoring the surface properties of membranes, and thus enhancing the UF performance. With this strategy, NMs can be fully exposed to the water environment rather than partially entrapped in the membrane matrix, so the functions of the NMs can be totally performed. Moreover, this approach mainly affects the

membrane surface, the membrane bulk structure isn't changed much. This gives people a chance to further improve the performance of commercial UF membranes.

A key point here is the binding agent as it bridges the substrate and NMs. Once NMs are tightly bound with polymeric UF membranes *via* binding agents, NMs endow UF membranes with extra optimization, *e.g.* improved permselectivity and elevated anti-bacterial properties, depending on the particular properties of NMs. Titanium dioxide (TiO_2) has been proven effective in enhancing membrane permeability.^{4,5} However, the aggregation of TiO_2 in membrane fabrication limits its optimization of membranes. To avoid this drawback, He's group bound TiO_2 upon functionalized PVDF membrane surfaces.⁶ They treated PVDF membranes with potassium hydroxide (KOH) followed by sodium bisulfite (NaHSO_3) and sulfuric acid (H_2SO_4) to plant hydroxyl groups ($-\text{OH}$) on the membrane. Then, the $-\text{OH}$ grafted membrane was immersed into a trimesoyl chloride (TMC)/*n*-hexane solution to further graft TMC on the membrane surface. A $-\text{OH}$ group can catch a TMC molecule *via* reacting with an acyl chloride group ($-\text{COCl}$) on TMC. The $-\text{OH}-\text{TMC}$ moieties are regarded as binding agents here. Afterward, the membrane was immersed into a TiO_2 suspension to bind TiO_2 onto the membrane surface. A TMC molecule has three $-\text{COCl}$ groups, thus spare $-\text{COCl}$ bound to the TiO_2 NMs, which usually have abundant $-\text{OH}$ groups on the surface. Further crosslinking was measured using polyvinylalcohol (PVA) and glutaraldehyde (GA) (Figure 4.2). Owing to the binding agents, 'TiO₂ boats' were anchored solidly in the 'PVDF sea' so that the NM aggregation was efficiently avoided. With TiO_2 binding, the PVDF- TiO_2 -PVA membrane exhibited much better hydrophilicity than the pristine PVDF membrane. The uniformly-bound TiO_2 NMs tend to induce the formation of a dense and stable hydration layer on the membrane surface and thus increase the fouling resistance.⁷ Meanwhile, the PVA crosslinked layer blocked or narrowed the membrane pores. Hence, compared with unmodified PVDF membranes, the resulting PVDF- TiO_2 -PVA membrane manifested enhanced permeability to water, promoted

rejection to bovine serum albumin (BSA) and an elevated anti-fouling performance.

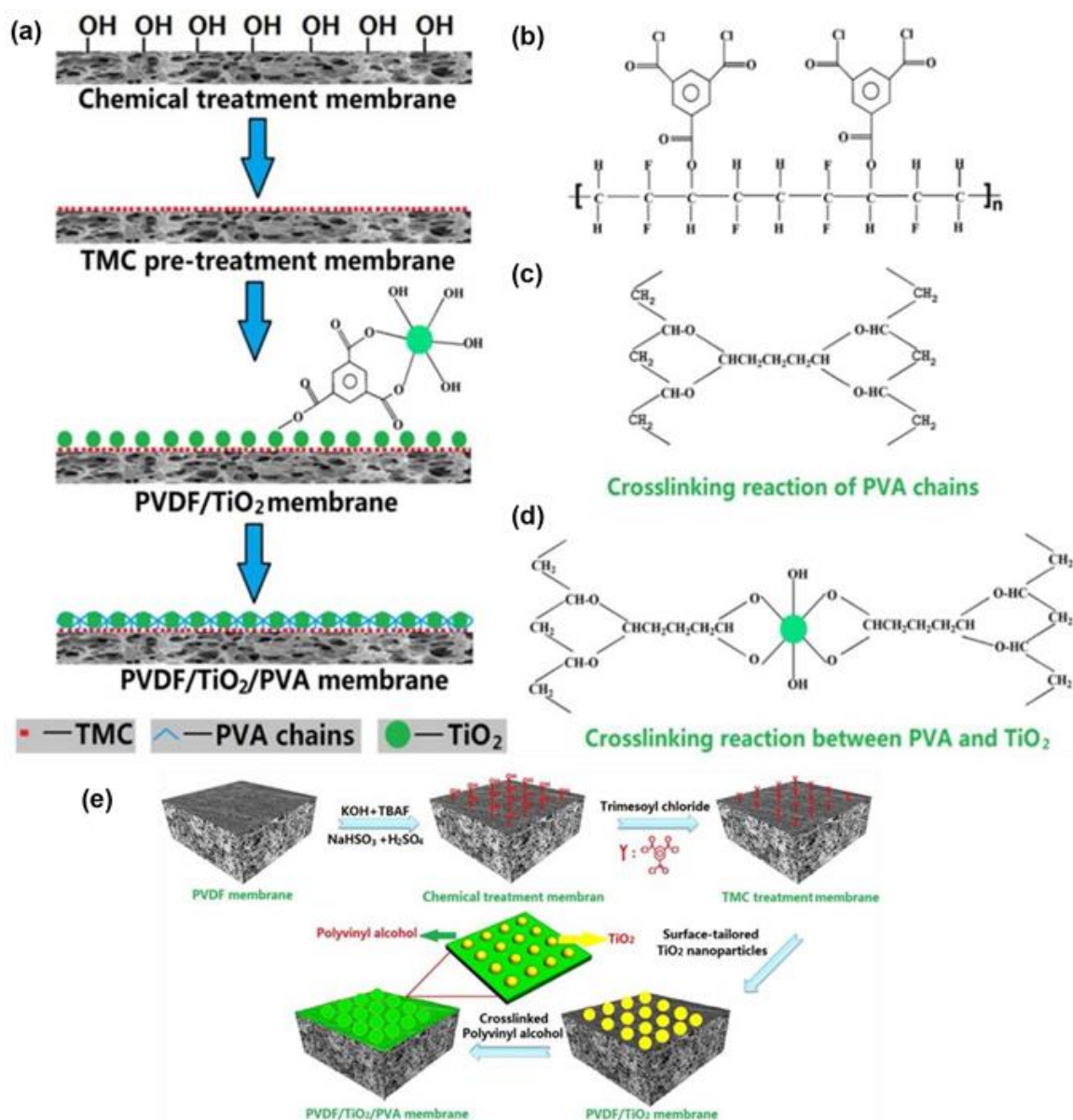


Figure 4.2 Proposed mechanism of PVA layer and TiO₂ nanoparticle binding process: (a) binding process of the PVA layer and TiO₂ nanoparticles; (b) reaction between the chemically treated membrane and TMC; (c) cross-linking reaction of PVA chains; (d) cross-linking reaction between PVA and TiO₂ nanoparticles; (e) 3D schematic illustration of the PVDF membrane surface modification. Reproduced from ref. ⁶ with permission from American Chemical Society, Copyright 2015.

Modifying the substrate to graft some functional groups as binding agents has another advantage in membrane fabrication, that is to protect the NMs from leaching during the membrane filtration. Because the coordination between NMs and the membrane matrix is strong. Silver nanoparticles (Ag NPs) are well known as microorganism killers. In order to tightly bind silver with membranes, Bandyopadhyaya's team introduced a binding agent *via* functionalizing the polymeric substrate.⁸ They sulfonated a PES substrate with concentrated H_2SO_4 to generate sulfonic acid groups ($-\text{SO}_3\text{H}$) as the binding agent. Subsequently, silver ions were bound by $-\text{SO}_3\text{H}$. Afterward, citrate was employed to reduce Ag^+ to Ag NPs in the presence of UV light (Figure 4.3). With optimized operation parameters (e.g. acid concentration and reaction duration), Ag NP-impregnated sulfonated PES (SPES) membranes without pore blockages were obtained. The as-prepared Ag-SPES membrane exhibited better anti-biofouling performance than the pristine PES membrane. When filtering *Escherichia coli* (*E. coli*) containing aqueous solutions, pristine PES membranes suffered from pore blockage brought about by *E. coli* attachment, while the Ag-SPES membrane killed the Ag-contacted cells, thus the membrane pores were less blocked. As a result, the PES and Ag-SPES membranes exhibited a flux decline of 80.4% and 14.7%, respectively. Moreover, thanks to the $-\text{SO}_3\text{H}$ binding, Ag stayed stable in the Ag-SPES membrane. The Ag release in both permeate and feed was no more than $10\text{ }\mu\text{g L}^{-1}$, which is obviously lower than the $100\text{ }\mu\text{g L}^{-1}$, World Health Organization (WHO) recommended limit for potable water.

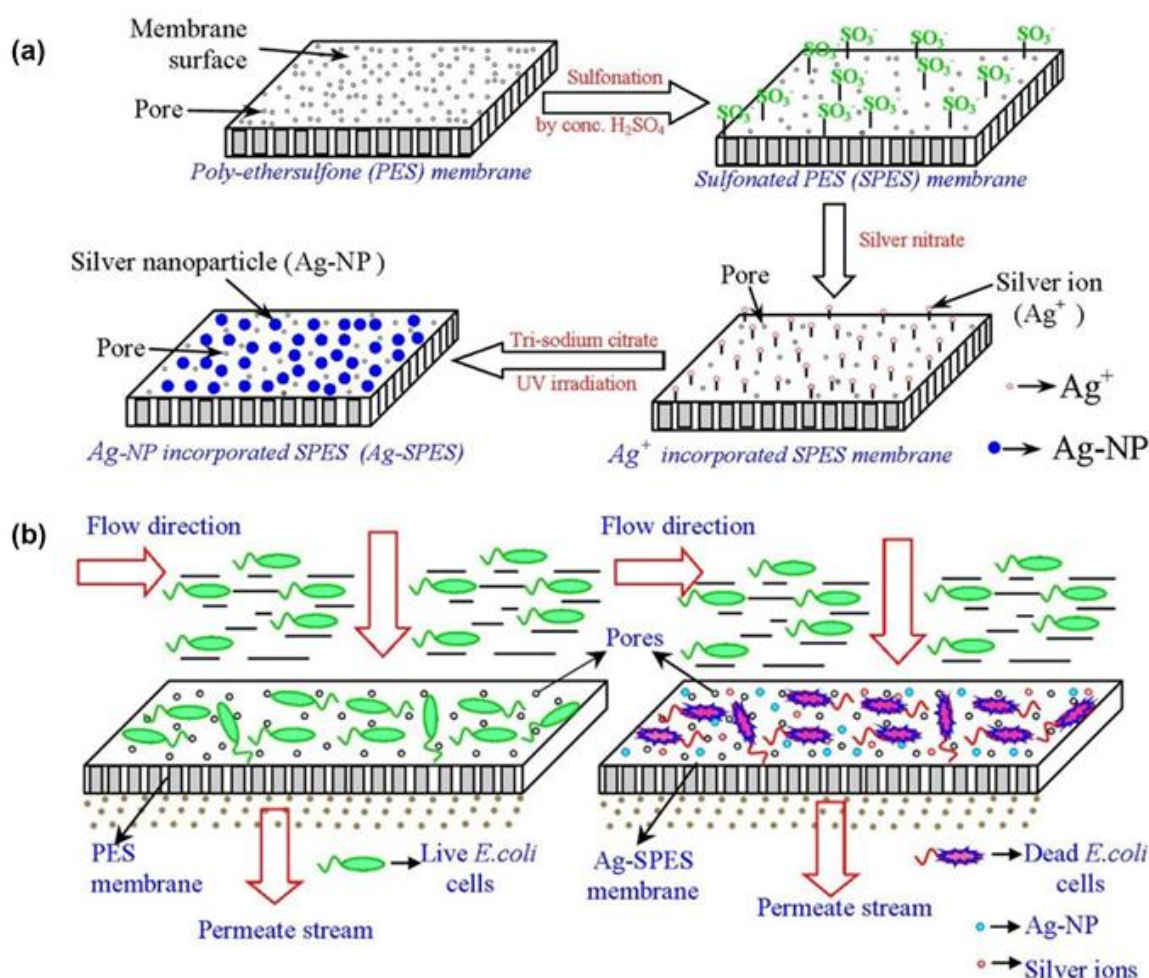


Figure 4.3 (a) Schematic representation of the sulfonation of a poly (ether sulfone) (PES) membrane followed by attachment of silver ions (Ag^+) and formation of Ag nanoparticles (AgNPs) via a UV-reduction method. (b) The killing of bacteria using a Ag-SPES membrane. Reproduced from ref. ⁸ with permission from Elsevier, Copyright 2017.

However, the above-mentioned formations of binding agent usually require harsh conditions (e.g. KOH and H_2SO_4) and this may confine the NM modification to UF membranes on a large scale. Attention has shifted to the NM itself. If a functional coating with adhesive force can be used to decorate NM and then glue it to a membrane, the conditions of whole manufacture will be milder. For instance, ferroferric oxide (Fe_3O_4) is also a fully inorganic NM, it has weak interaction with polymeric cellulose acetate

(CA) membranes. Low and coworkers coated Fe_3O_4 NMs with poly (diallyldimethylammonium chloride) (PDDA), a water-soluble cationic polyelectrolyte (denoted as f- Fe_3O_4 -PDDA).⁹ The f- Fe_3O_4 -PDDA NM suspension was dispersed onto a CA support to form a stable homogeneous thin film NM. Interestingly, the f- Fe_3O_4 -PDDA NM provides the membrane with good potential of humic acid (HA) fouling detachment. As Fe_3O_4 is magnetically responsive, an oscillating magnetic field can actuate the NM from the randomly oriented to a single direction. As a result, the magnetic field-induced Fe_3O_4 twisting detaches the HA fouling from the membrane surface. Moreover, the HA fouling detached membrane retained more than 85% of HA rejection, manifesting efficient fouling suppression.

As the function of retention is achieved by the rejection layer of membranes, traditional NMs are usually regarded as ‘ornaments’ on the membrane surface. In fact, some special NMs themselves can act as the rejection layer, such as two-dimensional (2D) NMs. Assembling 2D NMs to form a rejection layer has rapidly emerged as a hot research topic in the past few years.¹⁰ Generally, 2D NMs can be assembled as a rejection layer in two ways: (1) using one or a few layers of porous 2D NMs to sieve molecules; (2) stacking 2D nanosheets into laminates so that the interlayer channels can be regulated for molecule transport.² For the first method, the membrane pores are provided by either intrinsically porous structures (*e.g.* metal–organic frameworks (MOFs) and covalent organic frameworks (COFs)) or acquired drilling technologies (*e.g.* bombard graphene with ions¹¹). Although breakthroughs were made,^{12,13} big challenges still remain in this area. Technologies for exfoliating three-dimensional (3D) NMs into 2D nanosheets are limited. Moreover, scaling the several-atom-thick membranes to large areas with sufficient mechanical strength is troublesome. In comparison, stacking 2D nanosheets into laminates is much easier. In this mode, the interlayer spacing can be regarded as the membrane pore size and it can be tailored in many ways. Narrow enough interlayer spacing can exclude small ions for NF/RO, and suitable stacking also provides UF. Sun's team bound 2D kaolin nanosheets upon porous CA microfiltration (MF) membranes *via* a layer-by-layer approach.¹⁴ They dip-coated cationic polyacrylamide (CPAM) on the CA MF membrane and then

grafted 2D kaolin nanosheets by filtrating a kaolin aqueous suspension. Such steps were repeated 10 times to obtain multilayered 2D kaolin nanosheet membranes (see Figure 4.4). The as-prepared kaolin membrane remained stable under ultrasonic treatment, indicating its superb structure stability. Thanks to the hydrophilic nature and anti-compaction property of the rigid 2D kaolin nanosheets, the kaolin membrane exhibited an initial flux ($\sim 4000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (LMH bar^{-1})) that was approximately 10 times as that of the commercial PES UF membrane ($\sim 400 \text{ LMH bar}^{-1}$). Meanwhile, the kaolin membrane achieved similar selectivity to the commercial PES UF membrane in HA and BSA removal, demonstrating the usability of binding 2D NMs onto substrates to assemble UF level membranes. To accomplish rational NMs binding for UF, the methodology should ensure the structural stability of the entire membrane, avoid the aggregation of NMs and maximize the extra function which is brought by NMs.

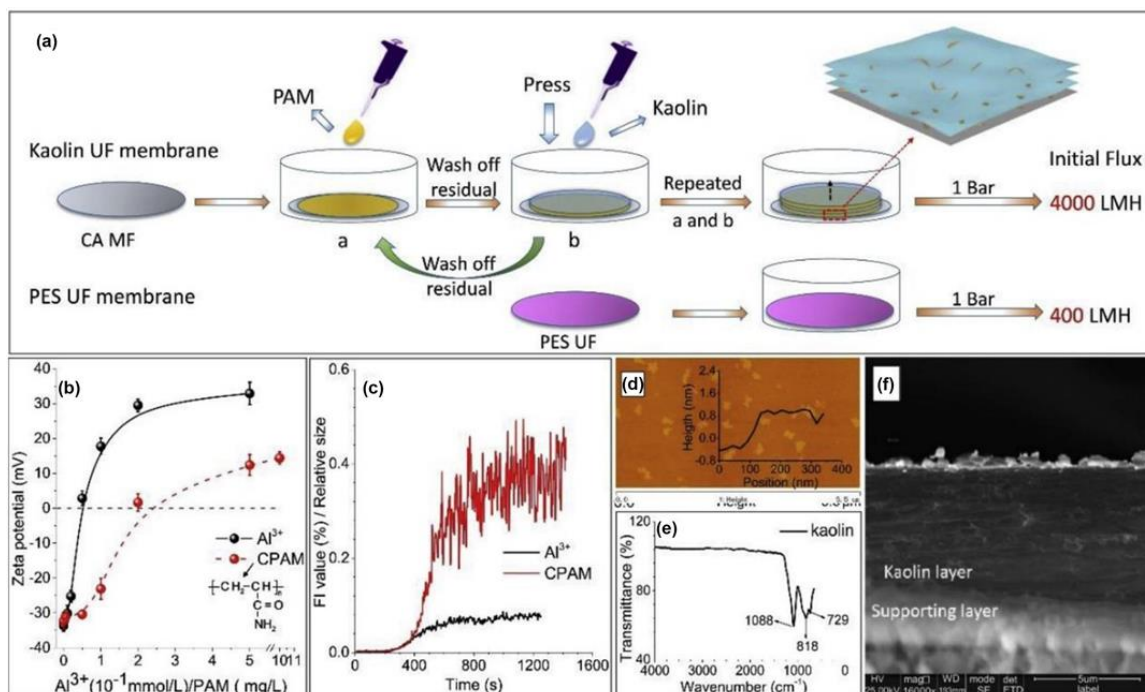


Figure 4.4 (a) The fabrication of kaolin membranes; (b) zeta potential and (c) floc size (FI) with the addition of CPAM and Al^{3+} at their respective doses of zero zeta potential; (d) AFM image and (e) FTIR-ATR spectrum of the kaolin sheets; (f) SEM cross-section

4.2.2 Blending NMs with the Membrane Matrix

Binding NMs onto membranes to optimize UF performance always requires a pre-synthesized substrate, which inevitably complicates the UF membrane manufacture. The manufacture has to be divided into two steps: (1) substrate fabrication; (2) NMs binding. In comparison, blending NMs with the membrane matrix can simplify the formation of NM-containing UF membranes within a single step. Commonly, polymeric UF membranes are produced *via* the classic NIPS method. Firstly, at least one polymer as the membrane matrix, *e.g.* PES, polysulfone (PSf), poly (acrylo nitrile) (PAN) and poly (vinylidene fluoride) (PVDF) is dissolved in an organic solvent (*e.g.* dimethylformamide (DMF), Dimethylacetamide (DMAc) or 1-methyl-2-pyrrolidinone (NMP)) to form a homogeneous dope solution. Sometimes, water-soluble additives *e.g.* poly (vinyl pyrrolidone) (PVP), poly (ethylene glycol) (PEG) and lithium chloride (LiCl) are also added as pore formers. Afterward, the dope solution is cast into a designed shape (flat thin film or hollow fiber) on a support. The shaped dope solution is then contact prepared in a coagulation bath, which contains the non-solvent or a poor solvent of the polymer. Such contact starts the phase separation process. During the process, the organic solvent exchanges into the coagulation bath so that the polymer precipitation takes place. Finally, a piece of porous polymeric membrane is obtained.^{15,16}

It is easy to come up with an idea of blending some NMs into the dope solution. After the phase separation process, the NM should be incorporated into the membrane matrix and then donate its extra function during water treatment. Such membranes are known as mixed matrix membranes (MMMs). Gohari *et al.* used metal oxides to successfully prepare MMMs with preferable UF performance.¹⁷ Hydrous manganese dioxide (HMO) NMs were synthesized and dispersed into a PES–PVP–NMP dope solution. The incorporation and coverage of HMO enhanced the membrane hydrophilicity and narrowed the pore size, resulting in promoted permselectivity and preferential antifouling performance compared with the pristine PES UF membrane. With the HMO : PES ratio increased from 0 to

1.5, the membrane flux boosted from 39.2 LMH bar⁻¹ to 496.5 LMH bar⁻¹, the BSA rejection also increased from 57% to 85%. Apart from manganese dioxide, other metal oxides with particular functions have been introduced in MMMs. For instance, TiO₂ can endow the UF membrane with the ability of self-cleaning and self-protecting. Lu's group introduced polydopamine (PDA)-modified TiO₂ NMs to produce TiO₂-PDA-PSf UF MMMs.¹⁸ The hydrophilic TiO₂-PDA NMs help promote the flux of the TiO₂-PDA-PSf UF membrane with a slightly decreased BSA rejection that was still ~90%. With the ultraviolet (UV) light irradiation, TiO₂ performed its photocatalytic property to clean the BSA fouled membrane surface and recover the flux. However, without the protection of PDA, UV irradiation would attack the membrane matrix and finally deteriorate the membrane selectivity. Here, PDA acted as a radical quencher to prevent PSf from being destroyed by UV light. As a result, the TiO₂-PDA-PSf UF membrane remained 72% of the initial flux and maintained selectivity after eight cycles of fouling-irradiating, indicating good stability of the NMs in the membrane and the ability of the membrane to self-clean and self-protect.

Metal oxides usually appear as solids. In comparison, porous hollow NMs seem to offer more room for flux improvement in MMMs. Li and coworkers developed a hollow mesoporous silica spheres (HMSS)-blended UF membrane and demonstrated its validity in improving the membrane's water treatment performance and the anti-fouling property.¹⁹ They used a Stöber system, an extremely classical and useful method for synthesizing porous Si-Si spheres, to prepare HMSS and blend HMSS with a PES dope solution (see [Figure 4.5](#)). The resultant HMSS-PES composite UF membranes showed better hydrophilicity than the pristine PSf UF membrane. As a result, the HMSS-PES composite UF membrane was shown to transport water much better than the pristine PSf UF membrane without sacrificing BSA rejection, together with a promoted anti-fouling performance. Owing to the abundant -OH groups around HMSS, the hydrophilicity of the HMSS-PES composite UF membrane was hence elevated. Hence, the anti-fouling performance of the HMSS-PES composite UF membrane was improved, the reversible fouling played a dominant role in HMSS-PES membrane. Moreover, a comparison of HMSS-PES

membrane and solid MSS–PES membrane was measured. The authors found that under the same molar blending, the flux of the HMSS–PES membrane was almost as twice much as the solid MSS–PES membrane with only a little difference in BSA rejection. The HMSS NMs possessed a cavity inside and therefore provided a reservoir and shortcuts for water permeation. Finally, the enhancement of hollow NMs in the performance of MMMs was soundly demonstrated. Other porous hollow NMs also deserve a try. Wu's group developed a hollow ZIF-8 (hZIF-8)-blended UF membrane and demonstrated its validity in improving the membrane's water treatment performance and anti-fouling property.²⁰ The synthesis of ZIF-8 was simple. After etching using tannic acid (TA), ZIF-8 became hollow. Based on the same principle, the hollow ZIF-8-blended UF membranes outperformed the solid ZIF-8 blended one in water treatment efficiency and fouling resistance.

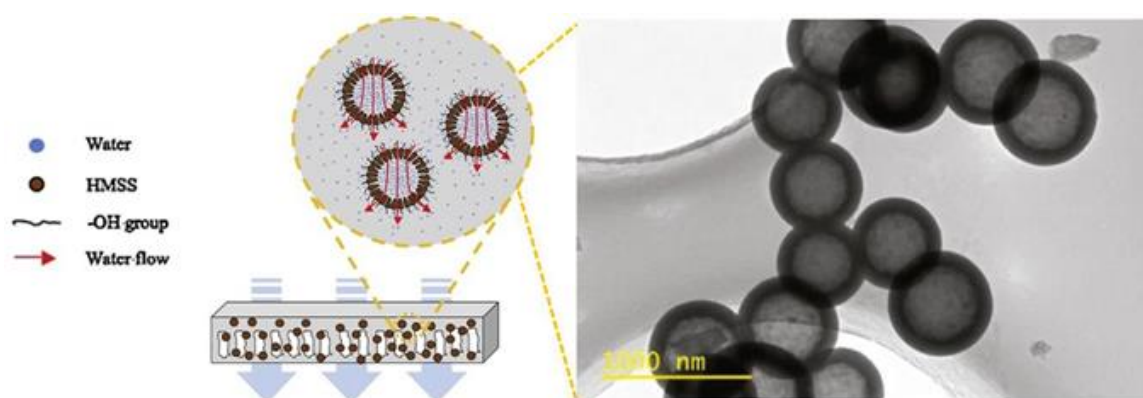


Figure 4.5 Schematic illustration of a hollow mesoporous silica spheres (HMSS)-blended UF membrane and a transmission electron microscope (TEM) image of HMSS. Reproduced from ref. ¹⁹ with permission from Elsevier, Copyright 2015.

In addition to these NMs, 2D NMs like graphene oxide (GO) also play their roles in MMMs. Ahn's team sulfonated GO with H_2SO_4 to graft GO with $-\text{SO}_3\text{H}$ groups.²¹ The sulfonated GO (SGO) was then employed for MMM preparation. A SGO–PVDF–PVP–NMP dope solution was formed and corresponding MMMs were fabricated *via* the NIPS method. The consequential PVDF–SGO membrane displayed generally better UF performance than the PVDF and PVDF–GO membranes. The PVDF–SGO

membrane showed a water flux of up to 740 LMH, which improved by approximately 146.6% compared with the PVDF membrane (290 LMH). The BSA rejection of the PVDF membrane was 90%, while that of the PVDF–SGO membrane was always higher than the former and can reach a peak of 98.8%. Moreover, the PVDF membrane suffered from severe irreversible fouling (the irreversible fouling ratio (R_{ir}) is 49.6%), while the PVDF–SGO membrane exhibited a much lower R_{ir} of ~11.2–24%. Besides the filtration reinforcement, GO was also reported to be effective in anti-bacterial applications due to its extremely sharp edges.²² With the sharp edges, GO can kill bacteria *via* direct contact because it acts as a cutter that hurts the cell membranes. Damaged cells release their intracellular contents and then die.^{11,23} Yu *et al.* modified GO with hyper-branched poly (ethylene imine) (HPEI) and mixed the HPEI–GO with a PES–PVP–DMAc system to synthesize the HPEI–GO–PES UF membrane.²⁴ Although the permeability of HPEI–GO–PES UF membrane decreased compared with the pure PES membrane due to the lower porosity caused by HPEI–GO, the HPEI–GO–PES UF membrane manifested a superior anti-fouling and anti-bacterial performance, which the pristine membrane didn't have. The flux recovery ratio (FRR) of the HPEI–GO–PES UF membrane was 92.1% and 88.7% for two fouling cycles, while the pure PES performance was 86.6% and 72.2%. HPEI–GO–PES UF membrane also gives a high bacteriostasis rate against *E. coli* of 74.88%. In comparison, the HPEI–PES hybrid membrane didn't show significant anti-bacterial properties.

Although blending is a facile manufacturing technique, there are apparent disadvantages for the corresponding UF membrane production. NMs tend to aggregate together during membrane fabrication, and that may result in defects for the passing or attachment of foulants. The incompatibility between inorganic NMs and the polymeric matrix also contributes to the generation of non-selective voids. If the interactions between NMs and membranes aren't strong enough, the NMs may leach out during the water filtration and lead to a secondary pollution.²⁵ Moreover, the blending method unavoidably renders some NMs completely embedded in the polymeric matrix, which severely obstructs NMs from playing their roles. With the development of UF membrane production, new approaches that combine the advantages of 'binding' and 'blending' are desired.

4.2.3 *In Situ* Generation of NMs

In situ generation of NMs in membranes has emerged as an advanced technology in UF membrane fabrication. This method compresses the membrane formation and the NM generation into a single-step NIPS process. The NM precursors are dispersed into the solvent, with the assistance of sol–gel or hydrolysis processes, the precursors are converted to NMs before or during the NIPS operation. Finally, UF membranes with *in situ* generated NMs are produced. The molecular level mixing of NMs precursors, polymers and solvents results in interpenetrating networks. This will possibly ease the NM aggregation and be beneficial for enhancing the compatibility between the polymer matrix and resultant NMs.²⁶ As a result, the stability and utility of the NMs can be promoted and exploited.

Metal oxides are prevalent in anti-fouling UF membrane fabrication. *In situ* generation of NMs makes such fabrication processes more facile. Li *et al.* *in situ* generated zinc oxide (ZnO) NMs in a PES UF membrane.²⁷ By preparing a ZnO sol using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as a precursor, they developed a ZnO sol containing dope solution and obtained ZnO hybrid PES UF membranes *via* a NIPS process (see Figure 4.6a). The ZnO–PES UF membranes were loaded with 0.25–0.75 wt% of ZnO NMs with an average radius of 10 nm. During water treatment tests, the flux of the ZnO–PES membrane reached as high as 365.8 LMH, while 46.4 LMH for the pristine PES membrane was achieved. Although the ZnO–PES membrane manifested a small decline in BSA rejection, its anti-fouling performance significantly outperformed that of the PES membrane (see Figure 4.6b). After further exploration, they found that the adhesion forces between foulant and ZnO–PES membrane were lower than that between foulant and PES membrane, indicating that fouling of the ZnO–PES membrane was more difficult. Similar work was finished by Pang *et al.*²⁸ They used zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) to prepare a zirconium dioxide (ZrO_2) sol *via* ion exchanging with an anion-exchange resin to replace Cl^- with OH^- . The ZrO_2 –PES hybrid UF membrane was found to possess ZrO_2 NMs with diameters of ~5–10 nm in the matrix. It was more hydrophilic than the pure PES membrane and manifested superior fouling resistance. The authors used BSA and ovalbumin (OVA) as model

foulants to investigate the anti-fouling performance of the membranes. With an appropriate ZrO_2 loading, the ZrO_2 -PES hybrid UF membrane performed a flux recovery percentage 1.8 times and 1.7 times higher than that of the pure PES membrane, in the cases of BSA and OVA fouling.

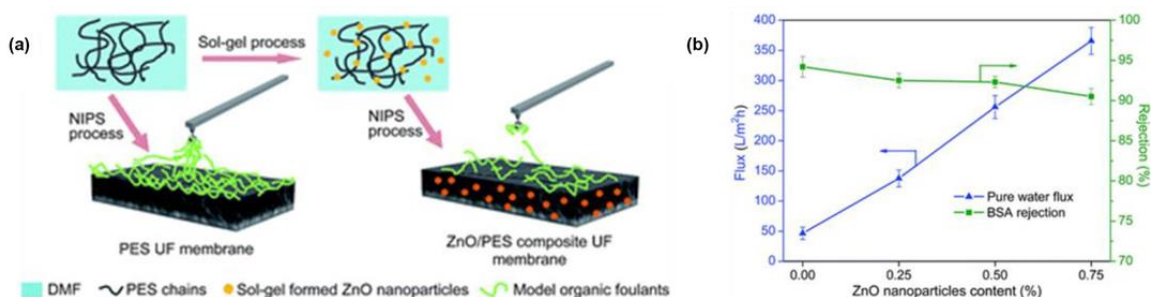


Figure 4.6 (a) *In situ* generation of ZnO NMs *via* a sol-gel and NIPS process for the manufacture of ZnO-PES UF membranes. (b) Performance of ZnO-PES UF membrane manufacture. Reproduced from ref. ²⁷ with permission from the Royal Society of Chemistry.

To further simplify the UF membrane fabrication, sometimes the formation of the solution and *in situ* generation of NMs can be measured simultaneously. By adding silver nitrate (AgNO_3) into the dope solution, Ag^+ can be reduced to Ag by DMF, the solvent, meanwhile, the polymer (PVDF) and the pore former (PVP) were dissolved to form a zero valent silver-containing uniform dope solution.²⁹ The Ag-PVDF UF membrane was produced *via* a NIPS process. In addition to the elevation of membrane hydrophilicity, the presence of Ag had a complicated influence on the kinetics of phase separation. On one hand, the presence of Ag blocked the pores on the UF membrane and therefore narrowed the pore size. On the other hand, Ag accelerated the solvent-nonsolvent exchange during phase separation and resulted in larger pore sizes. As a result of this balance, the Ag-PVDF UF membrane outperformed pristine PVDF membranes in both water flux and BSA rejection with a suitable Ag loading, signifying the potential of *in situ* generating methods in breaking the “trade-off” in membrane permeability and selectivity. Moreover, in this work, the leaching of silver during water filtration was detected to be below 100 ppb, the WHO guideline threshold for drinking water (2004). Thus, the leaching

wouldn't decrease the permeate safety, on the contrary, it protected the membrane from bacterial attack (see Figure 4.7).

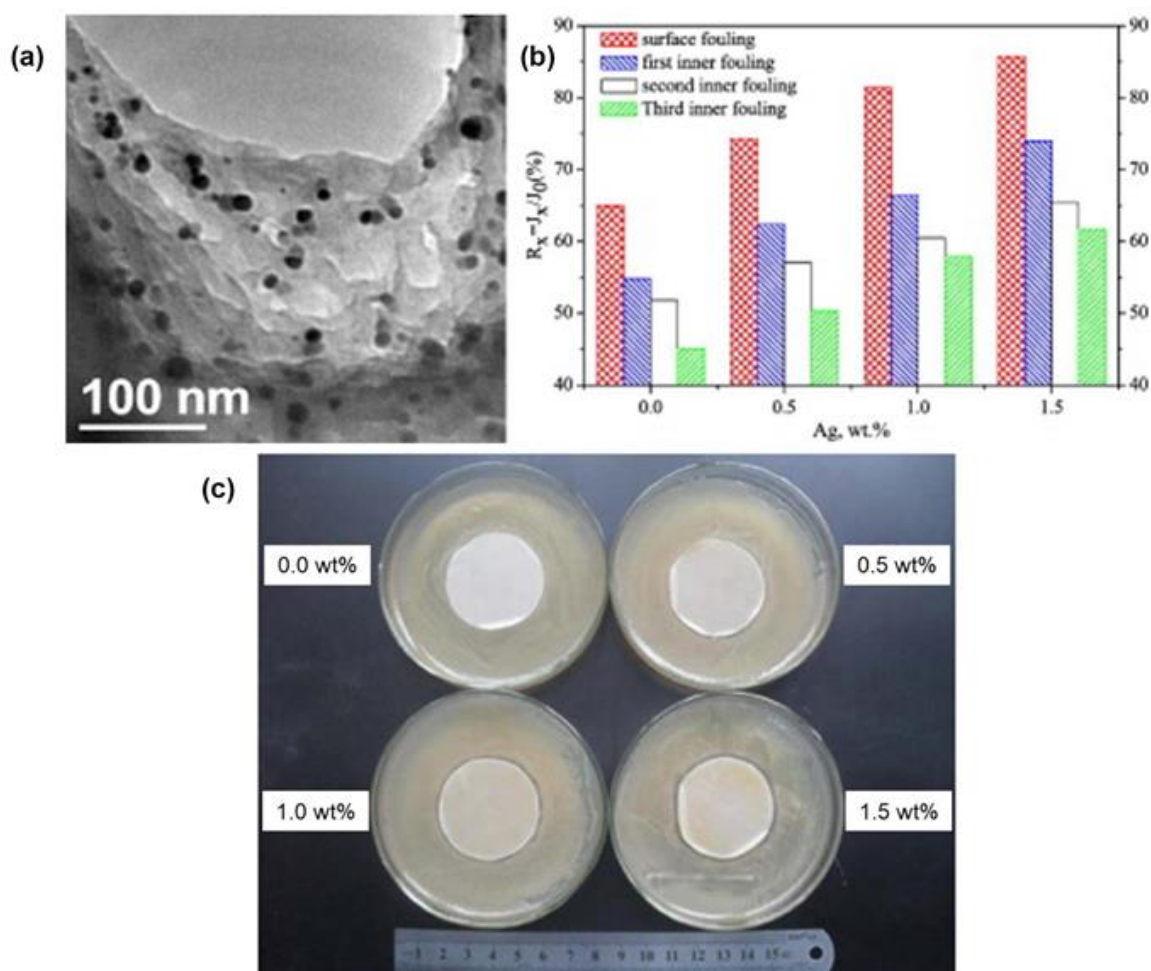


Figure 4.7 *In situ* generation of Ag NMs on PVDF UF membranes. (a) TEM image of *in situ* generated Ag NMs together with the PVDF matrix; (b) Anti-fouling and (c) anti-bacterial performances of different Ag loaded membranes. Halo zones can be found only around Ag-containing membranes. Reproduced from ref. ²⁹ with permission from Elsevier, Copyright 2013.

As membrane filtration is a time-consuming process, the reinforcement of membrane performance, brought by NMs, should also be sustainable. That requires minimal leaching of NMs during water filtration. Li's group combined the TiO₂ self-assembly, polymeric membrane formation and the binding between them into a NIPS process.³⁰ Tetrabutyltitanate (TBT) and a

PEO–PPO–PEO triblock copolymer Pluronic F127 served as source of TiO_2 and binding agent, respectively. They were both blended into the PES–PVP–DMF dope solution. During the phase separation, hydrolysis and condensation of TBT induced the self-assembly of TiO_2 with a size of $\sim 3\text{--}5$ nm around the membrane pores. Thanks to the presence of F127, the stability of TiO_2 NMs in the membrane was enhanced and the corresponding leaching was also remedied (see [Figure 4.8a](#) and b). With the assistance of TiO_2 and F127, the resultant TiO_2 –F127–PES UF membrane performed a higher flux of 235.9 ± 7.8 LMH, while the PES, F127–PES and TiO_2 –PES UF membranes presented water fluxes of 50.8 ± 4.1 , 126.6 ± 5.1 and 123.8 ± 4.0 LMH, respectively. All of these membranes manifested BSA rejections of roughly 96%, indicating such NM *in situ* generation minimally affects membrane selectivity. Moreover, TiO_2 and F127 jointly promoted the hydrophilicity not only of the membrane surface but also of the internal pores, resulting in a much better anti-fouling performance of the TiO_2 –F127–PES UF membrane than the other three counterparts (see [Figure 4.8c](#)). Further study revealed the anti-fouling mechanism.³¹ The adhesion force of the foulant–membrane and foulant–foulant were detected and found to be lower in the TiO_2 –F127–PES UF membrane than in the PES UF membrane. This made foulants like BSA more difficult to attach to the membrane surface. Considering the main fouling mechanism of filtration was standard blocking and cake layer formation, the self-assembly of TiO_2 around the membrane pores effectively remitted the foulant deposition on the membrane surface and membrane pore walls. Such an *in situ* generation attempt developed stable, functional NMs on the UF membrane surface and pore walls within a single-step NIPS method, indicating the combined advantages of binding and blending methodologies (see [Figure 4.8d](#) and e).

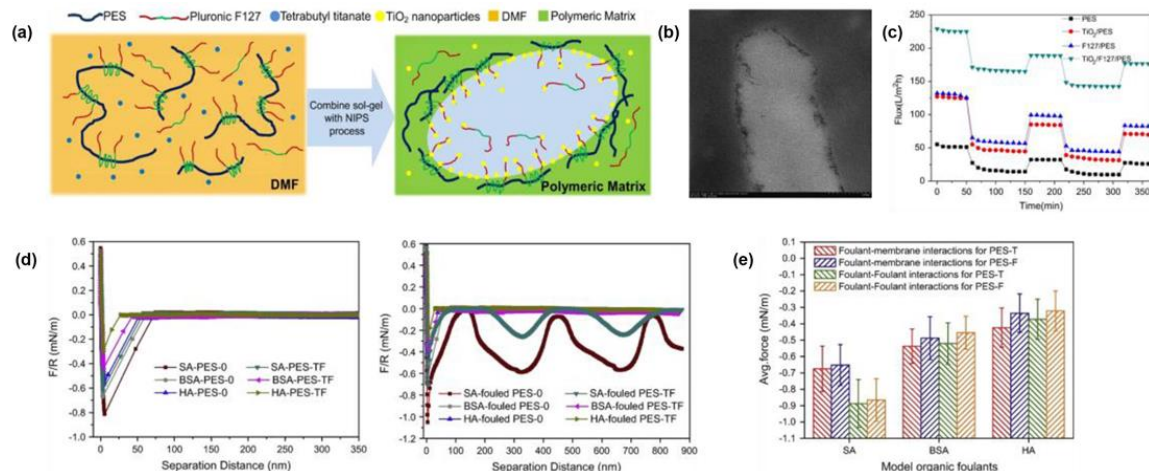


Figure 4.8 (a) Schematic illustration of the *in situ* generation of TiO_2 NMs on PES UF membranes with the assistance of Pluronic F127; (b) TEM image of self-assembled TiO_2 NMs around finger-like pores; (c) comparison of different membrane anti-fouling performances; Reproduced from ref. ³⁰ with permission from Elsevier, Copyright 2014. (d) Display of adhesion force of membrane-foulant and foulant-foulant, respectively; (e) comparison of membrane-foulant and foulant-foulant interactions of different membranes. PES-T represents membranes with TBT but no F127, and PES-F represents membranes with F127 but no TBT. Reproduced from ref. ³¹ with permission from Elsevier, Copyright 2016.

4.3 NM-assisted Dual-functional Membranes

Unfortunately, MF-UF membranes failed to reject many contaminants, such as heavy metals and some low molecular weight organics, from water even after some modification or optimization. In the frame of “membrane technology”, these pollutants are effectively removed by NF and RO approaches. However, compared with MF/UF, NF/RO requires higher pressure and contributes much lower flux. Without the restriction of “membrane”, adsorption and degradation also work well in removing these small contaminants. Driving by the goal of eliminating the small pollutants *via* high flux filtration, people started to prepare dual-functional membranes. Dual-functional membranes combine sieving and adsorption or catalysis *via* loading of adsorbents or catalyst within the membranes. When treating multi pollutant-containing wastewater, dual-functional membranes

reject contaminants of large sizes and adsorb or degrade smaller ones with the assistance of adsorbents or catalysts.

4.3.1 Adsorptive Membranes

The central point of constructing adsorptive membranes is the merging of adsorbents and membrane. Many simply blend the adsorbents with the dope solution to fabricate MMMs just as mentioned in Section 4.2.2 of this chapter. AlTi_2O_6 NMs were blended with PSf dope solutions and used to prepare MMMs *via* a NIPS method.³² The AlTi_2O_6 NMs enhanced the membrane hydrophilicity as well as the adsorption of heavy metal ions. As a result, the AlTi_2O_6 -containing PSf membrane exhibited efficient removal of lead, cadmium and arsenic ions. Adsorbents can also be crosslinked upon the membrane surface. Chen's team bound zirconium phosphate (ZrP) NMs on PVDF substrates *via* crosslinking.³³ The ZrP-loaded membrane worked very well in removing lead from water *via* adsorption. The loaded ZrP membrane, helped by a small piece of PVDF membrane (12.56 cm^2) treated 13.9 L of lead-containing wastewater ($224.5 \mu\text{g L}^{-1}$) to less than $15 \mu\text{g L}^{-1}$ through dead-end filtration. After regeneration using hydrochloric acid (HCl) and water, the membrane still manifested a similar adsorption capacity, presenting its superior reusability. Moreover, under the competition of zinc ions, the membrane displayed a reasonable selectivity to lead, unveiling its potential in selective lead removal. However, traditional construction of adsorptive membranes usually leads to loss of basic filtration performance, not many works report both of the molecular sieving and contaminant adsorption performance of their membranes. To chase a larger adsorption capacity, more nano-adsorbents are required, which alter the membrane formation inevitably. As a result, NMs aggregate together, trigger non-selective defects, block the selective pores and hence deteriorate the separation performance. Furthermore, blending NMs also causes the entrapment of adsorbents together with the invalidation of active sites.

The ideal building of adsorptive membranes should maximize the adsorbent loading and expose the active sites sufficiently without compromising the membrane filtration performance. Based on the structure

of asymmetric polymeric membranes, researchers realized that there is lots of unemployed space in the finger-like pores. If the finger-like pores can be fulfilled by adsorbents, the active sites will be fully exploited with a high loading. The main difficulty of this technology is how to infill the finger-like pores with NMs. Li's group focused on this problem and made some breakthroughs. They utilized the self-polymerization of dopamine (DA) to form PDA NMs in the finger-like pores of a PES substrate *via* reverse filtration of a DA solution.³⁴ DA molecules were brought into the finger-like pores using the reverse fluid and then self-polymerized as PDA NMs, a useful adsorbent for heavy metals (see [Figure 4.9a](#)). Finally, a PDA–PES UF membrane with an integral UF performance was obtained (water flux of 166 LMH and BSA rejection of 92.9%). When filtering a multi micro-pollutant solution including 100 ppb Pb^{2+} and 50 ppm BSA, a piece of PDA–PES UF membrane (13.4 cm^2) disposed of 1.5 L of solution to below 10 ppb Pb^{2+} and performed a BSA rejection of above 93.5%. The effective loading of PDA NMs was responsible for the efficient adsorption of Pb^{2+} (see [Figure 4.9b](#) and c). Moreover, after regeneration *via* sodium hydroxide (NaOH) solution, the PDA–PES UF membrane maintained a high-level of disposal capacity with unaffected UF performance. Given that reverse filtration has been proved useful in dual-functional UF membrane production, good adsorbents will indisputably promote the treatment capacity of the membrane. For example, a reported adsorbent (hollow porous $\text{Zr}(\text{OH})_x$ nanospheres (HPZNs)³⁵) was reversibly filtrated into the finger-like pores of a PES UF membrane followed by bottom sealing (see [Figure 4.10](#)).³⁶ The HPZN loading in the membrane reached as much as 68.9 wt%. Such a HPZN-infused dual-functional UF membrane showed a moderate water flux (slightly lower than 200 LMH) and normal BSA rejection of 95.3%. On the contrary, the HPZN blended UF membrane exhibited a high flux of 625.5 LMH and a significantly dropped BSA rejection of 72.5%, further demonstrating the selective deterioration of blending membranes. The HPZN-infused UF membrane was capable of removing $\text{Pb}(\text{ii})$ with the coexistence of colloidal gold (5 ppm, 25 nm) and PEG (600 kDa), and the capacity was detected as 4477.0 L m^{-2} , more than twice that of the blended membrane. Similar work was presented by Zhang

*et al.*³⁷ Fe_3O_4 microspheres were employed as adsorbents (see Figure 4.11). The as-constructed adsorptive membrane was able to reject BSA (rejection of 94.5%) and eliminate arsenic (1 m^2 of membrane can treat 2402 L of 97 ppb As water to below 10 ppb) synchronously, while the Fe_3O_4 -blended membrane possessed much lower BSA retention (69%) and treatment capacity (approximately 1500 L m^{-2}). The Fe_3O_4 microsphere-infused dual-functional UF membrane maintained a high level of UF-adsorption performance after regeneration using a NaOH solution, indicating its potential in removing BSA and arsenic from water sustainably.

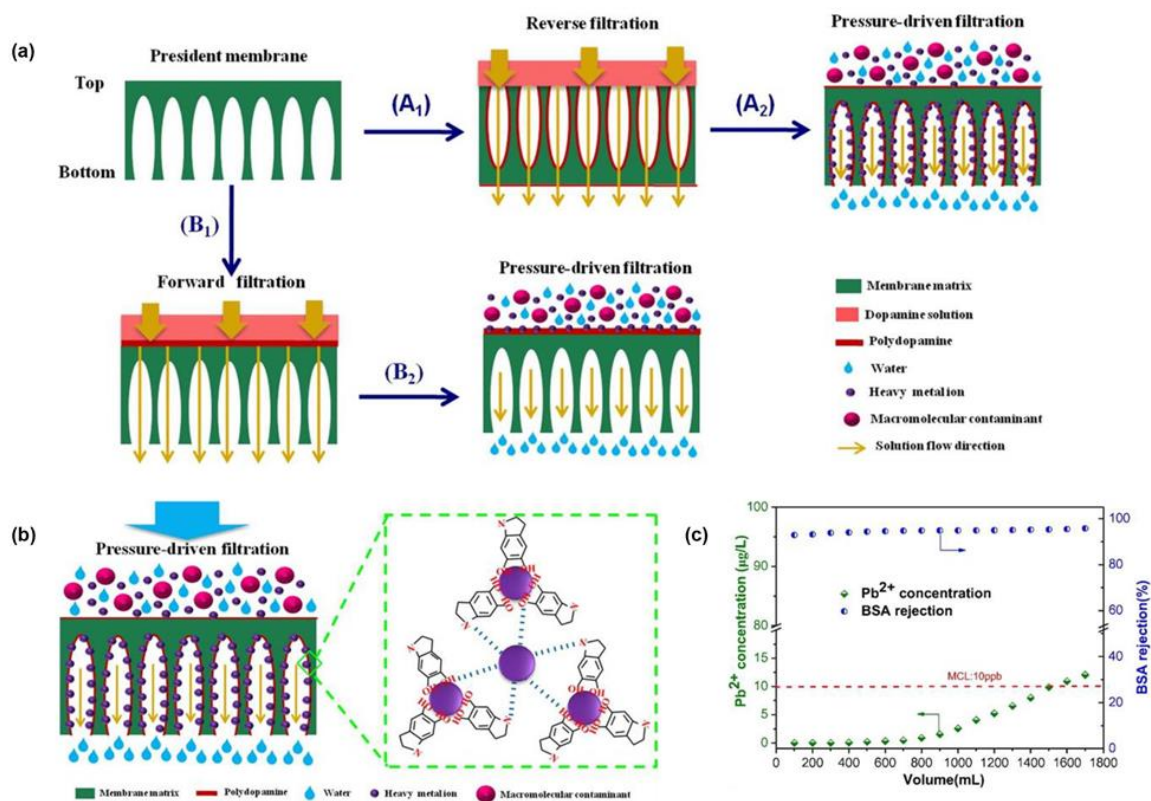


Figure 4.9 (a) Preparation of dopamine NM-containing adsorptive UF membranes; (b) a possible mechanism for heavy metal ion adsorption on PDA; (c) simultaneous removal of BSA and heavy metal ion using the adsorptive UF membrane. Reproduced from ref.³⁴ with permission from Elsevier, Copyright 2017.

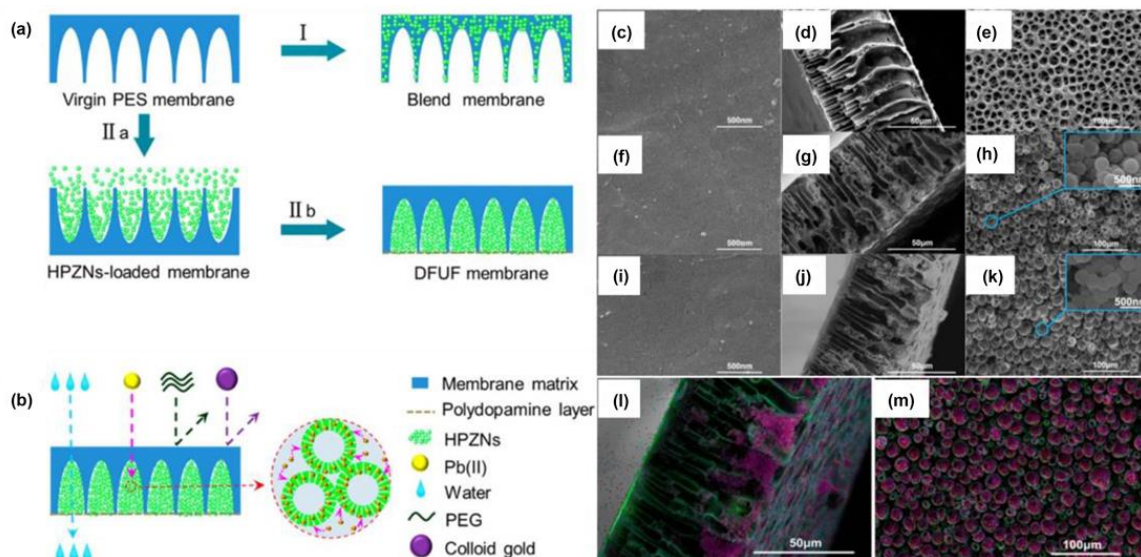


Figure 4.10 (a) Schematic representation of two fabrication methods for dual-functional UF membranes: traditional blending (I) and finger-like pore loading (II); (b) the process of removing pollutants with different sizes simultaneously within a one-step filtration; (c–k) SEM images of pristine and NM-loaded UF membranes from different angles (surface, cross-section and bottom); (l) and (m): EDS mapping of NM-loaded membranes. Reproduced from ref. ³⁶ with permission from American Chemical Society, Copyright 2017.

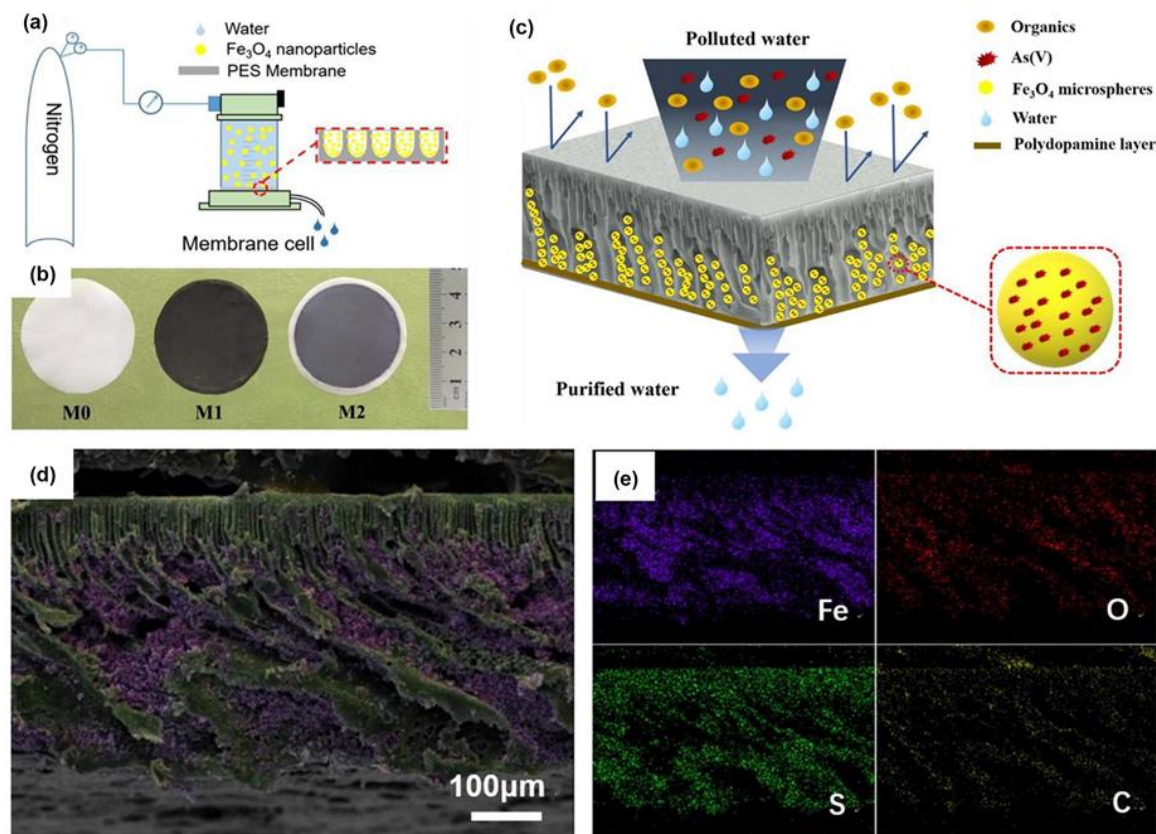


Figure 4.11 (a) The loading process of Fe_3O_4 ; (b) photographs of pristine (M0), blended (M1) and NM-loaded membrane (M2); (c) schematic representation of the removal of multiple pollutants *via* filtration; (d) and (e) EDS mapping of Fe_3O_4 -loaded UF membranes.

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An important factor for adsorption is the residence time of water in the membrane. From a pollutant removal point of view, the residence time should be longer. However, efficient water treatment requires a higher water flux and results in shorter residence times. Therefore, high-efficiency adsorbents and proper low-pressure operations are needed to find the balance. Liao *et al.* developed hollow mesoporous carbon nanospheres (HMCNs) as adsorbents. HMCNs were then loaded into the finger-like pores of PES UF membranes *via* the aforementioned reverse filtration method.³⁸ The HMCNs–PES membrane was capable of removing macro-pollutants (PEG, 600 kDa) and micro-pollutants (tetracycline (TCN) and 17β -estradiol (E2)) *via* rejection and adsorption, respectively (see [Figure 4.12](#)). Under a low pressure of less than 0.15 bar, the residence time of

water was estimated to be lower than 6s, the HMCNs–PES membrane successfully treated multi contaminant-containing tap water ($100 \mu\text{g L}^{-1}$ feed TCN, 50 mg L^{-1} feed PEG (600 kDa) and 0.02 mmol L^{-1} sodium chloride (NaCl) as background electrolyte). PEG was 100% rejected and TCN was found to be lower than $10 \mu\text{g L}^{-1}$ in the permeate with a large treatment capacity of more than 3000 L m^{-2} .

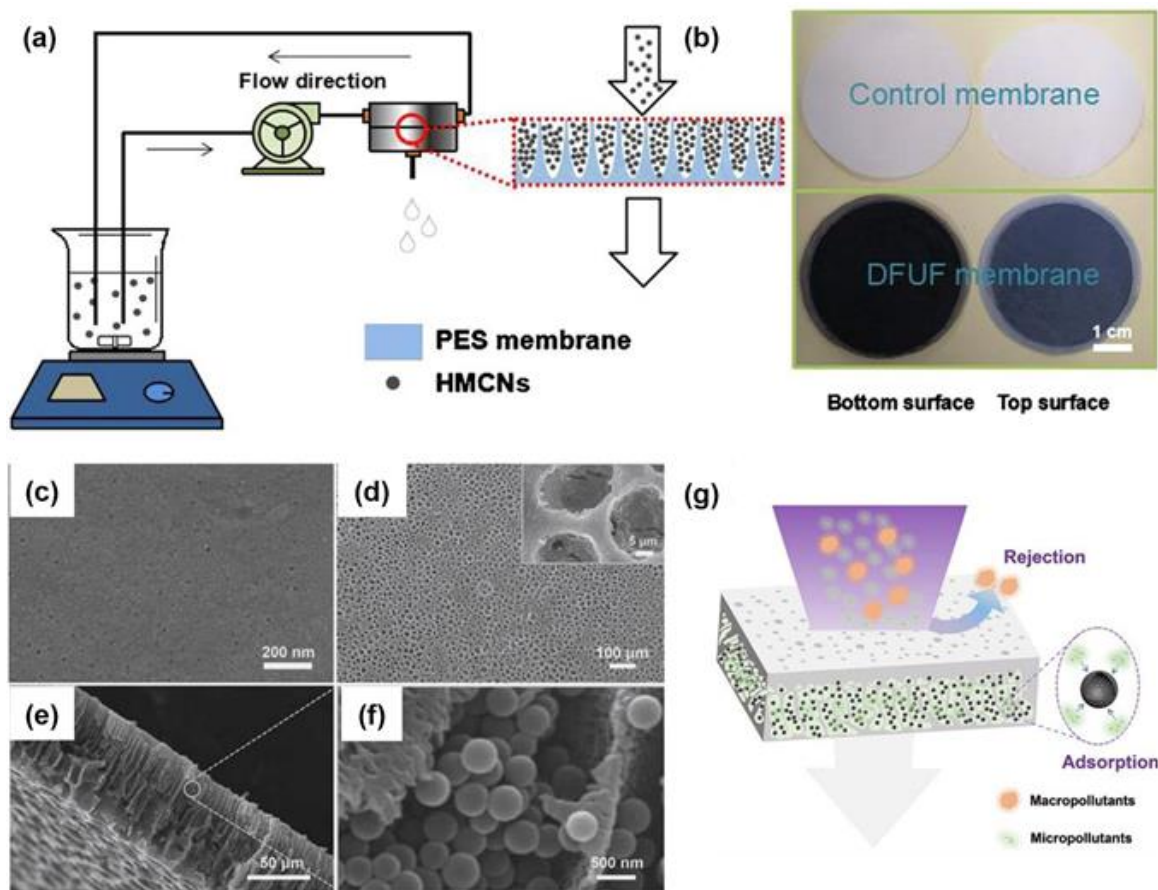


Figure 4.12 (a) The loading process of HMCNs; (b) photographs of control and dual-functional UF membranes; (c–f) SEM images of HMCN-loaded dual-functional UF membranes on surface (c), bottom (d), cross-section (e and f); (g) rejection–adsorption mechanism of the membranes. Reproduced from ref. ³⁸ with permission from Elsevier, Copyright 2020.

Loading adsorbents into the finger-like pores of the polymeric membrane was soundly proved useful in removing macro- and micro-pollutants simultaneously using UF membranes. The adsorbents loading is very high

(e.g. above mentioned 68.9 wt%) and the UF performance is well inherited. Nonetheless, optimizations are further expected. The reverse filtration and the following back sealing operation, namely the loading process, are time-consuming (usually several days). More rapid loading technology is required to simplify the membrane production. Moreover, there always exists an adsorption capacity for the dual-functional rejection–adsorptive membrane. Once the capacity runs out, regeneration is essential and the whole filtration system needs to be shut down for a break. In traditional filtration systems, such a break is usually for cleaning the fouled membrane. After cleaning, the system can run for another period. From the sustainable filtration angle, a larger adsorption capacity is desired. An ideal adsorption capacity ought to allow the regeneration frequency of adsorbents to meet the cleaning frequency of membranes. Further research should focus on these limitations.

4.3.2 Catalytic Membranes

Similar to adsorptive membranes, catalytic membranes consist of the membrane and nano-catalysts. Blending catalysts to form MMMs still suffers from poor filtration performance and NMs aggregation. Rationally loading catalysts on membranes has become the most important thing for researchers. Wan *et al.* functionalized PVDF membranes with poly (acrylic acid) (PAA) and then coordinated ferric ions (Fe^{2+}) to form zero valent iron (ZVI) followed by coating palladium(ii) acetate ($\text{Pd}(\text{OAc})_2$).³⁹ The as-prepared Fe/Pd–PAA–PVDF membrane possessed a reducing agent (ZVI) and a catalyst (Pd) in its pore channels (see [Figure 4.13a](#)). PCB 126 (3,3',4,4',5-pentachlorobiphenyl) can be degraded by a Fe–Pd–PAA–PVDF membrane *via* a single pass with a residence time of 15 s. To regenerate the Fe–Pd NMs, NaBH_4 immobilizing is an effective way. In an analogous work, Fe–Pd modified PVDF membrane was capable of treating site groundwater.⁴⁰ Trichloroethylene (177 ppb) and carbon tetrachloride (35 ppb) containing groundwater passed through the membrane and the permeate samples were detected containing 16 and 0.3 ppb, respectively. Moreover, after regenerated by NaBH_4 , the membrane possessed good pollutant degradation abilities again (see [Figure 4.13b](#)).

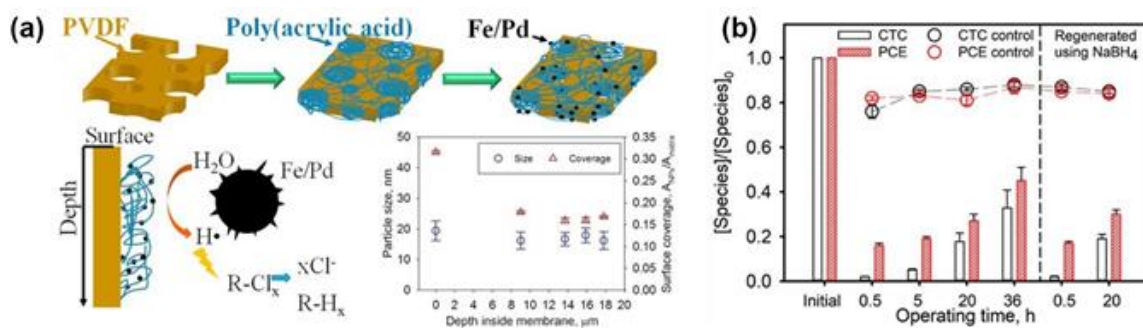


Figure 4.13 (a) Preparation of Fe–Pd NM hybrid UF membranes; Reproduced from ref. ³⁹ with permission from Elsevier, Copyright 2017. (b) Contaminant degradation and membrane regeneration performance (CTC and TCE represent carbon tetrachloride and trichloroethylene, respectively). Reproduced from ref. ⁴⁰ with permission from Elsevier, Copyright 2020.

However, environmental water systems contain macro-pollutants (*e.g.* HA and protein) and micro-pollutants (*e.g.* PCBs and nitrophenol). When degrading micro-pollutants with the assistance of catalysts, HA easily attaches to the catalyst surface and results in a significant drop in catalyst performance.^{41,42} Therefore, HA interference must first be eliminated by the membrane. Driven by this, Fang *et al.* fabricated TA–Fe–PES MMM followed by immersion in a silver ions solution. Ag NMs were thus reduced by TA and anchored on the UF membrane.^{43,44} Such PES–TA–Ag UF membranes displayed typical UF performance (239.8 LMH of water flux, 96.1% of BSA rejection and 87.3% of HA retention). When filtering a multiple pollutant solution (20 mg L⁻¹ HA and 0.3 mM 4-nitrophenol (4-NP)), the PES–TA–Ag UF membrane performed 89% rejection to HA and 98% conversion of 4-NP to 4-aminophenol (4-AP) with the support of NaBH₄ (see Figure 4.14). In contrast, dispersing only Ag NMs in the multiple pollutant solution resulted in an unsatisfying 4-NP conversion of 55.8%, confirming the necessity of constructing rejection-catalytic dual-functional UF membranes. In addition, during seven filtration cycles (regenerated using dilute NaOH solutions), the PES–TA–Ag UF membrane kept a 4-NP conversion of higher than 95% and a flux recovery ratio of 85–87%, demonstrating the reasonable reusability of the membrane.

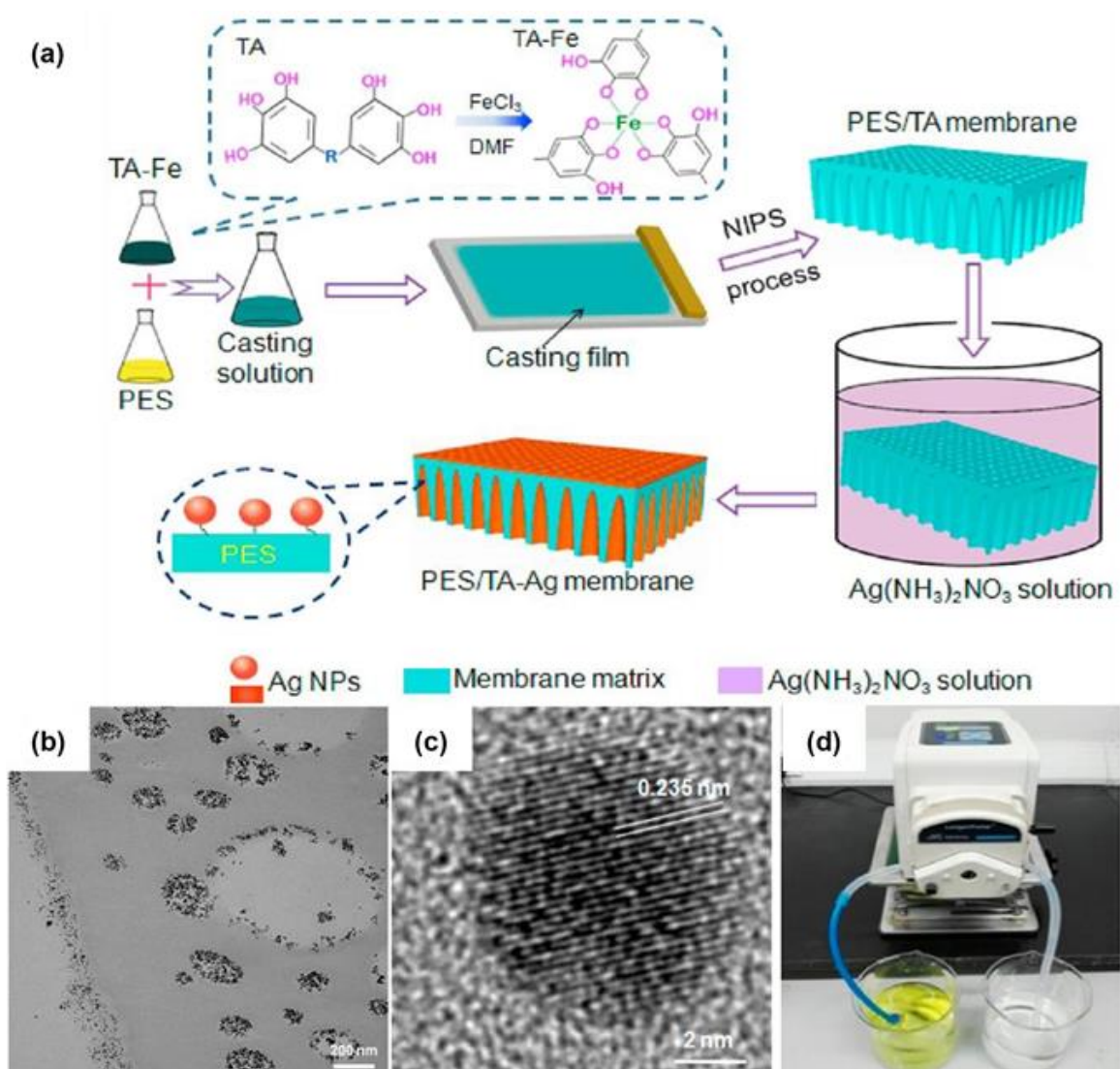


Figure 4.14 (a) Schematic illustration of a PES–TA–Ag UF membrane; (b) TEM image of PES–TA–Ag UF membrane; (c) HRTEM image of Ag nanoparticles in the PES matrix; (d) photograph of 4-NP catalysis *via* filtration using PES–TA–Ag UF membranes. Reproduced from ref. ⁴⁴ with permission from Elsevier, Copyright 2019.

The aforementioned degradation process can be reinforced *via* confined catalysis. Li's group designed a yolk–shell $\text{Co}_3\text{O}_4\text{--C@SiO}_2$ nanoreactors (YSCCSs) for confined advanced oxidation process (AOP).⁴⁵ Such YSCCSs, possessed a particle size of around 500 nm, had a 10 nm silica shell. The core of YSCCS was a 10–20 nm sized Co_3O_4 nanoparticle. The YSCCSs were further used to infiltrated the finger-like pores of UF membranes to

develop UF–catalysis membranes (see Figure 4.15).⁴⁶ The as-prepared UF–catalysis membrane manifested excellent decontamination performance by rejecting HA and degrading BPA simultaneously. Typically, HA will inhibit BPA from degrading by heterogeneous AOP *via* occupying the active sites of solid catalysts. However, with membrane filtration, HA can be removed, thus the inhibition disappears. As a result, with the existence of peroxymonosulfate (PMS), the UF–catalysis membrane achieved a flux of 229 LMH, HA rejection of 100% and BPA catalytic degradation of 95% under 0.14 MPa. It was noteworthy that the residence time of the feed solution in the membrane was only 3.1 s, indicating the highly efficient BPA degradation.

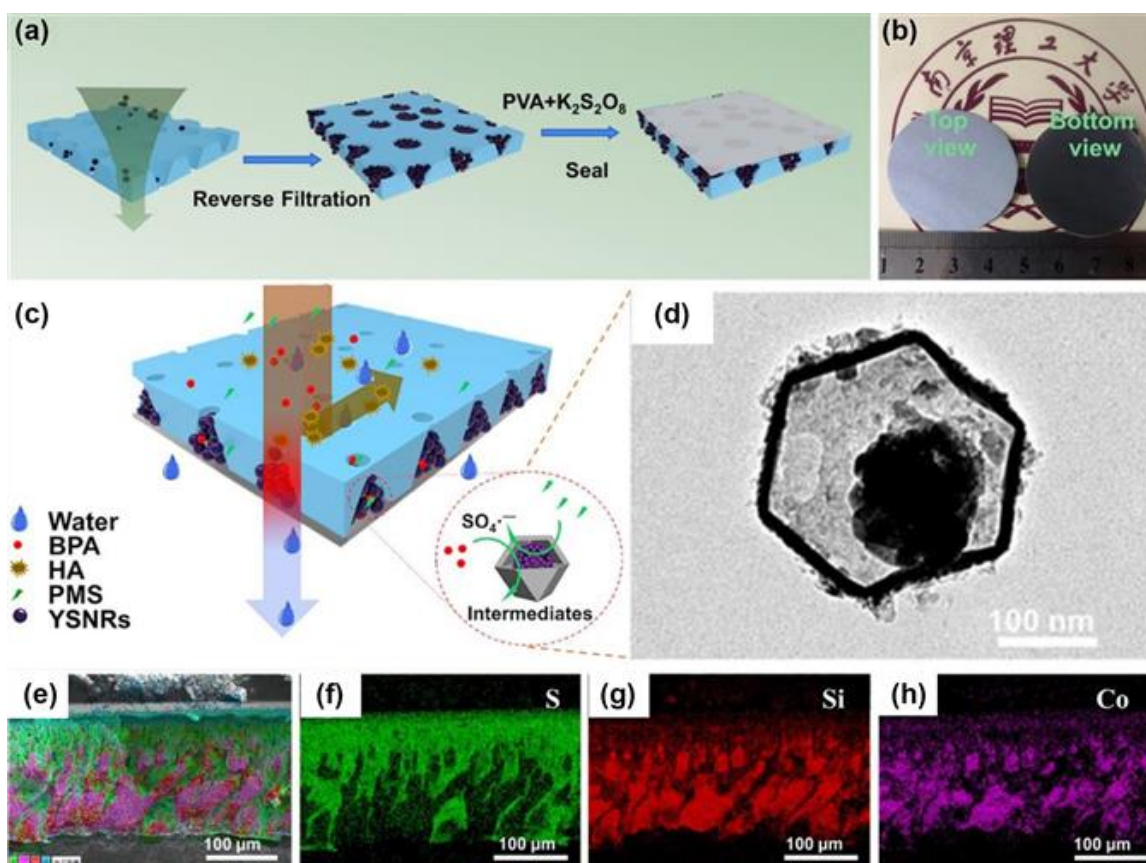


Figure 4.15 (a) Schematic representation of UF–catalysis membrane fabrication; (b) digital photographs of UF–catalysis membranes: top view and bottom view; (c) decontamination of UF–catalysis membrane; (d) TEM image of yolk–shell Co₃O₄–C@SiO₂ nanoreactors (YSCCSs) NM; (e–h): EDS mapping of YSCCSs NM-loaded

Considering the use of PMS and NaBH_4 leads to its presence in the permeate, which may cause secondary pollution, future work should focus on *in situ* generation of both the reductant/oxidant and catalyst on the membrane to preserve integral UF performance.

4.4 Marriage Between NMs and NF/RO Membranes

Nanofiltration (NF) and reverse osmosis (RO) are pressure-driven membrane technologies which aim at small organics and salt removal. Interfacial polymerization (IP) is the mainstream of NF–RO membrane manufacture. A skin layer with a complicated network is developed upon a substrate *via* reactions between amines in the aqueous phase and acyl chlorides in the organic phase. Functional NMs can also attend the fabrication of NF/RO membranes and make their contribution to corresponding water treatment.

4.4.1 In NF Membranes

IP is considered one of the most prevalent methodologies in NF membrane fabrication. The IP membranes are commonly called thin-film composite (TFC) membranes while their NM-assisted counterparts are thin-film nanocomposite (TFN) membrane. Promoting membrane permeability is the first revealed benefit of assisting IP process with NMs.⁴⁷ By dispersing NMs into the aqueous phase or organic phase, NMs can be covered or entrapped by the selective layer. NMs develop more channels for water transport and improve the surface hydrophilicity of TFN membranes, thus the membrane permeability is elevated.

Simply dispersing NMs into the aqueous or organic phase usually loosens the selective layer of TFN membranes. However, sometimes such loosening may be the key point of another special application. Carboxyl-functionalized graphene oxide (CFGO) was dispersed into aqueous solutions together with piperazine (PIP) and then cross-linked with TMC to

develop TFN NF membranes.⁴⁸ The addition of CFGO disturbed the packing of polymer chain, leading to more free volume and loosening the selective layer. The loose polyamide (PA) selective layer, derived from PIP–TMC polymerization, rejected dyes effectively (95.1% to New Coccine). Meanwhile, the CFGO-incorporated TFN membrane showed only 25% rejection to NaCl, indicating the potential of the membrane in dye/salt separation (also called loose nanofiltration).

Using loose TFN membranes to measure dye/salt separation is a little bit opportunistic, because the NM loosening effect is usually uncontrollable. Researchers still spare no efforts in improving the TFN membrane performance without sacrificing selectivity. Based on this, more variations were explored in NMs recently. For example, intrinsic porous NMs (*e.g.* MOFs) drew tremendous attention for TFN NF membrane synthesis. As a proven water stable MOF, UIO-66 and its analogs were widely introduced into TFN membrane manufacturing.⁴⁹ Shao's team dispersed UIO-66 into PEI aqueous solutions and then measured IP process with TMC.⁵⁰ Additional passageways were created by embedded porous UIO-66 NMs as the as-prepared UIO-66–TFN NF membrane presented a high flux (15.4 LMH bar⁻¹, 84% higher than that of the pristine TFC NF membrane), nearly 100% rejection to rose bengal (RB) and 97.6% rejection to azithromycin. In order to further improve the NF performance of TFN membranes, defect-engineered UIO-66–NH₂ (D-UIO-66–NH₂) was developed by replacing partial organic ligands (2-amino-1,4-benzenedicarboxylic acid (H₂BDC–NH₂)) with benzoic acid (HBC). Such D-UIO-66–NH₂ was used as an additive in IP processes (see [Figure 4.16a](#)).⁵¹ Thanks to the extra free volume brought by the defects on D-UIO-66–NH₂, the corresponding membrane NF flux was ~33% higher than that of solid UIO-66–NH₂-incorporated TFN membrane without sacrificing the rejection (see [Figure 4.16b](#)). In addition, good pH stability of the D-UIO-66–NH₂-incorporated TFN membrane was demonstrated (see [Figure 4.16c](#))

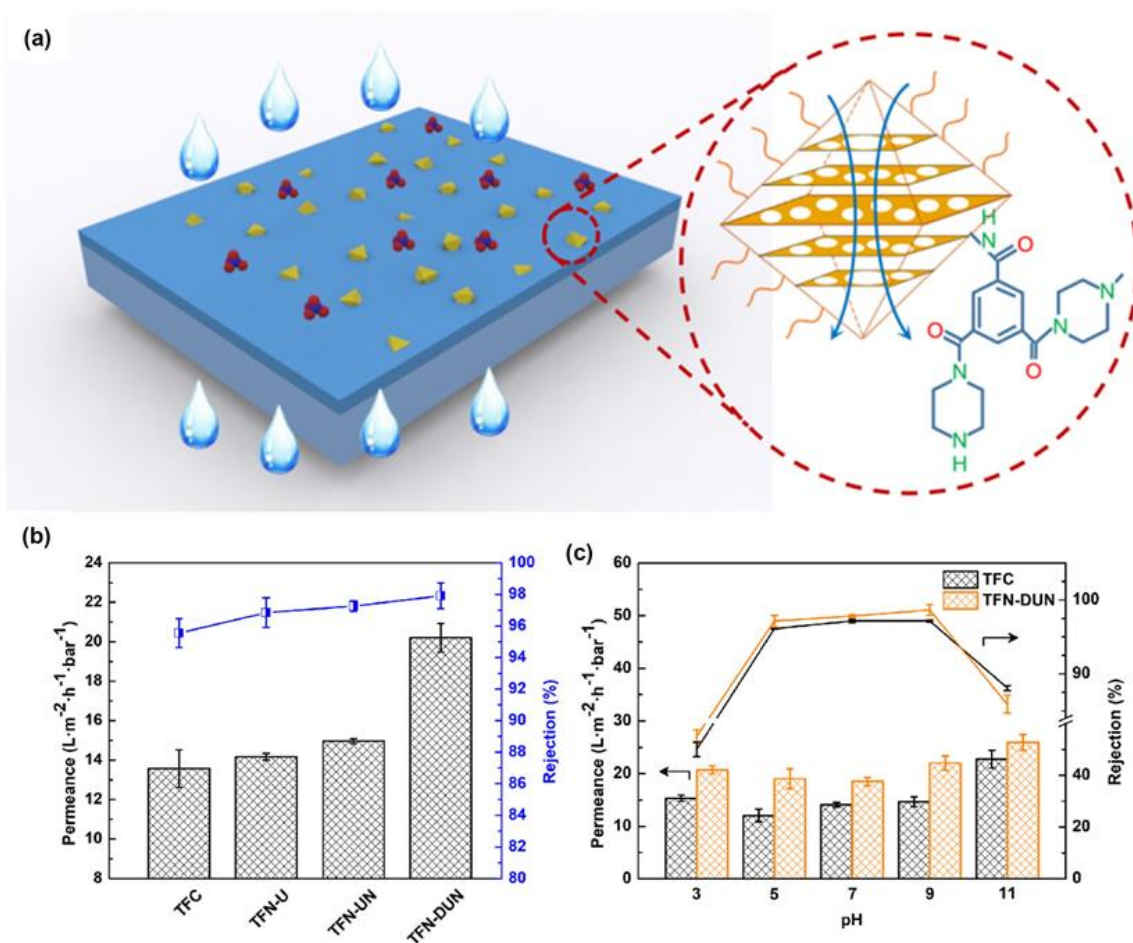


Figure 4.16 (a) The process of preparing a defect-engineered UIO-66-NH₂-containing TFN NF membrane; (b) comparison of NF performances of different NF membranes (TFN-U, TFN-UN and TFN-DUN represent UIO-66, UIO-66-NH₂ and defect-engineered UIO-66-NH₂-incorporated TFN membranes, respectively); (c) pH stability of TFN-DUN. Reproduced from ref. ⁵¹ with permission from the Royal Society of Chemistry.

Hollow porous NMs seem preferable for TFN membrane production as they can bring large cavities that enhance membrane permeability. The aforementioned hollow ZIF-8 was incorporated into the PIP-TMC IP system to form a TFN NF membrane *via* dispersion of the NMs into the organic phase.⁵² The cavity in hollow ZIF-8 created a substantial space for water passing (see Figure 4.17a). Moreover, residual TA outside ZIF-8 helped the membrane reinforce its negative surface charge and thus strengthen its repulsive force to high-valence anions. Accordingly, the

hollow ZIF-8-incorporated TFN membrane exhibited an increased salt rejection and almost two fold higher flux (19.4 ± 0.6 LMH bar⁻¹) than those of pristine TFC membranes (see Figure 4.17b).

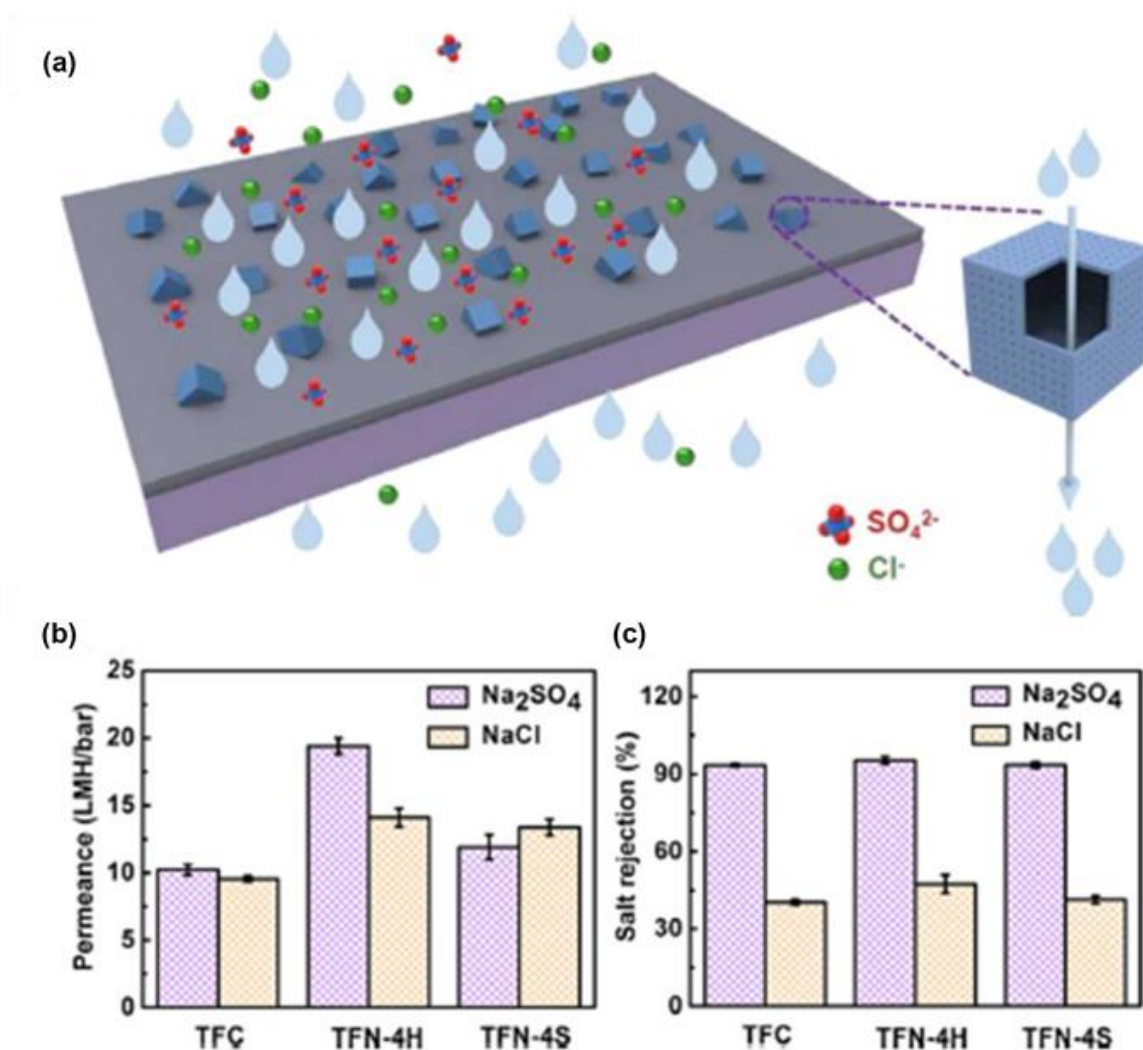


Figure 4.17 (a) Schematic illustration of a hollow ZIF-8-incorporated TFN NF membrane; comparison of permeability (b) and rejection (c) in NF of different membranes. (TFN-4H/TFN-4S represent 0.04 wt% hollow/solid ZIF-8 added into the organic phase for IP). Reproduced from ref. ⁵² with permission from American Chemical Society, Copyright 2019.

Apart from MOFs, there are other kinds of NMs can create interspaces to reinforce mass transfer. Liao *et al.* synthesized resorcinol–formaldehyde nanobowls (RFBs) *via* a modified Stöber method and embedded them into

PIP–TMC IP membranes.⁵³ The nanobowls dispersed on the membrane surface with reasonable cavities. The distinctive structure of the RFB-incorporated TFN membrane logically enhanced the flux by nearly 50% compared with the TFC counterpart without compromising the rejection (see Figure 4.18).

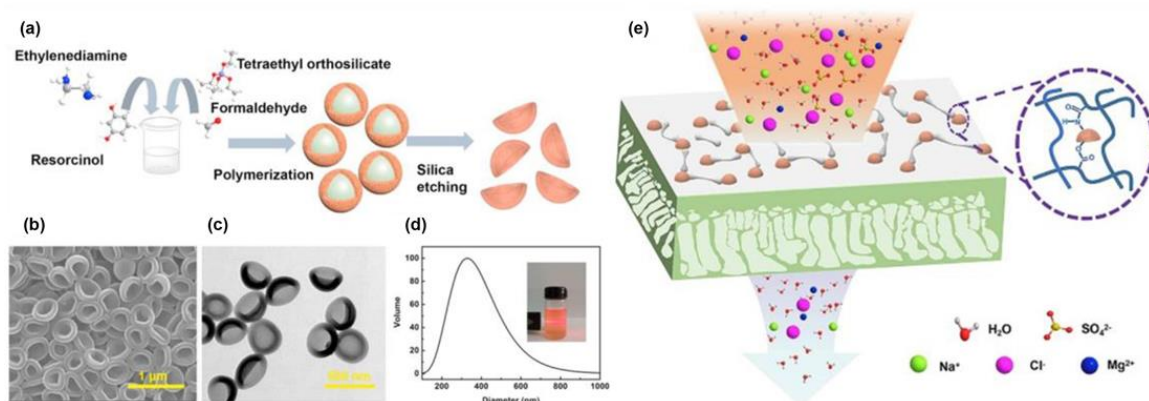


Figure 4.18 (a) Synthesis of resorcinol–formaldehyde nanobowls (RFBs); (b–d) SEM, TEM and dynamic light scattering (DLS) consequences of RFBs; (e) schematic representation of the RFB-incorporated TFN membrane. Reproduced from ref. ⁵³ with permission from Elsevier, Copyright 2020.

4.4.2 In RO Membranes

RO, as a popular technology in eliminating monovalent salt (NaCl) from water, has already been applied on a large scale. *m*-Phenylenediamine (MPD) and TMC are the predominant monomers for RO membrane fabrication *via* IP process. Predictably, with the assistance of NMs, there are many TFN RO membranes that have showcased better permeability than the pristine TFC RO membranes. Most of these efforts tended to improve the porosity of the selective layer, and thus NMs were introduced and stayed. A unique attempt is to remove the NMs after incorporating them into TFN membranes.⁵⁴ Copper ions were reduced into Cu NMs on the PSf substrate using NaBH₄. Then the MPD–TMC IP process was measured upon the Cu-impregnated substrate. The sandwiched Cu NMs were then removed by placing the membrane into nitric acid (HNO₃). Finally, nanovoid-containing RO membranes were prepared (see Figure 4.19a).

With the increase of Cu loading, more nanovoids appeared in the final RO membrane (Figure 4.9b), which manifested higher flux. However, Cu overloading jeopardized the integrity of PA selective layer and resulted in decline of salt rejection (Figure 4.19c).

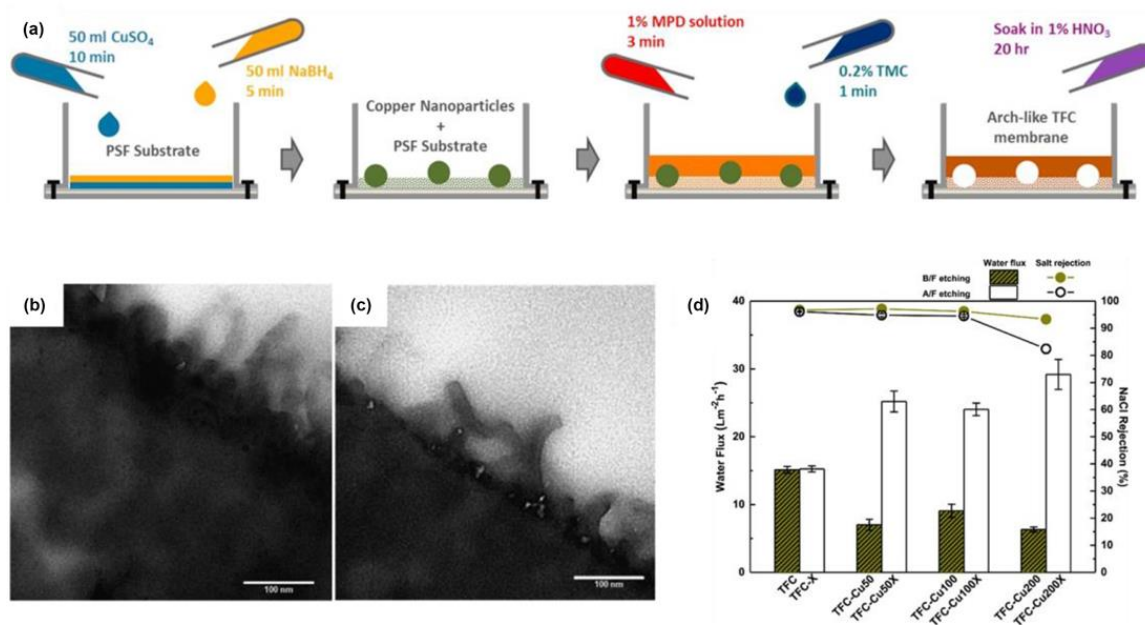


Figure 4.19 (a) Schematic illustration of a nanovoid-containing TFC RO membrane; cross-section TEM images of (b) Cu NM-incorporated TFN membrane and (c) Cu eliminated TFC RO membrane, voids can be clearly observed in (c); (d) desalination performance of membranes before and after Cu etching. X represents HNO_3 etching and TFC refers to the control without Cu embedding. Reproduced from ref. ⁵⁴ with permission from Elsevier, Copyright 2019.

Aside from chasing higher permselectivity, improving anti-bacterial and anti-chlorine performance of RO membranes is also of great significance. To elevate the anti-bacterial performance of RO membranes, Tang's group coated RO membranes with PDA, followed by immersion of the membrane into Ag^+ solutions to *in situ* form Ag NMs on the RO membrane surface (see Figure 4.20).⁵⁵ The Ag NMs had a size distribution of 10–20 nm and were dispersed uniformly upon the RO membranes (see Figure 4.20b and e). Compared with the unmodified RO membrane, the PDA/Ag loading led to a reduction of $62.7 \pm 9.3\%$ for viable *B. subtilis* and $42.4 \pm 5.7\%$ for *E. coli*, manifesting better anti-bacterial performance. Nonetheless, such

loading actually requires extra manufacturing processes after obtaining the RO membrane. To simplify the production of NM-assisted RO membranes, multi-functional NMs are desired to prepare TFN RO membranes. For instance, polypyrrole (PPy) was found to be versatile in anti-bacterial and antioxidant applications.^{56–58} Such PPy NMs were successfully introduced into the organic phase for IP, followed by incorporation into a MPD–TMC derived PA layer.⁵⁹ The PPy NMs acted as a sacrifice and a biocide in the TFN RO membrane (see Figure 4.21a). As a sacrifice, the abundant amino groups on PPy made the NMs more sensitive to chlorine-free radicals than the PA layer (see Figure 4.21c). Thus, PPy NMs can protect the PA layer from attack and ensure its integrity. As a biocide, PPy NMs were intrinsic positively charged and able to induce the leakage of nutrition in negatively charged cells (see Figure 4.21d–j). Moreover, the fully organic nature of PPy endows itself with better compatibility with polymers and helps the TFN RO membrane maintain its desalination performance (see Figure 4.21b).

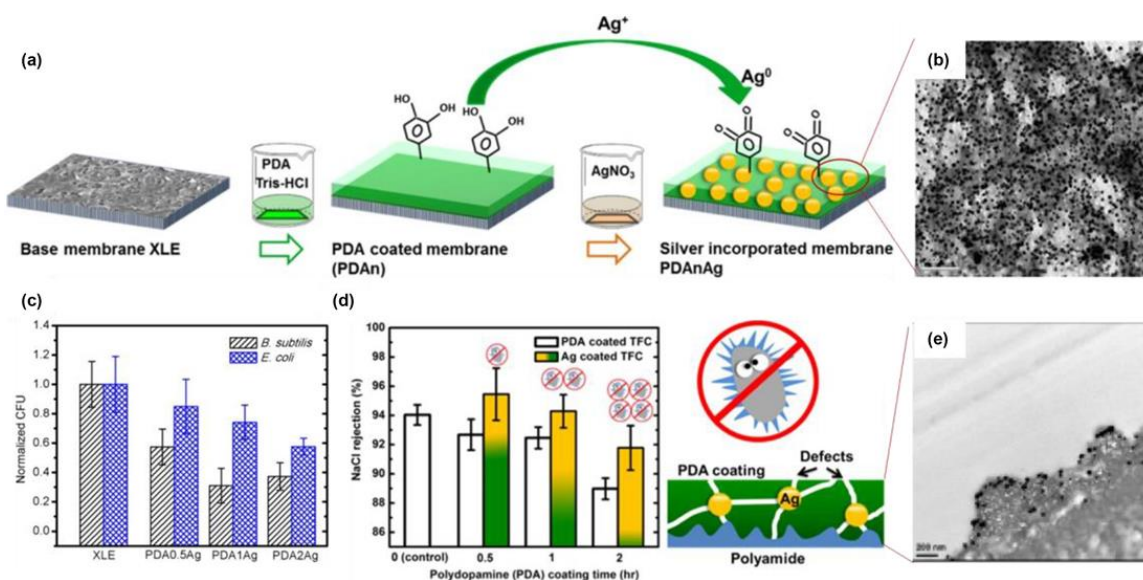


Figure 4.20 (a) Fabrication of silver-incorporated RO membranes; (b) TEM vertical view of silver-incorporated RO membranes; (c) anti-bacterial performance of RO membranes with (PDA0.5Ag, PDA1Ag and PDA2Ag) and without (XLE) silver on the surface; (d) desalination performance of the control membrane, PDA-coated membranes and PDA–Ag coated membranes; (e) TEM cross-section of silver-incorporated RO

membranes. Scale bars in the TEM images are both 200 nm. Reproduced from ref. ⁵⁵ with permission from American Chemical Society, Copyright 2016.

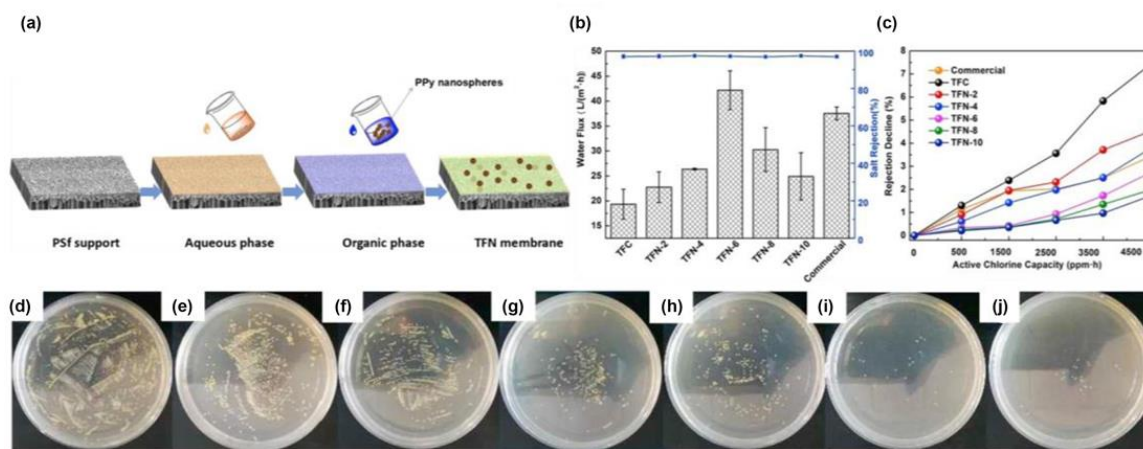


Figure 4.21 (a) Manufacture of PPy NM-incorporated TFN RO membranes; (b) RO performance and (c) chlorine resistance of TFC and PPy-containing TFN membranes; (d–j) *E. coli* colonies after being in contact with TFC and TFN membranes, later letters refer to higher PPy contents in the membrane. Reproduced from ref. ⁵⁹ with permission from Elsevier, Copyright 2018.

4.5 NM-supported Non-pressure-driven Membrane Processes

Non-pressure-driven membrane processes usually include MD, PV and FO. In this section, we will have a brief review on how NMs assist these emerging membrane processes.

4.5.1 NM-supported Membrane Distillation (MD)

MD is a thermally driven membrane process. In MD, water vapor molecules pass through the pores of hydrophobic membranes and such a process can be enhanced by the temperature differences across the membrane.⁶⁰ Thus, NMs are used to enhance the membrane hydrophobicity, anti-wettability and mechanical strengths. Activated carbon (AC), a cost effective and easily available NM, was introduced into corresponding membrane fabrication. No matter in NIPS⁶¹ or

electrospinning (see Figure 4.22a),⁶² blended AC provided more pathways for the transport of water vapor without affecting the membrane hydrophobicity as AC possessed a porous and hydrophobic nature (see Figure 4.22b and c). With the support of AC, the corresponding membranes outperformed their neat counterparts in vacuum MD (VMD) and direct contact MD (DCMD) fluxes (see Figure 4.22d). Although other NMs (*e.g.* silicon dioxide (SiO₂), graphene and carbon nanotubes (CNT)) were also reported to improve the desired properties in MD,^{63–65} more efforts are expected. For example, thermophilic bacteria were observed during the MD process while seldom work reported the attempt of introducing anti-bacterial NMs into the corresponding membrane manufacture.⁶⁰ In addition, the commercial use of NM-supported MD is still proceeding at a slow rate, breakthroughs in such commercialization are highly desired.

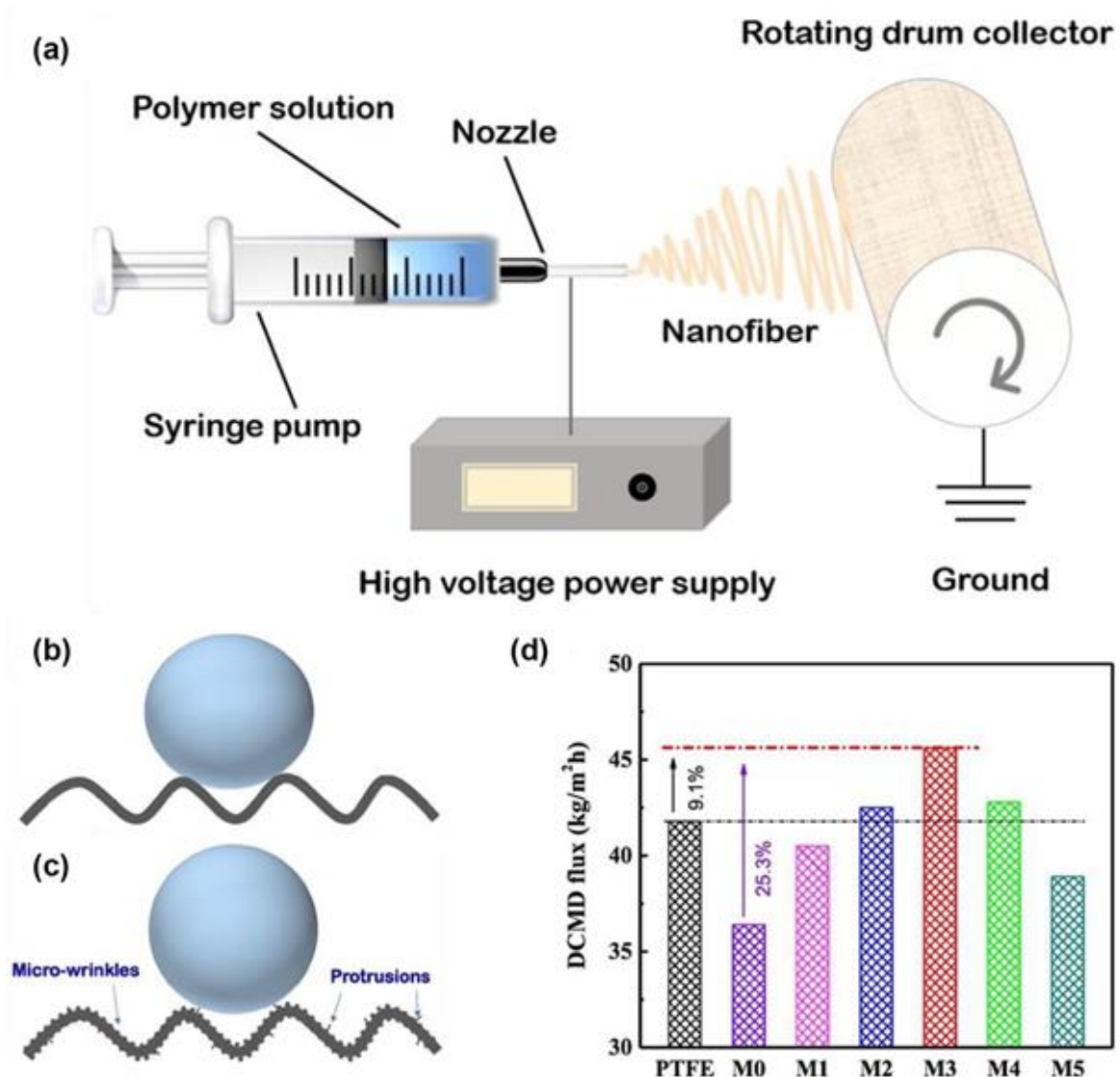


Figure 4.22 (a) Schematic illustration of electrospinning; (b) and (c) the effect of activated carbon (AC) on fiber membrane hydrophobicity; (d) MD fluxes of electrospun membranes and PTFE membranes. M0 didn't contain AC. From M1 to M5, the dosage of AC increased. Reproduced from ref. ⁶² with permission from Elsevier, Copyright 2018.

4.5.2 NM-supported Pervaporation (PV)

Pervaporation is based on the differences of chemical potential across the semi-permeable membrane. A feed solution contacts one side of the membrane, while the sweep gas or vacuum is used at the other side, namely the permeate side, to let the separation happen. The solution diffusion model is the most prevailing transport mechanism in PV.⁶⁶ In water

treatment, PV can be applied in organic solvent dehydration (removing water to purify the solvent) and organic solvent recovery (removing solvent from water). Depending on different demands in PV, super-hydrophilic or super-hydrophobic membrane surfaces are needed, and NMs can help develop the corresponding surfaces.

For organic solvent dehydration, the membrane surface should be as hydrophilic as possible to allow the water molecules to diffuse through the membrane more easily. PEG-functionalized polyhedral oligomeric silsesquioxanes (PEG@POSS) are expected to be an ideal auxiliary for organic solvent dehydration as there are abundant absorption sites for water molecules on the NMs (see Figure 4.23a). After blending with sodium alginate (SA), the PEG@POSS NMs were spin-coated and cross-linked on the PAN substrate to form the nanocomposite membrane.⁶⁷ The homogeneous dispersion of PEG@POSS NMs endowed the as-prepared membrane better hydrophilicity together with larger free volume for water permeation (see Figure 4.23b). As a result, the membrane achieved a flux of $2500 \text{ g m}^{-2} \text{ h}^{-1}$ and a separation factor of 1077 in the dehydration of 90/10 wt% ethanol–water mixture.

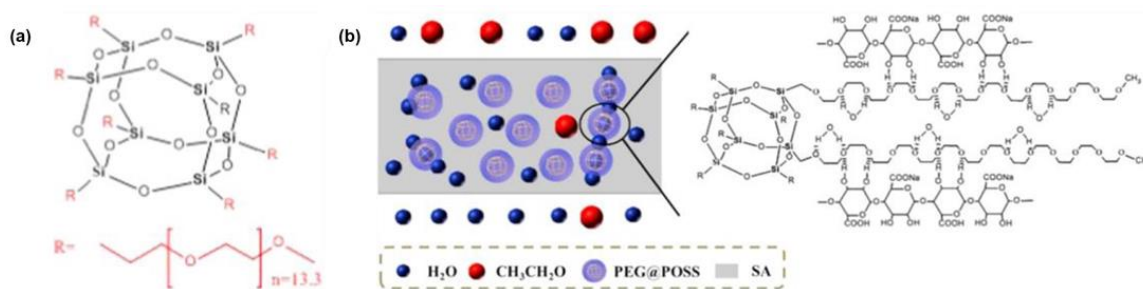


Figure 4.23 (a) Structure of PEG-functionalized polyhedral oligomeric silsesquioxanes (PEG@POSS); (b) PV process via the PEG@POSS composite membrane.

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In contrast, membranes used for solvent recovery should show high affinity to the solvent and hydrophobicity. A SiO_2 -blended polydimethylsiloxane (PDMS) suspension was synthesized to coat a PSf UF substrate with the assistance of ultrasonic treatment.⁶⁸ Thanks to the presence of SiO_2 , the membrane hydrophobicity was higher (water contact

angle of 135.5° to 146.3°) than the neat PDMS–PSf membrane (water contact angle of 110.2°). Meanwhile, the PDMS–SiO₂ hybrid membrane exhibited better affinity with ethanol (ethanol contact angle of lower than 20°) than the pristine one (ethanol contact angle of higher than 25°). In pervaporation with a 5% ethanol–water mixture, the PDMS–SiO₂ hybrid membrane manifested a lower flux with a promoted selectivity compared with the neat PDMS–PSf membrane.

NMs can help tailor the membrane surface properties to meet the particular demand in PV. They are anticipated to overcome some drawbacks of PV such as low permeation rate and membrane swelling. With an in-depth understanding of the merging of NMs and PV membranes, the wide application of PV is expected.

4.5.3 NM-supported Forward Osmosis (FO)

FO is an osmosis pressure-driven process and requires no or low extra hydraulic pressure in providing clean water. The porous membrane faces the feed solution with back contact of draw solution. The draw solution usually possesses ultrahigh osmosis pressure and draws water from the feed solution *via* the differences of osmosis pressure between two sides of membrane.

The membrane used in FO process should perform high permeability and solute rejection. Hydrophilic NMs are incorporated into TFN membranes^{69,70} or blended into MMMs⁷¹ to improve the FO performance. In addition, proper NMs like carbon nanoparticles can provide the membrane with enhanced mechanical strength to withstand the high osmosis pressure.⁷²

One interesting usage of NMs in FO is to let the NMs, especially magnetic NMs, be the draw agent. Magnetic NMs are qualified to serve as the draw agent. They can be modified to manipulate the osmotic properties. Their superparamagnetic properties make them easy to be recycled. Moreover, their particle appearance can prevent them infiltrating the feed solution.⁷³ Pectin, PAA and oleate were once used to coat Fe₃O₄, a well-known magnetic NM, to form draw agents to enhance the FO performance and ease the internal concentration polarization (ICP) of FO process.^{74–76}

However, in some work, it has been pointed out that polymer-coated magnetic NMs didn't elevate the osmotic pressure in the draw solution very much compared with a solely polymer-containing draw solution.⁷⁷ From a flux promotion point of view, better marriage between NMs and draw solutions is still highly desired.

4.6 Summary

In this chapter, we reviewed how NMs help membranes improve the efficiency in water treatment. Hydrophilic NMs can enhance the hydrophilicity of membranes to help membranes enhance the permeability and anti-fouling performance. In contrast, hydrophobic NMs can deteriorate the membrane wettability and play an important role in MD. NMs like silver can act as anti-bacterial agent to protect membranes from biofouling. Absorptive/catalytic NMs are used to assemble dual-functional membranes and achieve the removal of multiple contaminants from water. 2D NMs themselves can generate a selective layer for separation. In addition, some NMs inherently possess multiple properties, with their assistance, perhaps multiple improvements can be achieved in one-step modification techniques. Whether in pressure-driven (MF, UF, NF and RO) or non-pressure-driven membrane process (MD, PV and FO), NMs always have a superior position.

To a large extent, the development of NM-assisted membrane water treatment depends on the intrinsic properties of NMs. By attending to the construction of membrane–membrane processes, the NM properties become part of the membrane properties and NMs play their role in membrane water treatment. Therefore, rationally designed NMs are greatly needed. Such designing at least includes structural manipulation and interfacial tailoring. For instance, hollow NMs provide more cavities for water transport and negatively charged interfaces enhance the rejection of sodium sulfate (Na_2SO_4) of membranes. We look forward to witnessing more innovations in NM-assisted membrane water treatment.

Abbreviations

–COCl	acyl chloride groups
–OH	hydroxyl groups
–SO ₃ H	sulfonic acid groups
2D	two-dimensional
AOP	advanced oxidation process
BSA	bovine serum albumin
CA	cellulose acetate
CNT	carbon nanotube
COFs	covalent organic frameworks
CPAM	cationic polyacrylamide
DMAc	dimethylacetamide
DMF	dimethylformamide
<i>E. coli</i>	<i>Escherichia coli</i>
E2	17β-estradiol
Fe ₃ O ₄	ferroferric oxide
FO	forward osmosis
FRR	flux recovery ratio
GA	glutaraldehyde
GO	graphene oxide
H ₂ SO ₄	sulfuric acid
HA	humic acid
HCl	hydrochloric acid
HMO	Hydrous manganese dioxide
HPZNs	hollow porous Zr(OH) _x nanospheres
KOH	potassium hydroxide
LiCl	lithium chloride
LMH	liters per square meter per hour
MD	membrane distillation
MF	microfiltration
MMMs	mixed matrix membranes
MOFs	metal–organic frameworks
MPD	<i>m</i> -phenylenediamine
Na ₂ SO ₄	sodium sulfate
NaCl	sodium chloride
NaHSO ₃	sodium bisulfite

NaOH	sodium hydroxide
NF	nanofiltration
NIPS	non-solvent-induced phase separation
NMP	1-methyl-2-pyrrolidinone
NMs	nanomaterials
OVA	ovalbumin
PAA	poly (acrylic acid)
PAN	poly (acrylo nitrile)
PCB 126	3,3',4,4',5-pentachlorobiphenyl
Pd(OAc) ₂	palladium(ii) acetate
PDA	poly (dopamine)
PDDA	poly (diallyldimethylammonium chloride)
PDMS	poly (dimethyl siloxane)
PEG	poly (ethylene glycol)
PEI	poly (ethylene imine)
PES	poly (ether sulfone)
POSS	polyhedral oligomeric silsesquioxanes
PPy	polypyrrole
PSf	polysulfone
PV	pervaporation
PVA	poly (vinyl alcohol)
PVDF	poly (vinylidene fluoride)
PVP	poly (vinyl pyrrolidone)
RFBs	resorcinol–formaldehyde nanobowls
R_{ir}	irreversible fouling ratio
RO	reverse osmosis
SA	sodium alginate
SiO ₂	silicon dioxide
TA	tannic acid
TBT	tetrabutyltitanate
TCN	tetracycline
TiO ₂	titanium dioxide
TMC	trimesoyl chloride
UF	ultrafiltration
UV	ultraviolet

WHO	World Health Organization
ZnO	zinc oxide
Zn(NO ₃) ₂ ·6H ₂ O	zinc nitrate hexahydrate
ZrO ₂	zirconium dioxide
ZrOCl ₂ ·8H ₂ O	zirconyl chloride octahydrate
ZrP	zirconium phosphate
ZVI	zero valent iron

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Chapter 5

Tuning Iron Oxide-based Nanomaterials as Next Generation Adsorbents for Environmental Applications

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5.1 Introduction

Globally, addressing water pollution is a critical engineering challenge.¹ Among such pollutants, metals and metalloids are widely distributed in the environment due to increased industrial usage, including mining, metallurgy, tannery, chemical manufacturing, battery manufacturing, among others.² Due to their persistence and toxicity, metals and metalloids not only pose a threat to ecosystems, but their transportation and accumulation through food chains also presents significant risk to human health.^{3–6} To

address such risk(s), the World Health Organization (WHO) has proposed a drinking water guidance for a number of metals and metalloids, including 0.05 mg L⁻¹ for chromium, 0.03 mg L⁻¹ for uranium, 0.01 mg L⁻¹ for lead, and 0.01 mg L⁻¹ for arsenic.⁷

Currently, ion-exchange, membrane separation, coagulation–flocculation, chemical precipitation, electrochemical, reverse osmosis, air floating, and bioremediation methods are used to remove metals from the aqueous phase.^{6,8–16} However, such methods are costly and/or sometimes unsuitable for the removal of low-level metals and metalloids, not to mention they can generate toxic sludge and other secondary pollutants.^{17,18} Adsorption has emerged as a promising, alternative method for the separation of metals/metalloids (as contaminants or high-value rare earth elements) from wastewater in recent years.^{19,20} The advantages of adsorption are low cost, simplicity, and little need to use large amounts of water or other additional chemicals.²¹ A variety of natural and synthetic adsorbents such as activated carbon, metal oxides, clays, zeolites, and biomaterials have been applied for the removal of metals/metalloids.^{22–24} Among these, iron oxides show some of the highest affinities toward metals/metalloids, making them a preferred sorbent. However, adsorption capacities of bulk iron oxides are generally limited due to the low surface area of the material. The adsorption capacity of an adsorbent is generally affected by the specific surface area, which is proportional to the active/favorable sites available to the adsorbate during the adsorption process. However, iron oxide adsorbents can be size engineered to maximize the total surface area and thus increase the active sites.^{25,26} In particular, nanoscale iron oxide materials, which allow for high surface area, numerous functional groups (and types), ease of modification and recyclability/separation have gained considerable attention as next generation adsorbents for metals/metalloids.²⁷ To realize such advantages, numerous methods to prepare nanoscale iron oxides have been reported. Herein, we provide a review of recent synthesis methods for iron oxide-based nanomaterials, various surface coating strategies, and discussion of their sorption performance for a variety of metals/metalloids in the aqueous phase.

5.2 Synthesis Methodologies

A number of methods have been developed to synthesize nanoscale iron oxide/iron oxide nanocomposites, including physical,²⁸ chemical,²⁹ and biological methods.³⁰ Among these, chemical methods are the most popular preparation routes that allow for a variety of efficient routes for size/shape-controlled, highly dispersed iron oxide nanoparticles (IONPs), such as co-precipitation, microemulsions, hydrothermal, thermal decomposition, electrochemical methods, sonochemical, microwave-assisted, chemical vapor deposition, and laser pyrolysis synthesis.^{29,31–37} Iron oxide nanocomposites with various compositions, sizes, and structures/morphologies have also been synthesized for a number of applications.^{37–41} According to the structure/morphologies, iron oxide nanocomposites can be classified into three types: one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) structures, as described below.

5.2.1 Synthesis Methods for Iron Oxide Nanoparticles

5.2.1.1 Co-precipitation Methods

Co-precipitation of ferric and/or ferrous ions in an alkaline solution is a classic, convenient, cheap, and eco-friendly method to synthesize IONPs. For this method, IONPs are usually produced in an aqueous medium, and the reaction mechanism can be written as follows:³²
$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_3\text{O}_4 \downarrow + 4\text{H}_2\text{O}$$

The size, shape, and composition of IONPs are affected by a variety of factors including the type of iron salt, the $\text{Fe}^{2+} : \text{Fe}^{3+}$ ratio, temperature, pH, alkali type and addition (titration) rate.^{31,42,43} Rajput *et al.*⁴⁴ demonstrated IONPs by adding ammonium hydroxide (NH_4OH) to a mixture of FeCl_2 and FeCl_3 in a 1 : 2 molar ratio under inert conditions. Iida *et al.*⁴⁵ prepared Fe_3O_4 nanoparticles in an aqueous solution containing Fe^{2+} and Fe^{3+} with the addition of 1,6-hexanediamine as the base. They found that as the molar ratio of ferrous ions relative to total iron ions increased from 33% to 100%, the average diameter of Fe_3O_4 nanoparticles increased from 9 nm to 37 nm,

respectively.⁴⁵ Wilson *et al.*⁴⁶ synthesized Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles *via* co-precipitation using 1.5 mol L^{-1} NaOH and 25% NH_4OH as precipitants, respectively. They found that compared with NaOH, IONPs prepared by NH_4OH had a narrower size distribution and smaller mean particle size.⁴⁶ Petcharoen *et al.*⁴³ prepared hexanoic acid and oleic acid coated iron oxide nanoparticles using co-precipitation at different temperatures using ammonium hydroxide as the precipitant. They discovered that particle size can be controlled by reaction temperature and surface coating. Although co-precipitation is a relatively easy and environmentally friendly method to prepare iron oxide nanoparticles, it is difficult to precisely control the size and monodispersity. Further, as nanoparticles produced using co-precipitation methods are bare, surfactants are usually added during/after the reaction process to hinder aqueous agglomeration.⁴⁷

5.2.1.2 *Microemulsion Methods*

Microemulsions are liquid mixtures comprised of an aqueous phase, an oil phase, and surfactant(s).⁴⁸ In water-in-oil microemulsions, iron salts/precursors are dissolved in the aqueous phase, which are wrapped in surfactants and uniformly distributed in the oil phase.³² The aqueous phase microdroplets act as nano-reactors, which keep colliding, repeating the process of merging and breaking, and finally forming a precipitation of iron oxide nanoparticles.⁴⁹ In 1992, Lee *et al.*⁵⁰ first prepared Fe_3O_4 nanoparticles with an average radius smaller than 15 nm using water-in-oil microemulsions composed of Aerosol OT (AOT)–water–isooctane. Du *et al.*⁵¹ prepared size-controllable Fe_3O_4 nanoparticles coated with SiO_2 *via* a water-in-oil microemulsion route. In the reaction system, FeCl_2 and FeCl_3 solutions were encapsulated by the amphiphilic hexadecyltrimethylammonium bromide (CTAB) surfactant, and excess toluene acted as the oil phase. They found Fe_3O_4 nanoparticle size was controlled by the molar ratio of deionized water to CTAB (Wo): values of Wo were 26, 40, and 80 resulted in average IONP sizes of *ca.* 4.5, 6.3, and 8.7 nm, respectively. Nourafkan *et al.*⁵² reported that uniform IONPs with a

mean particle size of 2.1 ± 0.49 nm can be synthesized using the reverse microemulsion method (water-in-oil). Although various sizes of IONPs can be generated through microemulsion methods, the problem of low yield and high solvent demand hinder its widespread use.

5.2.1.3 *Hydrothermal Methods*

Among the various synthesis techniques used to produce IONPs, hydrothermal-based methods allow for process control by adjusting the pressure and temperature of the reaction. Hydrothermal synthesis is conventionally conducted by adding an organic metal salt precursor to an aqueous solvent, which is sealed into a pressured container (often an autoclave). Under high temperature (130–250 °C) and high pressure (0.3–4 MPa), nanoparticle growth is promoted.³² The solvothermal method is a similar high pressure/high temperature process used to synthesize IONPs, with the key difference being that the precursor salts are added to nonaqueous solvents, such as ethylene glycol and benzyl alcohol.^{53,54} One significant advantage of hydrothermal-based methods is that they can be used to prepare nanoparticles of various shapes without the need for surfactants. Wang *et al.*⁵⁵ reported a generalized hydrothermal method for synthesizing a variety of nanocrystals, including IONPs, *via* a phase transfer and separation mechanism(s) based on liquid (ethanol–linoleic acid)–solid (metal linoleate)–solution (water–ethanol) interfaces. Zhang *et al.*⁵⁶ employed both hydrothermal and solvothermal methods to synthesize spindle, ellipsoidal, spherical, and quasi-cubic Fe₃O₄ nanoparticles using various catalysts. Wu *et al.*⁵⁷ demonstrated both solid and hollow IONPs with controlled size and morphology by varying the ratios of the iron salts, phosphate, and sulfate ions. While hydrothermal methods are capable of producing highly crystalline nanoparticles with various morphologies, in general, such methods suffer from slow reaction kinetics, resulting in long preparation times. Microwave-assisted hydrothermal synthesis circumvents this issue by rapidly, uniformly, and selectively heating. Hu *et al.*⁵⁸ synthesized magnetite, maghemite, and hematite nanoparticles in a very short time (2–6 min) by integrating microwave heating with an autoclave-based reaction.

5.2.1.4 Thermal Decomposition Methods

Thermal decomposition, a chemical decomposition process induced by heat, is a synthesis technique capable of precisely producing highly monodispersed IONPs. IONPs are synthesized through the rapid decomposition of iron precursors, such as $\text{Fe}(\text{CO})_5$,⁵⁹ iron carboxylate salt,⁶⁰ ferrocene,⁶¹ iron oxyhydroxide,⁶² and iron acetylacetonate⁶³ in an organic solvent. These precursors decompose easily under relatively mild conditions (such as heating) due to their metastable nature. Highly dispersed IONPs with precise control over size, shape, and composition can be achieved by adjusting reaction conditions, including the initial precursors, reaction time, reaction temperature, heating rate, and the additives.²⁶ In 1999, Rockenberger *et al.*⁶⁴ were the first to produce monodisperse $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles *via* decomposition of $\text{Fe}(\text{cup})_3$ at 180 °C. In 2002, Sun *et al.*⁶⁵ produced Fe_3O_4 nanoparticles with diameters less than 20 nm through the thermal decomposition of $\text{Fe}(\text{acac})_3$ in a mixed solution of 1,2-hexadecanediol, oleic acid, and oleylamine. Li *et al.*⁶⁶ synthesized monodisperse IONPs through a high temperature (*ca.* 320 °C) decomposition of iron carboxylate in a mixed solution of oleic acid and 1-octadecene. They demonstrated that precise control of the size of IONPs could be achieved by changing the concentrations of oleic acid and the initial iron precursor while keeping the volume of solvent fixed. By systematically increasing the amount of $\text{FeO}(\text{OH})$ from 2 to 10 mmol, they observed that the diameter of the IONPs increased from 8 to 25 nm, respectively (see Figure 5.1). It was further reported that additives played an important role with regard to the final shape of the resulting nanoparticles, including cubes,³⁸ octahedra,³⁹ tetrapods,⁴¹ potato- and flower-like structures.³⁷ For instance, Alexey *et al.*³⁹ produced octahedral IONPs *via* the thermal decomposition of iron oleate in the presence of tetraoctylammonium bromide. Li *et al.*³⁷ found that the addition of L-arginine and L-arginine monohydrochloride resulted in IONPs with irregular potato- and flower-shaped nanoparticles, respectively. Thermal decomposition is frequently used synthesis method to produce high quality IONPs due to the scalability of the process, high yield, reproducibility, and control of IONP shape and size.

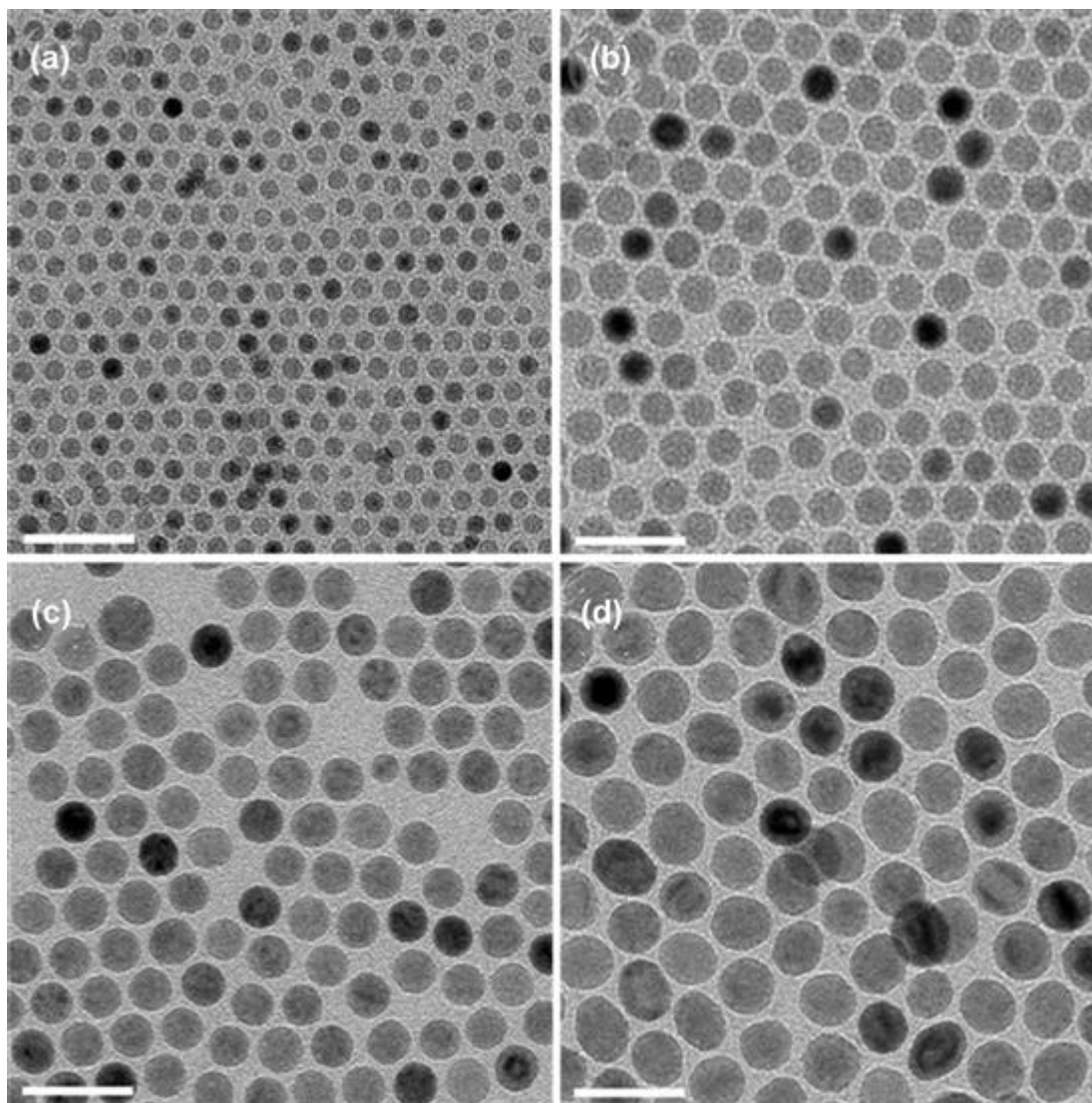


Figure 5.1 TEM micrographs of (a) 8 nm, (b) 15 nm, (c) 19 nm, and (d) 24 nm IONPs in hexane. All scale bars are 50 nm. Reproduced from ref. ⁶⁶, <https://doi.org/10.1021/acsami.7b01042>, with permission from American Chemical Society, Copyright 2017. Further permissions related to the material excerpted should be directed to the ACS.

5.2.1.5 *Electrochemical Methods*

Electrochemical methods provide a means of synthesizing IONPs with well-controlled particle size, (narrow) size distributions, and excellent magnetic properties. Electrochemical techniques are based on applying either an external voltage or current between two electrodes, which are

immersed in an electrolytic solution. Electrochemical synthesis of IONPs uses either iron salts or a metallic iron electrode as the precursor material. In the case of metallic iron, the electrode acts as the anode of the electrochemical cell and produces Fe ions as a result of oxidation. The Fe ions dissolve in the electrolyte solution and undergo complexation with other ions in order to form IONPs. Morphology, structure, size, and size distribution of IONPs synthesized electrochemically can be adjusted by varying experimental conditions such as electrode separation,⁶⁷ current density,⁶⁸ applied potential,⁶⁸ and the electrolyte composition.⁶⁹ Pascal *et al.*⁷⁰ electrochemically synthesized γ -Fe₂O₃ nanoparticles using an iron electrode in an organic medium, incorporating a cationic surfactant to prevent particle aggregation. They found that as the applied current density decreased from 25 to 1.5 mA cm⁻², the mean particle size increased from 3.2 to 7.8 nm, respectively. Starowicz *et al.*⁷¹ synthesized magnetic IONPs using an iron anode in a LiCl solution containing a mixture of ethanol and water. They found that the average diameter of their round nanoparticles could be controlled in the range of 5 to 40 nm by adjusting the water-to-ethanol ratio of the solution. Taimoory *et al.*⁷² synthesized spherical IONPs using stainless-steel electrodes and FeSO₄·7H₂O as an iron precursor. They also evaluated the influence that the inter-electrode spacing had on the mean diameter of the IONPs and found that as the spacing between the anode and cathode increased from 2 to 6 cm, the mean diameters of the resulting nanoparticles decreased from 33 to 19 nm, respectively.

5.2.1.6 Plasma-assisted Electrochemical Methods

While plasma–liquid interaction research is still a relatively new synthesis frontier, the use of plasma–liquid systems to synthesize nanomaterials has already been well established for a variety of metal and metal oxide nanoparticles including Au,^{73,74} Ag,^{74,75} ZnO,⁷⁶ and TiO₂.⁷⁷ A plasma is a partially ionized gas comprised of free electrons, radicals, and ions. Closely related to electrochemical synthesis, a plasma can be used to replace one (or both) of the electrodes, acting as a gaseous electrode in contact with an aqueous solution containing an iron salt. The plasma source used for these electrolysis reactions is a microplasma, which is a plasma with sub-

millimeter dimensions. Plasma-assisted electrochemistry has the advantages of being able to operate under ambient conditions, not requiring surfactants, and the ability to synthesize nanoparticles in short timescales. Wang *et al.*⁷⁸ synthesized well-dispersed, water-soluble Fe₃O₄ nanoparticles with a mean diameter of 12.5 ± 2.4 nm by treating an aqueous solution containing 2 mM FeCl₃ and 1 mM FeCl₂ with an Ar microplasma. Though the system had not been optimized for high throughput, they observed a IONP production rate of 0.37 mg min^{-1} . Shirai *et al.*⁷⁹ synthesized magnetic Fe₃O₄ nanoparticles used a Fe anode as the iron precursor and treated an aqueous solution containing 15 wt% NaCl using a He plasma as the cathode. After 30 minutes of plasma treatment, the synthesized nanoparticles showed a narrow size distribution centered at about 11.8 nm. Nolan *et al.*⁸⁰ synthesized magnetic Fe₃O₄ nanoparticle–hydrogel composites by using a He plasma to treat a pH 5 aqueous solution containing 5 mM FeCl₃, 2.5 mM FeCl₂, and the hydrogel precursors. The average size of the IONPs formed for such a one-step synthesis hydrogel composite was found to be 9 ± 0.97 nm.

5.2.1.7 Other Methods

In addition to the methods described, various other methods used to synthesize IONPs have been reported including sonochemical,⁸¹ biosynthesis,³⁰ microwave heating,⁵⁸ among others.^{82–84} Sonochemical methods utilize cavitation to induce or enhance chemical reactions. Acoustic cavitation results in rapid heating, allowing nanoparticles to be prepared over short time scales without the need for high temperatures or pressures.⁸¹ The main drawback of sonochemical synthesis is the difficulty in controlling the shape and size of the product. Biosynthesis offers a platform for green synthesis of IONPs, using organisms such as bacteria, fungi, plants, *etc.* to prepare the nanoparticles. Bharde *et al.*⁸⁵ synthesized γ -Fe₂O₃ with an average size of 19 nm by feeding the bacteria *Actinobacter* sp. with a ferric chloride precursor under aerobic conditions.

5.2.2 One-dimensional Iron Oxide Nanocomposites

Iron oxide nanocomposites with higher dimensional structures are attractive materials based on potential synergistic effects between the high surface area of the template material and the magnetic properties of IONPs. Such nanocomposites typically have a higher absorption capacity compared to the constituent materials due to an increased number of available absorption sites. A number of nanocomposites comprised of magnetic iron oxide and 1-D nanomaterials such as nanotubes,⁸⁶ nanoworms,⁸⁷ nanowires,⁸⁸ nanofibers,⁸⁹ and nanosticks⁹⁰ have been reported. Magnetic 1-D nanocomposites are prepared by depositing IONPs onto a 1-D template material. For example, carbon nanotubes are often utilized as 1-D templates for nanocomposites due to their high adsorption capacity and ability to support metal oxides. Nanocomposites comprised of IONPs and carbon nanotubes have been successfully prepared using a simple and efficient, one-step method in which ferrocene was pyrolyzed and subsequently deposited onto carbon nanotubes under high temperature conditions.⁸⁶ Gupta *et al.*⁹¹ synthesized magnetic multi-walled carbon nanotubes, which have superior adsorption performance compared to activated carbon and single-walled carbon nanotubes. Mao *et al.*⁹² produced α -Fe₂O₃ nanorod arrays through electrodeposition of Fe onto gold nanorod arrays with the assistance of an anodic aluminum oxide (AAO) template, which was thermally annealed under an oxygen atmosphere to convert Fe to Fe₂O₃. Nanofibers have also been investigated as a 1-D nanocomposite template material for adsorption due to the high porosity, high surface area, and cost-effective preparation. One method of preparing magnetic composite nanofibers, using an adaptation of the hydrothermal method, has been developed by adding electrospun fibers to the aqueous solution containing the iron salt precursor, resulting in an IONP-coated electrospun nanofiber composite.^{93,94} The chemical composition of the fiber can also be changed depending on the intended application (*e.g.*, targeting a specific adsorbate). For example, Karamipour *et al.*⁹³ synthesized cellulose acetate and cellulose chitosan nanofibers coated with Fe₃O₄ nanoparticles. Muhammad *et al.*⁹⁵ prepared maghemite glass fiber nanocomposites *via* the thermal decomposition of ferric nitrate in a mixture containing urea and a non-woven glass fiber.

5.2.3 Two-dimensional Iron Oxide Nanocomposites

More recently, research focused on combining iron oxides with 2-D template materials has attracted attention due to the large surface-to-volume ratio of the 2-D matrices. Examples of 2-D template structures that have been used to prepare magnetic iron oxide nanocomposites include graphene-based materials (*e.g.*, graphene,⁹⁶ graphene oxide,⁹⁷ and reduced graphene oxide⁹⁸), MXenes,⁹⁹ layered double hydroxides (LDHs),¹⁰⁰ and fabrics.¹⁰¹ Similar to the case of 1-D composites, preparation of magnetic 2-D composites can be achieved using IONPs and/or iron salt precursors as the starting material. For example, IONPs can be surface modified and directly attached to the oxygen-containing functional groups of graphene oxide.¹⁰² Such 2-D iron oxide–graphene oxide nanocomposites have been demonstrated to be excellent adsorbents due to abundance of functional groups (*e.g.*, hydroxyl, epoxy, carboxyl, and carbonyl groups) and high aqueous dispersibility.¹⁰³ Iron oxide–graphene oxide nanocomposites can be chemically converted to iron oxide–graphene nanocomposites by reduction of graphene oxide with hydrazine hydrate.⁹⁶ Zhang *et al.*⁹⁹ fabricated a sandwiched MXene–iron oxide (MXI) nanocomposite, which was comprised of alternating layers of MXene, $\gamma\text{-Fe}_2\text{O}_3$, and Fe_3O_4 . In this process, ultrafine $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were embedded within the interior layers of MXene while magnetic Fe_3O_4 nanoparticles were mainly distributed in the gaps between multiple layers of MXene and on the MXene surface. Yan *et al.*¹⁰⁰ reported a calcined $\text{Fe}_3\text{O}_4\text{--ZnAl-LDH}$ prepared by synthesizing ZnAl-LDH in the presence of ferric oxide followed by a subsequent calcination at elevated temperatures. It was noted that the calcination of ZnAl-LDH resulted in the disorder of the stacking layers. However, adsorption of Cr(IV) using calcined $\text{Fe}_3\text{O}_4\text{--ZnAl-LDH}$ resulted in the reconstruction of layered structures, which was ascribed to the so-called memory effect of LDHs.¹⁰⁰

5.2.4 Three-dimensional Iron Oxide Nanocomposites

3-D iron oxide nanocomposites can also be synthesized by additional processing of the aforementioned 1-D/2-D nanostructures. Vadahanambi *et*

*al.*¹⁰⁴ reported a 3-D graphene–carbon nanotube–iron oxide ternary nanocomposite in which vertically-oriented carbon nanotubes were anchored onto graphene sheets with IONPs uniformly distributed on the surface of both carbon allotropes. This nanocomposite was generated using a one-pot microwave method, involving the sublimation of graphene modified by organometallic ferrocene under microwave radiation. Ye *et al.*¹⁰⁵ prepared a 3-D Fe₃O₄ graphene oxide aerogel (GAs) *via* the hydrothermal method, in which FeC₂O₄·2H₂O was added to a graphene oxide (GO) suspension followed by hydrothermal, freeze-drying, and thermal treatments. They found that IONPs were attached to the graphene aerogel, which displayed an interconnected mesoporous network allowing for access and diffusion of ions. Jiang *et al.*¹⁰⁶ adopted an aerosol route to synthesize a ternary, aggregation-resistant nanocomposite comprised of crumpled graphene–TiO₂–Fe₃O₄. In this hybrid material, TiO₂ and Fe₃O₄ were functionally wrapped inside the crumpled graphene oxide (see [Figure 5.2](#)). Lyu *et al.*¹⁰⁷ adopted a simple chemical oxidation method to prepare a 3-D hierarchical coral-like, magnetic polyaniline adsorbent consisting of short nanowires. Due to the mesoporous structure and abundance of surface-active sites, Fe₃O₄ coated with hierarchical coral-like polyaniline exhibited better adsorption performance compared to polyaniline nanorod. Interestingly, iron oxide can also be integrated into 3-D structures without the need for any substrate. Jia *et al.*¹⁰⁸ successfully synthesized shape-controlled, hollow magnetic porous Fe₃O₄– α -FeOOH microspheres through a facile template-free, one-step solution method. The microspheres were fabricated by adding urea to a solution containing a mixture of FeSO₄ and ethylene glycol, which was subsequently stirred and heated to 100 °C. Due to the abundant surface hydroxyl groups and carbonate-like complexation species (*e.g.*, FeO(CO₃)[−]), the microspheres exhibited excellent adsorption properties for metals and metalloids (As, Cr, Cd, and Hg).

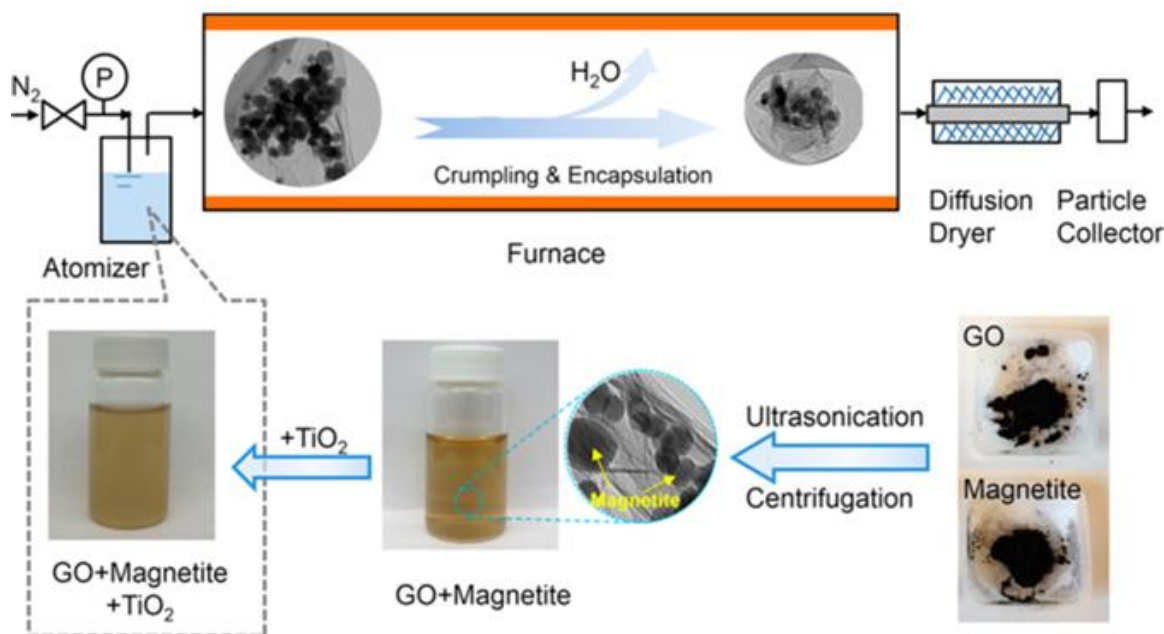


Figure 5.2 Synthesis process for crumpled graphene–TiO₂–Fe₃O₄ ternary nanocomposites.

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5.3 Surface Modification

As mentioned, iron oxide nanoparticles/nanocomposites with uniform shape, controllable size, and defined structures can be readily obtained by varying the reaction conditions used in the synthesis procedure.²⁶ However, these nanomaterials typically have high specific surface energies, inevitably leading to the aggregation of particles in solution. Subsequently, formation of aggregates limits their optimization in aqueous environments.¹⁰⁹ For environmental applications, the ability to synthesize/modify nanoparticles that remain stable within aqueous phase has been an important issue/goal, particularly for the adsorption of heavy metal ions.¹¹⁰ As such, determining suitable surface coatings/strategies to produce nanoparticles that demonstrate high stability in aqueous environments is necessary for material integration in real-world treatment systems. The two general strategies used for surface modification of nanoparticles are performed *in situ* (*i.e.*, coating is applied during synthesis)

and post-processing (*i.e.*, coating is applied in additional steps following synthesis).¹¹¹ It should be noted that the latter is typically the preferred method, as such processing does not limit the growth of nanoparticles.²⁶ Coatings used for the surface modification can be broadly classified as either organic (small organic molecules, surfactants, and macromolecules) or inorganic (silica, metals, and metal oxides).^{17,26,112}

5.3.1 Organic Surface Coatings

5.3.1.1 Monolayer Coatings

For a monolayer coating, surface modification can be achieved using small organic molecules either during the synthesis or in a subsequent step following the synthesis of the IONPs. For instance, when synthesizing iron oxide in polar solvents, small organic molecules such as arginine, tyrosine, and lysine are added directly for *in situ* coating.^{17,26,113} In contrast to unmodified, aggregated IONPs, the hydrophilic end groups of the amphiphilic molecules used for the coating process allow the IONPs to be stably dispersed in water.¹¹² Karimzadeh *et al.*¹¹⁴ obtained lysine and tyrosine-coated IONPs by adding either 1 g L⁻¹ lysine or tyrosine to the reaction mixture of FeCl₂–FeCl₃ (molar ratio of 1 : 2). The average diameter of the bare IONPs was 8 nm, while the average diameters of the lysine-coated and tyrosine-coated IONPs were approximately 10 nm, indicating the coating layer was thin. Small organic molecules can also be attached to the surface of IONPs after the synthesis through chemical–physical interactions. For example, citric acid (CA) can be linked to the surface of IONPs *via* carboxylic groups, as demonstrated by Sahoo *et al.*¹¹⁵ Upon functionalization, carboxylic groups from the citric acid are effectively exposed (facing) to the water, making the nanoparticles hydrophilic and stable in the aqueous phase. The average size of stabilized particles ranged from 12 to 15 nm, depending on the pH value ($5 \leq \text{pH} \leq 7$). Li *et al.*¹¹⁶ utilized a plasma-induced technique for the grafting of β -cyclodextrin (β -CD) to the surface of iron oxide and formed a water dispersible material (Fe₃O₄– β -CD) for adsorbing pollutants in water. The

average size of Fe_3O_4 - β -CD microspheres was 200 nm and remained unchanged after coating with β -cyclodextrin.¹¹⁶

5.3.1.2 *Bilayer Coatings*

When IONPs are prepared *via* thermal decomposition methods using oleic acid as a surfactant, the hydrophilic carboxyl group of oleic acid forms a chemical bond with the iron oxide, while the long hydrophobic alkyl chain is reoriented radially outward during particle ripening. Thus, the synthesized IONPs are hydrophobic and cannot be directly applied for the adsorption of metals/metalloids in aqueous solutions.^{26,110} However, an additional layer of amphiphilic surfactant can be readily assembled onto the original layer (*e.g.* oleic acid) with the assistance of additional energy inputs (*e.g.*, probe sonication), forming a double layer structure with the hydrophilic functional groups interfacing with the aqueous phase (see [Figure 5.3](#)).^{26,117} A series of unsaturated and saturated fatty acids can be used to functionalize IONPs with carboxyl end groups, including oleic acid (OA), ricinoleic acid (RA), elaidic acid (EA), stearic acid (SA), palmitic acid (PA), myristic acid (MA), and lauric acid (LA). Sulfate end groups can be grafted to the IONPs by adding sodium dodecyl sulfate (SDS) or sodium dodecylbenzenesulfonate (SDBS) during the mixing process. Cationic surfactants such as CTAB and dodecyltrimethylammonium bromide (DOTAB) introduce positive charge to the bilayer structure. Zwitterionic surfactants like *N,N*-dimethyl-*N*-dodecylglycine betaine (EMPIGEN) can produce IONPs with hydrophilic end groups. After phase transfer from a nonpolar solvent to an aqueous phase, IONPs with bilayer coatings were observed to be well dispersed in water.^{26,117} As demonstrated, the hydrodynamic diameters of the 8 nm core IONPs with bilayer coatings range from 15–25 nm, depending on the choice of surfactant used for the outer layer.^{117–120}

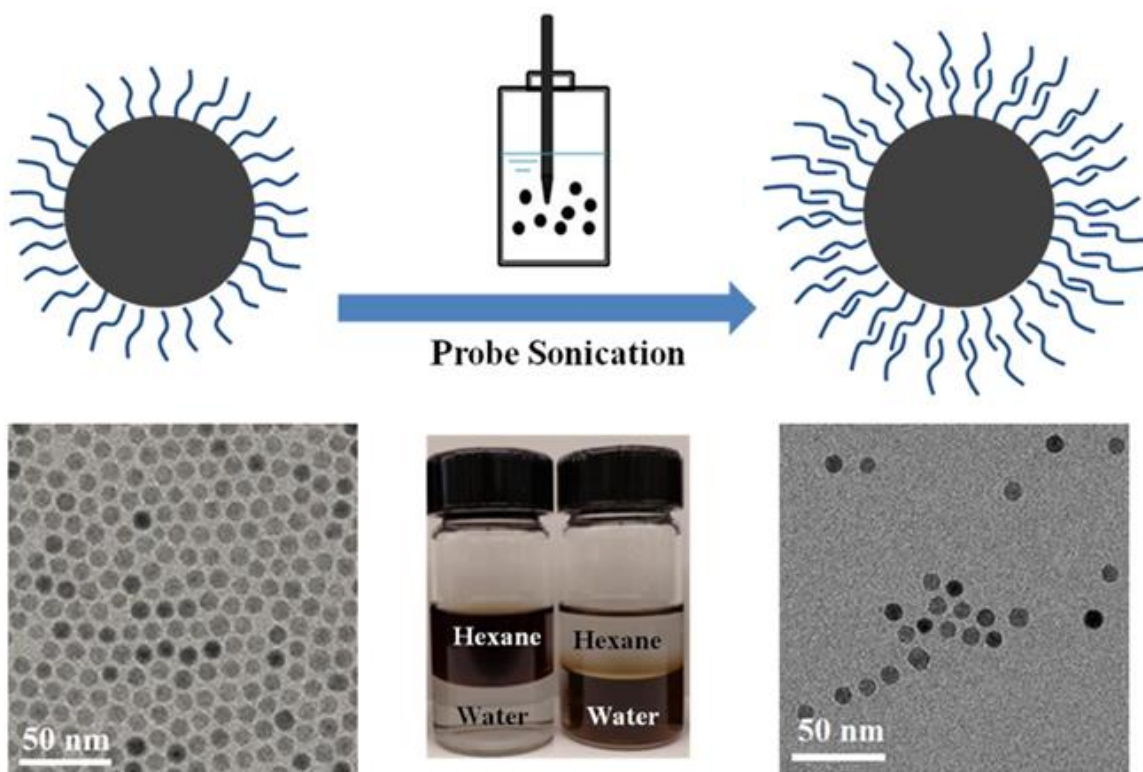


Figure 5.3 Scheme illustrating the bilayer coating strategy. Reproduced from ref. ¹¹⁷ with permission from the Royal Society of Chemistry.

5.3.1.3 Macromolecule Encapsulation Methods

In addition to small organic molecules, researchers have implemented large organic molecules for coating IONPs, such as humic acid (HA), polymers, sugars, esters, and *etc.*^{121–128} Fe_3O_4 particles coated with humic acid ($\text{Fe}_3\text{O}_4\text{-HA}$) were synthesized by Liu *et al.*¹²⁹ for the removal of toxic metals in water. Humic acid was attached to the iron oxide surface by ligand exchange using a co-precipitation reaction. The hydrodynamic diameter of $\text{Fe}_3\text{O}_4\text{-HA}$ was 140 nm, which was significantly smaller than that of bare Fe_3O_4 nanoparticles (250 nm), indicating that the HA coating played a role in minimizing particle aggregation.¹²⁹ Using a reverse suspension cross-linking method, Li *et al.*¹³⁰ synthesized $\text{Fe}_3\text{O}_4\text{-CTS}$ by covalently bonding chitosan (CTS) to the surface of iron oxide. The resulting $\text{Fe}_3\text{O}_4\text{-CTS}$ was spherical with a diameter of 25 nm and a shell

thickness of 1 nm. Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were used to verify the bonding of CTS onto the surface of iron oxide.¹³⁰ Wu *et al.*¹³¹ obtained magnetic microspheres (Fe_3O_4 -PDAPs) that were rich in carboxyl groups by coating poly-2,3-diaminophenol (PDAP) onto the surface of IONPs using ultrasonication. Polymers, such as polyethylene glycol (PEG) and polyethylene imine (PEI) have also been reported to fully encapsulate the IONPs, producing hydrophilic nanoparticles.^{26,132} Zhou *et al.*¹³³ synthesized polyacrylic acid (PAA)-coated Fe_3O_4 nanocomposites (Fe_3O_4 -PAA) through a reaction of iron oxide with PAA using a polyol-media solvothermal method. The synthesized Fe_3O_4 -PAA was highly water dispersible with a spherical shape that was 400 nm in diameter. Song *et al.*¹³⁴ coated polyacrylamide (PAM) onto iron oxide and obtained magnetic microspheres (Fe_3O_4 -PAM) that could adsorb U(vi) from radioactive wastewater. The diameter of the bare IONPs was 190 nm, whereas the PAM coating increased the diameter of Fe_3O_4 -PAM to 250 nm.¹³⁴

5.3.2 Inorganic Coatings

5.3.2.1 Silica

As a robust surface coating material, silica (SiO_2) is highly stable and corrosion resistant with a large number of hydroxyl groups on the surface. There are generally four methods for the synthesis of silica-coated IONPs (Fe_3O_4 - SiO_2), which include the Stöber method,¹³⁵ microemulsion,¹³⁶ sodium silicate solution-based methods,¹³⁷ and aerosol pyrolysis.¹³⁸ Among them, the Stöber method can efficiently prepare Fe_3O_4 - SiO_2 to have a uniform and adjustable particle size.^{112,135-138} A silica shell was successfully decorated on the surface of iron oxide through the hydrolysis of tetraethyl orthosilicate (TEOS), as reported by Yang *et al.*¹³⁹ The complete hydrolysis of TEOS and subsequent condensation of silicic acid formed a uniform silica shell around iron oxide.¹⁴⁰ Similarly, Kurnaz *et al.*¹⁴¹ coated TEOS on the surface of iron oxide and obtained Fe_3O_4 - SiO_2 with fluorescent properties. They found that as the amount of TEOS was

increased, the thickness of the silica shell also increased. For instance, when the amount of TEOS increased from 0.5 to 5 mL, the size of $\text{Fe}_3\text{O}_4\text{-SiO}_2$ increased from 15.1 nm to 412.3 nm, respectively.¹⁴¹ Additionally, the hydroxyl groups from the silica coating provided binding sites for different functional groups through covalent interactions, allowing for an additional layer to be chemically linked to $\text{Fe}_3\text{O}_4\text{-SiO}_2$, forming a stable, double-layer structure.^{111,142–147} As an example, Behjati *et al.*¹⁴⁶ prepared dithiocarbamate-functionalized magnetic microspheres by adding an additional layer to $\text{Fe}_3\text{O}_4\text{-SiO}_2$ using tetraethylenepentamine (TEP) and carbon disulfide. Sun *et al.*¹⁴⁴ developed $\text{Fe}_3\text{O}_4\text{-SiO}_2$ -porphyrin with a core-shell structure for monitoring, adsorption, and aqueous recovery of mercury (Hg^{2+}). For this, magnetic nanocomposites were made by mixing $\text{Fe}_3\text{O}_4\text{-SiO}_2$ and 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin ($\text{NO}_2\text{-TPP}$) in anhydrous toluene.¹⁴⁴

5.3.2.2 Metal Coatings

Gold (Au) and silver (Ag) are the two most frequently used metal elements to modify the surface of IONPs. An inert layer of Au or Ag can effectively shield the magnetic core from oxidation and improve the stability of iron oxide under extreme conditions.¹¹² Yang *et al.*¹⁴⁸ synthesized Ag-coated iron oxide microspheres ($\text{Fe}_3\text{O}_4\text{-Ag}$) by heating a mixture of silver acetate with IONPs under an inert atmosphere. Instead of forming a uniform layer of Ag, Ag nanoparticles (30–50 nm) were distributed on the surface of iron oxide. Zhang *et al.*¹⁴⁹ first prepared Ag-modified IONPs by treating thiol-functionalized IONPs with Ag solutions. A solid shell of Ag was formed on IONPs surface upon the addition of NaBH_4 as the reducing agent. The hybrid structure of silver-coated iron oxide is considered a very promising material, due to its high stability and antibacterial properties.¹⁵⁰ Similar to the mechanism of Ag coatings, reduction of Au^{3+} on the surface of iron oxide leads to the formation of a dense gold shell.^{151–153} Reductants commonly used include, but are not limited to, sodium citrate, sodium borohydride, hydroxylamine hydrochloride, oleylamine, and 1-hexadecanol.^{112,154–156} Zhou *et al.*¹⁵⁷ reported the coating of 10–20 nm Au

shells on IONPs, forming $\text{Fe}_3\text{O}_4\text{-Au}$ nanocomposites. Here, citrate was introduced to the Fe_3O_4 surface before the addition of a HAuCl_4 solution. Upon the addition of HAuCl_4 , citrate induced the reduction of Au^{3+} to Au, forming a continuous layer over the IONP surface.¹⁵⁷ Dong *et al.*¹⁵⁸ developed a simple and efficient way to synthesize core-shell structured nanocomposites with a layer of Au on a Fe_3O_4 core. The authors first prepared thiol-modified Fe_3O_4 -silica nanospheres by self-assembly, whereby Au nanoparticle seeds (*ca.* 2 nm) were anchored onto the outer surface through *in situ* reduction of Au^{3+} and the continued growth of Au nanoparticles led to the formation of a Au nanoshell.¹⁵⁸

5.3.2.3 Metal Oxide Coatings

In addition to silica and precious metals, many researchers have also discovered that some other inorganic materials can also be used to coat IONPs, such as inorganic salts, elemental carbon, sulfides, metal oxides, and ionic liquids.^{159–163} Among them, metal oxides are often used as another class of surface modification materials based on their unique physiochemical properties.¹¹² Tungsten trioxide (WO_3), which is acid resistant and thermally stable, exhibits a special open tunnel structure. A core-shell, microsphere structure of $\text{Fe}_3\text{O}_4\text{-WO}_3$ was obtained by coating WO_3 onto the surface of Fe_3O_4 using the hydrothermal method.¹⁶⁴ After the coating, the particle size of $\text{Fe}_3\text{O}_4\text{-WO}_3$ was *ca.* 100 nm, which was significantly larger than the bare Fe_3O_4 nanoparticles. Wen *et al.*¹⁶⁵ synthesized flower-like Fe_3O_4 nanocomposites coated with a thin-film of magnetic MnO_2 using an ultrasonic treatment. The nanocomposites had a 3-D layered morphology with dozens of 2-D nano petals. Considering the excellent adsorption capacity of iron-rich ferrite materials toward heavy metals, core-shell $\text{Fe}_3\text{O}_4\text{-Mn}_x\text{Fe}_y\text{O}_4$ nanocomposites were synthesized through thermal decomposition.¹⁶⁶ By decomposing the manganese oleate in the mixture of IONP seeds, oleic acid, and 1-octadecene, a ferrite layer of *ca.* 1 nm thickness was formed around the IONPs.

5.4 Sorption of Metals/Metalloids

Metals and metalloids, even at trace levels, pose a risk to human health due to being non-degradable and toxic.^{2,4,6,17} Iron oxides exhibit a strong affinity for heavy metals, making them promising heavy metal sorbent candidate materials.²⁶ The high specific surface area and large number of active sites of nanoscale iron oxide enhance its adsorption performance, especially when modified with suitable functional groups. The main interaction mechanisms between iron oxide adsorbents and heavy metal ions are electrostatic attraction, complexation, and ion exchange.¹⁷ The following sections provide a brief review of the adsorption mechanisms between iron oxide-based nanomaterials and select metals and metalloids.

5.4.1 Arsenic

Arsenic (As) is both toxic^{167–171} and widely present in nature^{167,170} with both natural (*e.g.*, dissolution of pyrite mineral) and anthropogenic exposure routes, including the usage of pesticides/herbicides and discharge of industrial wastewater.^{172,173} Arsenic can accumulate in the human body through drinking water and/or consuming produce grown in contaminated soil.^{172,174,175} To address this, a number of research groups have demonstrated iron oxide-based materials as an efficient adsorbent for arsenic removal.^{176–179} Wen *et al.*¹⁶⁵ synthesized microspheres by coating flower-like Fe₃O₄ with magnetic MnO₂ nanosheets as a sorbent for arsenic. Here, MnO₂ acts as a strong oxidant, effectively transforming the more soluble As(III) species into a less soluble form As(V). As a reaction product, As(V) was further adsorbed by iron oxide through inner-sphere complexation. These synergistic effects from iron oxide and manganese oxide made this nanocomposite an excellent adsorbent material for both As(III) (76.73 mg g⁻¹) and As(V) (120.50 mg g⁻¹).¹⁶⁵ Morillo *et al.*¹⁸⁰ prepared 3-mercaptopropionic acid (3-MPA)-coated IONPs to remove As(V) over a wide range of pH values (2 to 11). The best adsorption performance was found at pH 3.8, which was attributed to the existence of a large number of deprotonated surface groups. For these materials, the maximum loading capacity of As(V) was calculated to be 2 mmol g⁻¹, which

corresponded to 54% (molar basis) of the total binding sites on 3-MPA IONPs.¹⁸⁰ Vadahanambi *et al.*¹⁰⁴ demonstrated graphene–CNT–iron oxide nanocomposites, whereby uniformly-dispersed IONPs were distributed on the graphene sheets and CNT surfaces, offering a large number of adsorption sites for arsenic sorption. They also found that arsenic adsorbed onto iron moieties and formed inner-sphere arsenate complexes.¹⁰⁴ Sigdel *et al.*¹⁸¹ used porous alginate beads to immobilize IONPs for As removal. The maximum adsorption capacities of the magnetic beads for As(III) and As(V) were 68.4 and 42.8 mg g⁻¹, respectively. This hybrid material demonstrated excellent recyclability with less than 50% decrease in the adsorption performance even after 16 cycles.

5.4.2 Chromium

Like arsenic, chromium (Cr) is another pollutant that poses serious risks to human health.¹⁸² The main source of chromium pollution is due to anthropogenic inputs, such as metallurgy, chemical production, electroplating, leather tanning, and chemical fertilizers.^{183,184} Excessive intake of chromium can cause a series of diseases such as nasal mucosal damage, tissue necrosis, allergic contact dermatitis, and cancer.¹⁸⁵ Similar to As, iron oxide-based nanomaterials with high surface-to-volume ratios and high adsorption capacities offer significant potential for Cr treatment.¹¹⁰ Burks *et al.*¹⁸⁶ reported a loading capacity of 45 mg g⁻¹ for Cr(VI) using nanoscale magnetic balls that were comprised of IONPs coated with 3-MPA. The carboxyl groups from 3-MPA bonded to the IONPs, providing aqueous stability, while the thiol groups of 3-MPA were oxidized to sulfonate groups, allowing for the formation of complexes with Cr(VI).¹⁸⁶ Nematollahzadeh *et al.*¹⁸⁷ evaluated the sorption performance of polydopamine-coated iron oxides (MNP–PDA) toward Cr(VI) in water. Due to the protective polydopamine layer, this adsorbent was found to be suitable for working under acidic environments. For these materials, the removal efficiency was found to be maximized at pH 3. Additionally, after four cycles, the sorption efficiency of MNP–PDA remained above 90%.¹⁸⁷ Yuan *et al.*¹⁸⁸ used diatomaceous earth as the support material(s) to synthesize magnetic microspheres with iron oxides decorated on the surface

and inside the pores of diatom frustules. Cr(vi) was not only concentrated near the microspheres through electrostatic attraction, but also partially reduced to Cr(iii) through redox reactions with magnetite surfaces.¹⁸⁸ Magnetite was irreversibly oxidized to maghemite after three cycles of elution/adsorption. Zhu *et al.*¹⁸⁹ successfully designed a core-shell structured nanocomposite with amine-functionalized Fe₃O₄ nanoparticles (as the core) with a poly(*m*-phenylenediamine) encapsulation shell *via* oxidation polymerization. These core-shell nanocomposites offered substantial nitrogen-containing functional groups for high-capacity sorption (508 mg g⁻¹) and reduction of Cr(vi). The adsorbents could be regenerated with 1 M NaOH and exhibited a sorption capacity of at least 330 mg g⁻¹ after five cycles.¹⁸⁹

5.4.3 Uranium

Nuclear power has become a prevalent global energy source.¹⁹⁰ Uranium (U) is an important component in nuclear reactors, serving as the fuel for nuclear fission. Mining and processing of uranium ore, nuclear waste disposal, and unintentional release have led to environmental exposure events, posing a threat to human health.¹⁹¹ Uranium is not only highly toxic, but the radioactive element is widely known to cause various types of cancer^{134,192} as well as kidney and liver damage.¹⁹³ Under oxic conditions, uranium is usually present in the environment in the form of hexavalent U(vi).¹¹¹ Song *et al.*¹³⁴ coated polyacrylamide onto iron oxide to synthesize magnetic microspheres (PAM-Fe₃O₄) that can adsorb U(vi) in radioactive wastewater. The microspheres showed a strong adsorption capacity ($Q_{\max} = 220.9 \text{ mg g}^{-1}$) as a result of the complexation of the nitrogen-containing groups with U(vi). Li *et al.*⁶⁶ systematically compared the effect of IONPs size, coating type, and solution pH on the uranium sorption (see [Figure 5.4](#)). The maximum adsorption capacities decreased from 635 mg g⁻¹ to 260 mg g⁻¹ when the IONPs size increased from 8 nm to 25 nm, respectively, which was due to the decrease of specific surface area (when particle size increased). IONPs with oleic acid and monododecyl phosphate coatings exhibited higher uranium sorption capacities than IONPs with monododecyl phosphate and lauric acid coatings, indicating the importance of surface

coatings. Further, higher sorption capacities were found at pH 5.6 due to favorable electrostatic attractions between IONPs and uranium species.⁶⁶ Kim *et al.*¹⁶⁶ prepared oleyl phosphate (OP) stabilized core-shell $\text{Fe}_3\text{O}_4\text{-Mn}_x\text{Fe}_y\text{O}_4$ nanocrystals for ultra-high uranium sorption. This study showed that a maximum sorption capacity of 1438 mg g^{-1} toward $\text{U}(\text{vi})$ was achieved when the Mn : Fe ratio was 0.28. The authors attributed this to the enhanced reduction of $\text{U}(\text{vi})$ to $\text{U}(\text{iv})$ from the higher concentration of Fe(ii) and Mn(ii) on the nanocrystal surface. Owing to strong chelation between amidoxime (AO) and $\text{U}(\text{vi})$, AO surface coatings have been demonstrated with IONPs to sorb and separate $\text{U}(\text{vi})$ more effectively. Additionally, Zhao *et al.*¹¹¹ synthesized magnetic microspheres by grafting AO to $\text{Fe}_3\text{O}_4\text{-SiO}_2$ core-shell structures and observed a maximum sorption capacity of $0.441 \text{ mmol g}^{-1}$ at pH 5.

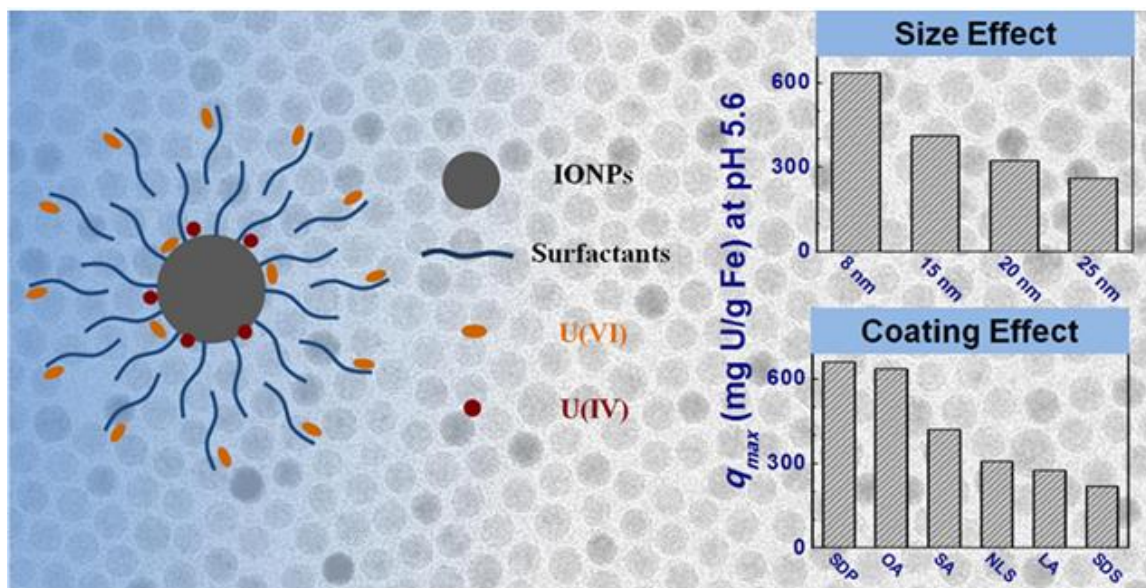


Figure 5.4 Bilayered IONPs for uranium sorption. Reproduced from ref. ⁶⁶, <https://doi.org/10.1021/acsami.7b01042>, with permission from American Chemical Society, Copyright 2017. Further permissions related to the material excerpted should be directed to the ACS.

5.4.4 Rare Earth Elements

Due to their unique physical, chemical, magnetic, optical, and electrical properties, rare earth elements (REE) have a wide range of applications in the fields of catalysis, electronics, metallurgy, photonics, aerospace, among others.^{194–202} Further, with rapidly increasing demand for rare earth elements, the supply of these non-renewable resources is diminishing relatively fast.²⁰³ Mining and refining of rare earth elements produces low-concentration residual materials that not only pose a severe environmental impact if not properly handled, but also contribute to pollution and waste generation. Therefore, separation and recovery of rare earth elements are of significant environmental importance.^{204,205} Rare earth elements act as Lewis acids that can be chelated with oxygen-containing and phosphine-containing functional groups, such as hydroxyl, carboxyl, phosphate, amide, and carbonyl groups.^{206,207} Further, such functional groups on the surface of iron oxide-based nanomaterials have been demonstrated to enhance their adsorption properties toward REEs. Zhang *et al.*²⁰⁸ prepared Fe₃O₄-alginate microcapsules to capture neodymium (Nd³⁺) with a maximum adsorption capacity of 149.3 mg g⁻¹. They observed that Nd³⁺ sorption was accompanied by the release of calcium ions, thus it was assumed the adsorption mechanism was related to ion exchange-type processes. Wu *et al.*²⁰⁹ synthesized magnetic Gaomiaozi (GMZ) bentonite, which showed an adsorption efficiency of 97.7% toward Eu(III) within two minutes. They found that the negatively charged oxygen groups preferentially attracted lighter rare earth ions, leading to higher sorption of Yb³⁺ compared to Eu³⁺ and La³⁺. Basualto *et al.*²¹⁰ developed Fe₃O₄ nanosorbents modified by organophosphorus acid extractants (CYANEX 272, D2EHPA, and CYANEX 301) for the sorption of lanthanide elements, which exhibited an adsorption capacity of ~12–14 mg g⁻¹. Patra *et al.*²¹¹ reported a 100% efficiency for europium adsorption using magnetic IONPs that had been modified with graphene oxide and silane.

5.4.5 Removal of Multi-contaminants

With regard to real world pollution, it is widely known that various heavy metal ions (such as Cu(II), Hg(II), Cd(II), Pb(II), Zn(II), Ni(II), Co(II), U(VI), and As(V)) are often simultaneously present in water, thus the complex

interactions between various heavy metals must be considered. As metal/metalloid ions compete for adsorption sites, favorable adsorption for one ionic species over other ions must be understood and managed. For instance, Ozmen *et al.*²¹² synthesized Fe_3O_4 nanoparticles that were modified using 3-aminopropyltriethoxysilane (APTES) and glutaraldehyde (GA). They reported that in the presence of coexisting ions, including Pb(II) , Co(II) , Ni(II) , Zn(II) , and Cr(III) , the sorption percentage of Cu(II) decreased from 75% to about 35%. Thus, in order to adsorb different ionic contaminants, various functional groups must be rationally grafted/attached to the IONPs. Peng *et al.*²¹³ prepared magnetic CNT–iron oxide nanocomposites, which were modified to contain oxygen-containing functional groups *via* chemical oxidation using nitric acid. The synthesized nanocomposites demonstrated high adsorption capacity for both Pb(II) and Cu(II) . Kim *et al.*²¹⁴ prepared positively charged PEI and CTAB modified IONPs, which showed a superior adsorption for anions such as arsenate (AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^-) and chromate (CrO_4^-). It was found that the primary sorption sites were the amine functional groups (in PEI) and the terminal methyl ammonium groups (CTAB head groups). Guo *et al.*²¹⁵ synthesized amino-modified Fe_3O_4 –graphene nanocomposites for multi-contaminant sorption, which showed sorption capacities of 17.29, 27.95, 23.03, 27.83, and 22.07 mg g^{-1} for Cr(VI) , Pb(II) , Hg(II) , Cd(II) , and Ni(II) , respectively. Here, the initial pH of the solution also influences adsorption capacities, due to the protonation of the functional groups of the adsorbent, the degree of ionization, and speciation of heavy metals in solution.^{216–218} Shen *et al.*²¹⁶ synthesized 8 nm Fe_3O_4 nanoparticles for heavy metal ion sorption and found the adsorption capacities to be 41.86, 47.44, 45.86, and 43.59 mg L^{-1} for Ni^{2+} , Cu^{2+} , Cd^{2+} , and Cr^{6+} , respectively. They also observed that the adsorption of heavy metal ions was greatly affected by solution pH, with the exception of Cu^{2+} , which could exchange with the H^+ on the surface of iron oxide particles. At lower pH (2–4), IONPs become protonated, adopting a positively charged surface. While this was beneficial for the adsorption of the negatively charged Cr(VI) ion *via* electrostatic attraction, it made the adsorption of positively charged Ni^{2+} and Cd^{2+} much less favorable. Conversely, the adsorption rate of Ni^{2+} and Cu^{2+} increased

significantly at higher pH, but the adsorption capacity of Cr(vi) decreased due to electrostatic repulsion. In order to simultaneously absorb these heavy metal ions, the optimized solution pH was found to be 4.

5.5 Conclusion

This review systematically introduced recent synthesis techniques, surface modification strategies, and environmental sorption-based applications of engineered iron oxide-based nanomaterials. First, an overview of the fabrication of iron oxide nanoparticles and their hierarchical nanocomposites with 1-D, 2-D, and 3-D structures was provided. Next, a detailed summary of the common approaches for synthesizing iron oxide nanoparticles including co-precipitation, microemulsion, hydrothermal methods, thermal decomposition, and electrochemical methods was covered. To obtain higher dimensional structures, iron oxide nanocomposites are prepared using template materials, such as nanotubes, nanofibers, MXenes, graphene, and graphene oxide aerogels. In order to utilize these materials in aqueous environments, proper surface modification is required to improve dispersivity, and thus sorption capacities. Typical coating methods (*e.g.*, organic and/or inorganic coatings), modification schemes and mechanisms were presented. Finally, the application of iron oxide-based nanomaterials as adsorbents to separate and recover metals/metalloids (as contaminants or high-value rare earth elements) in water treatment was briefly discussed. The adsorption mechanisms, working environments, and sorption efficacy of these materials on metals/metalloids (arsenic, chromium, uranium, multi-contaminants, and rare earth elements) were introduced. Taken together, this review not only provides a comprehensive framework outlining the various synthesis, surface functionalization, and adsorption methods applied to iron oxide-based nanomaterials, but also highlights the high potential of such materials for environmental applications, particularly in terms of water treatment. We see future research in this field focusing on the development of more efficient and economical methods to fabricate iron oxide-based nanomaterials. Further, this research area will likely shift to nanocomposite materials with improved sorption performance and higher selectivity toward dissolved metals/metalloids. Based on the current state of the art and high

potential, we expect that iron oxide-based nanomaterials can provide applicable strategies for treating metal pollution and recovery, thus improving global water quality paradigms.

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Chapter 6

Novel Nanoadsorbents for the Separation of Hazardous Pollutants from Water

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6.1 Hazardous Pollutants in Water

With the expansion of the human sphere of influence, many hazardous substances have entered water, air, and soil and caused great harm to the environment. During the last few decades, water contaminants have caused the most extensive and direct damage on Earth. Polluted water harms not only humans but also the whole ecological chain.¹

In the second decade of the 21st century, the composition of pollutants in the water has changed dramatically from the past. The present worldwide water shortage mainly results from two aspects: (1) insufficient natural water resources that cannot satisfy the requirements from local places (physical water shortage) and (2) unsuccessful administration of applicable water resources (economic water shortage). The situation of current global

water scarcity is summarized in Figure 6.1a.² In addition, the distribution of the most hazardous species of environmental poisons is also listed on this chart, including radionuclides, obsolete pesticides, and heavy metals (e.g., chromium, mercury, and lead).³ The composition of the major pollutants existing in industrial and commercial places of Europe is shown in Figure 6.1b, while the normalized amount of treated water by the area of application is indicated in Figure 6.1c.⁴

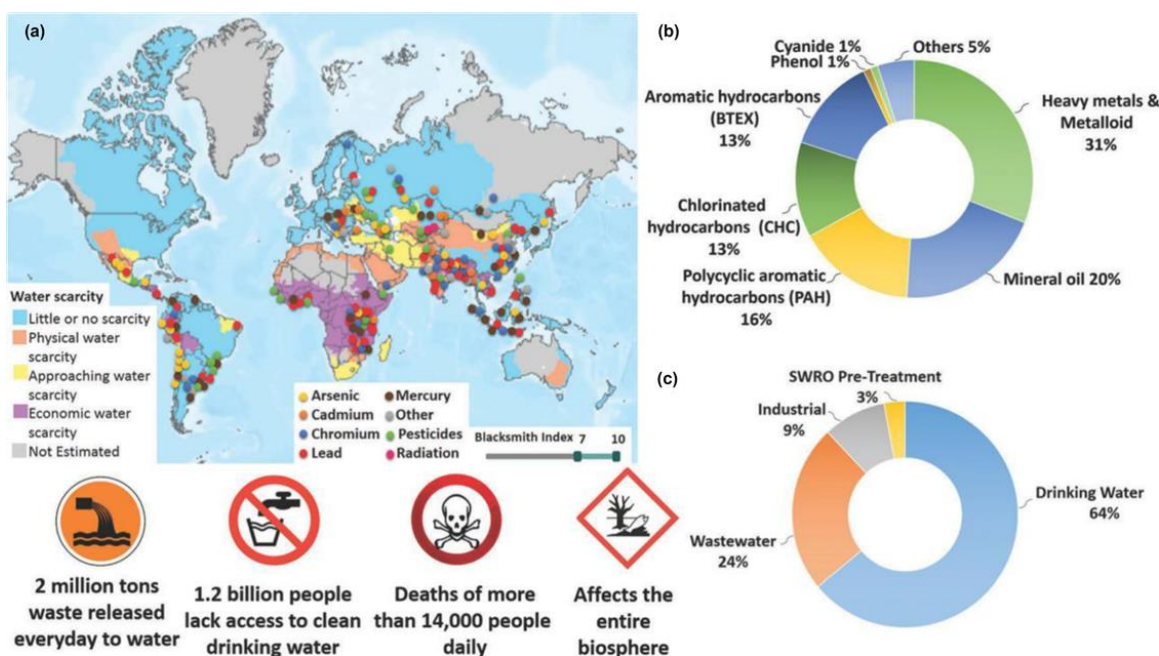


Figure 6.1 Synopsis of global water contaminant distribution. (a) The geographical distribution of water shortages and pollution by major contaminants, including radionuclides, pesticides, and heavy metals. (b) Normalized composition of water contaminants in treated and reused water streams. (c) Normalized amount of treated water by area of application. Adapted from ref. ² with permission from the Royal Society of Chemistry, Copyright 2018.

6.1.1 Heavy Metal Pollutants

Many industries leak heavy metal ions into the environment, such as metal mining operations, plating facilities, and tanneries. They can biologically accumulate upon cumulative exposure. Heavy metals are not biodegradable and can enter the food chain and deteriorate human health by causing various diseases and disorders.^{3,5}

Copper (Cu) is a common heavy metal that has been widely applied in human society for many centuries. It can enter the environment from Cu-utilizing industries, including batteries, fertilizers, semiconductors, electronic chips, cell phones,⁶ and mining. Cu is an essential trace element for human beings. There is approximately 100–200 mg of Cu in a healthy human body, approximately 50–70% of which exists in muscle and bones, approximately 20% in the liver, and approximately 5–10% in the blood. Cu participates in critical physiological processes in the human body, including creating hemoglobin and oxygen-conveying enzymes. However, excessive ingestion of Cu, for example, surpassing 64 mg per day, may result in serious diseases such as hematuria, hemolytic anemia, intense tubular rot, gastrointestinal bleeding, and hepatocellular putrefaction and can cause demise.⁷ Consequently, as hazardous heavy metal ions, the concentration of copper ions in drinking water is strictly limited by many countries. For instance, the limitation of Cu ions in drinking water given by the Bureau of Indian Standards is 2 mg L⁻¹.⁸

Cadmium (Cd) has been broadly used in many industries, such as pigments, ceramics, insecticides, petroleum products, electroplating, and textiles.⁹ Cd is an extremely toxic metal that can accumulate in the human body and result in irreversible damage to various organs even at very low concentration levels.¹⁰ The two most important ways that Cd enters the human body are eating routines and cigarette smoking. For example, the Cd concentration in some consumable crabs was reported to be approximately 30–50 mg L⁻¹.¹¹ Cd containment levels in one cigarette are approximately 1–2 µg, and a man smoking a pack of cigarettes every day purportedly intakes 1 µg of Cd each day. When Cd enters the human body, it is considerably challenging to exclude. The natural half-life of Cd in the body is approximately 20 years.¹² Chronic exposure to excessive levels of Cd can produce outcomes such as renal dysfunction, bone damage, liver ramification, blood degeneration, and cancer.¹³ Furthermore, the permissible maximum level of Cd in drinking water given by the United States Environmental Protection Agency is 10 ppb.

Mercury (Hg) is a global contaminant and is among the top three hazardous substances proposed by the Agency for Toxic Substances and Disease Registry.¹⁴ Hg enters the environment *via* mining and other

anthropogenic industries. Hg mainly exists in aquatic systems as organic Hg, which is the most toxic form of mercury. Organic Hg can easily penetrate the biological membrane and hence indicates high bioaccumulation.¹⁵ It finally accumulates in assorted aquatic animals and can enter human bodies through food chains, a common method of high level mercury exposure in humans.¹⁶ Hg toxicity can dramatically damage the nervous system, causing hallucinations, depression, extreme irritability, autism.¹⁷ It can poison the kidney, leading to renal cancer, glomerulonephritis, and nephrotic syndrome,¹⁸ and Hg can also harm various organs, including the heart, pituitary gland, pancreas, and testicles.¹⁹ The concentration of Hg in the environment is strictly restricted. The limitation standard proposed by the United States Environmental Protection Agency is $2\text{ }\mu\text{g L}^{-1}$ of Hg for water and soil.²⁰

6.1.2 Nonmetallic Inorganic Pollutants

In addition to heavy metal pollutants, the toxicity of some nonmetallic inorganic pollutants cannot be ignored. Furthermore, some nonmetallic inorganic pollutants are even more difficult to handle.

Phosphorus is a normal in the composition of fertilizers, either from mineral or manure. Phosphorus is a nutrient that can cause serious eutrophication of water bodies such as lakes, rivers, and seas worldwide due to the extraordinary growth of algae.²¹ Phosphorus is widely used to promote agricultural crop yields. Nevertheless, it is common that a large part is not completely absorbed by the target plants, and excess phosphorus enters the environment and remains a pollutant. It either accumulates in the soil or flows out into water bodies such as groundwater, rivers, lakes, and seas, increasing the eutrophication risk. The total P content in discharge water is limited to below 0.5 mg L^{-1} , as proposed by the Chinese Ministry of Ecology and Environment.

Ammonium is another crucial factor responsible for the eutrophication of water bodies.²² Ammonia is generally discovered in trace quantities in nature.¹ Commonly, it originates from nitrogenous waste from animals and organic food matter. Ammonia and ammonium salts can be detected in minimal amounts in rainwater, while NH_4Cl and $(\text{NH}_4)_2\text{S}$ are primarily

discovered in volcanic zones. Additionally, similar to phosphorus, ammonia is also widely applied as agricultural fertilizer, and its overuse also brings about leakage-based contamination. This may result in a considerable rise in ammonia concentration in related water bodies. The overdose of ammonia and its salts in water resources is hazardous because the excessive use of ammonia could result in physical poisoning and may also cause disorders in the blood and circulatory systems.²³

Fluoride is a dangerous nonmetallic inorganic contaminant.²⁴ Fluoride enters the environment through many human activities, such as coal mining, glass and ceramics, aluminum and zinc smelters, and superphosphate fertilizers. These industries can produce large amounts of wastewater containing high fluoride concentrations every year worldwide. Excess consumption of fluoride can cause skeletal fluorosis and other terrible illnesses. As suggested by the World Health Organization (WHO), the maximum F^- concentration in drinking water should be $\sim 0.5\text{--}1.5\text{ mg L}^{-1}$.

6.1.3 Organic Pollutants

Emerging contaminants as new organic pollutants have gained significant attention and recognition over the past few decades.^{25–27} Emerging contaminants refer to those newly discovered in the environment, although they may have been recognized earlier but have only recently attracted attention. The existence level, detection frequency, or source of these substances in the environment is unknown, which may pose potential risks to human health and the ecological environment. Most emerging contaminants have not yet been regulated, including pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and psychoactive substances (PSs). The massive/uninterrupted use and discharge of emerging contaminants cause their persistence for an extended period in the environment. In recent years, worldwide relevant investigations and studies have shown that various emerging contaminants have been detected in sewage treatment plants, rivers, groundwater, and even drinking water.

At present, the number of chemicals registered in the United States has reached more than 70 million, and the growth rate in recent years has increased by millions or even tens of millions every year. These chemicals

enter the environment in various ways. With the development of environmental analysis technology, people are continually discovering that some of the chemicals entering the environment have the characteristics of emerging contaminants, such as EDCs and PSs.

Traditional organic water pollutants are mainly removed using advanced oxidation techniques such as photocatalysis,²⁸ the Fenton process,²⁹ and persulfate oxidation processes.³⁰ The trouble is that the current general sewage treatment plants are not designed to remove emerging contaminants. Therefore, the most effective way to reduce the potential impact of these pollutants is to expand and optimize the wastewater treatment process.

6.2 Novel Nanoadsorbents for Water Pollutant Elimination

Adsorption is a suitable strategy to remove pollutants in water because of its low cost and convenience. It can be widely applied in areas with relatively regressive economic and technological conditions, such as rural and remote mountain areas, because it has minimal operational requirements. Nanosized materials demonstrate different advantages for use as adsorbents, and the surface area effect is one of the most important ones. A high active surface area means a high ratio of surface atoms compared to the total atoms in the material, so many accessible and high-energy surfaces are available. Therefore, the rate of chemical or surface reactions can be accelerated by increasing the surface area.³¹

Recently, various novel nanoadsorbents have emerged and exhibited excellent performance for pollutant removal from water. Herein, we introduce the recent developments of adsorption technology from the following five kinds of nanoadsorbents: selective nanoadsorbents, regenerable and separable nanoadsorbents, nanoadsorbents equipped with indicators, rare earth nanoadsorbents and broad-spectrum nanoadsorbents.

6.2.1 Selective Nanoadsorbents

In natural water bodies, various other substances usually coexist with the primary pollutants. These coexisting substances usually negatively affect the adsorption treatment because they could compete for active adsorbent

sites with the primary pollutants during adsorption, depressing the removal efficiency. Therefore, the selectivity of adsorbents is usually essential for high removal efficiency in treating complex water bodies. Furthermore, highly selective adsorbents are fundamental for the directional recycling of high-value resources in multicomponent industrial wastes.³²

Ma *et al.*³³ prepared a nanocomposite denoted MoS₄-LDH (Figure 6.2), which consisted of a Mg/Al layered double hydroxide (Mg/Al-LDH) intercalated with MoS₄. The MoS₄-LDH exhibited an exceptionally high capacity of selective capture toward lethal oxoanions such as As(iii)/As(v) (HAsO₃²⁻/HAsO₄²⁻) and Cr(vi) (CrO₄²⁻). This nanocomposite indicated a very high elimination efficiency (> 99%) toward As(iii), As(v), and Cr(vi) from complicated solutions. In coexistence with various rival nontoxic anions, for example, NO₃⁻, SO₄²⁻, and Cl⁻, excellent selectivity toward HAsO₃²⁻, HAsO₄²⁻, and CrO₄²⁻ was found. High concentrations of As(iii) and Cr(vi) ions in solution could be rapidly reduced to below 10 ppb, much lower than the allowable standard in drinking water. The maximum adsorption abilities toward As(iii), As(v), and Cr(vi) were 99, 56, and 130 mg g⁻¹, respectively. Adsorption isotherms for As(iii) and As(v) could be fitted using the Langmuir model, suggesting monolayer adsorption behavior onto the adsorbent. The sorption of As(v) and Cr(vi) was extremely fast, indicating more than 93% elimination within 1 min, and more than 96% elimination occurred within 5 min. The adsorption kinetics for these oxoanions agreed with a pseudo second-order model, indicating chemisorption involving probable As-S and Cr-S bonding. Cr(vi) sorption co-occurs *via* a redox reaction with MoS₄²⁻, producing Cr(iii) species.

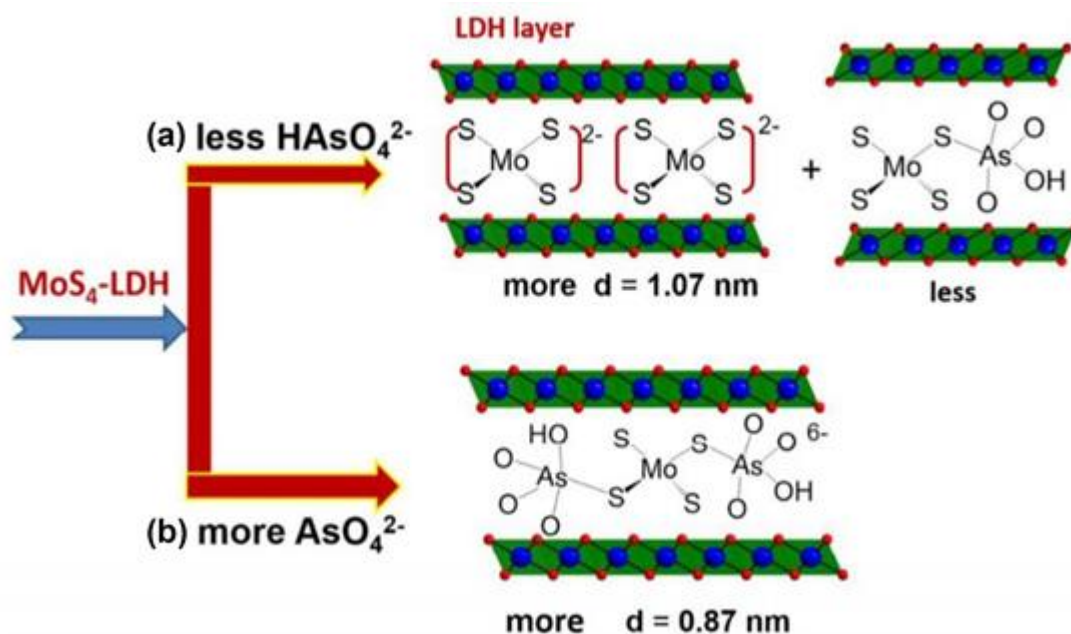


Figure 6.2 The dominant phases and probable binding modes of MoS_4^{2-} with HAsO_4^{2-} in LDH galleries. Adapted from ref. ³³ with permission from American Chemical Society, Copyright 2017.

Zr and Al are commonly applied as effective sorbent components for F^- elimination due to their high affinities. Traditionally, these sorbents are usually synthesized by deposition from soluble sources of Zr or Al. Nevertheless, the preparation conditions for deposition require careful control. Furthermore, the precipitants used were commonly strong bases, which could easily remain and cause secondary pollution. Wang *et al.*³⁴ synthesized a composite of $(\text{ZrO}_2\text{-Al}_2\text{O}_3)\text{-GO}$ using a facile sonochemical strategy (Figure 6.3). A particular three-dimensional (3D) network was built, which generated a large surface area and metal oxide nanoparticle dispersion. This material showed a maximum F^- adsorption ability of 62.2 mg g^{-1} . Furthermore, its adsorption ability reached 13.80 mg g^{-1} when the fluoride balance concentration was 1 mg L^{-1} . Furthermore, it exhibited high anti-interfering ability toward the coexisting ions Cl^- , NO_3^- and SO_4^{2-} . Due to the high adsorption performance toward F^- , $(\text{ZrO}_2\text{-Al}_2\text{O}_3)\text{-GO}$

could be employed to treat large amounts of drinking water containing F^- to meet the WHO limit.

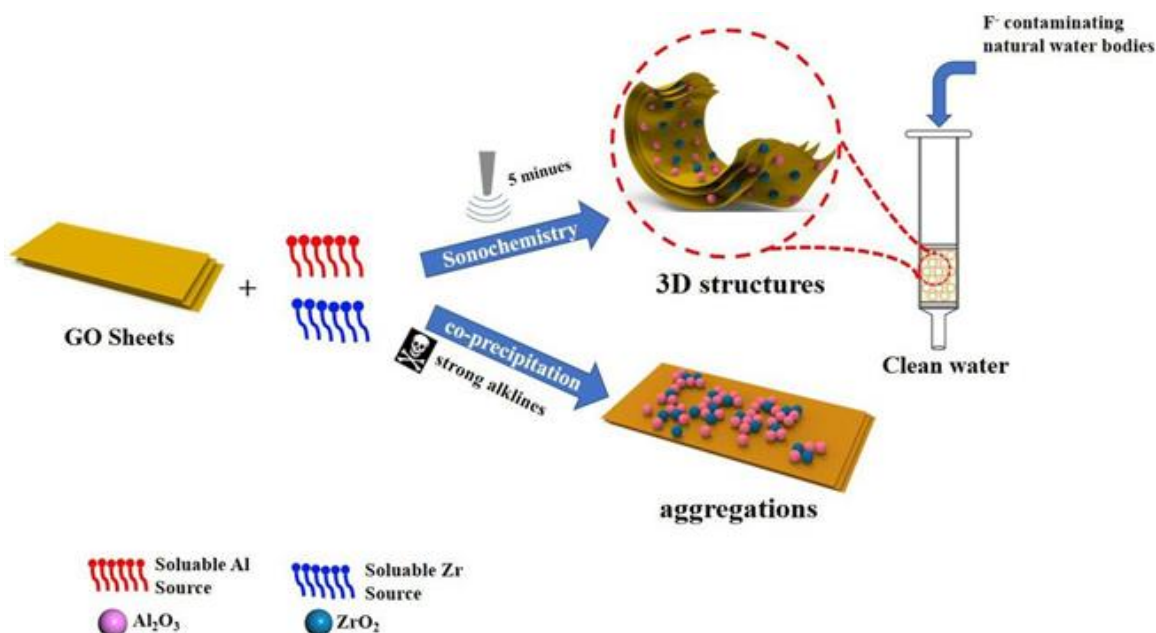


Figure 6.3 Schematic illustration of the synthesis of (ZrO₂-Al₂O₃)-GO. Adapted from ref. ³⁴ with permission from Elsevier, Copyright 2020.

The ion-imprinted polymer (IIP) technique is conventionally employed to selectively remove and recycle pollutants, usually for heavy metal ions. Liu *et al.*³⁵ demonstrated a highly discriminating and high-performance adsorbent using free radical polymerization of thiolactone-functionalized acrylamide (denoted PAM-TL) (Figure 6.4). PAM-TL indicated a high Ag(i) adsorption ability (145.2 mg g⁻¹), which was 5.8 times that of the related NIP (nonimprinted polymer) (25.07 mg g⁻¹). Furthermore, the distribution coefficient of PAM-TL (576.1) was 4.1 times greater than that of NIP (113.8). Moreover, the PAM-TL adsorbent also exhibited outstanding stability and reusability (excellent sorption performance after six recycles).

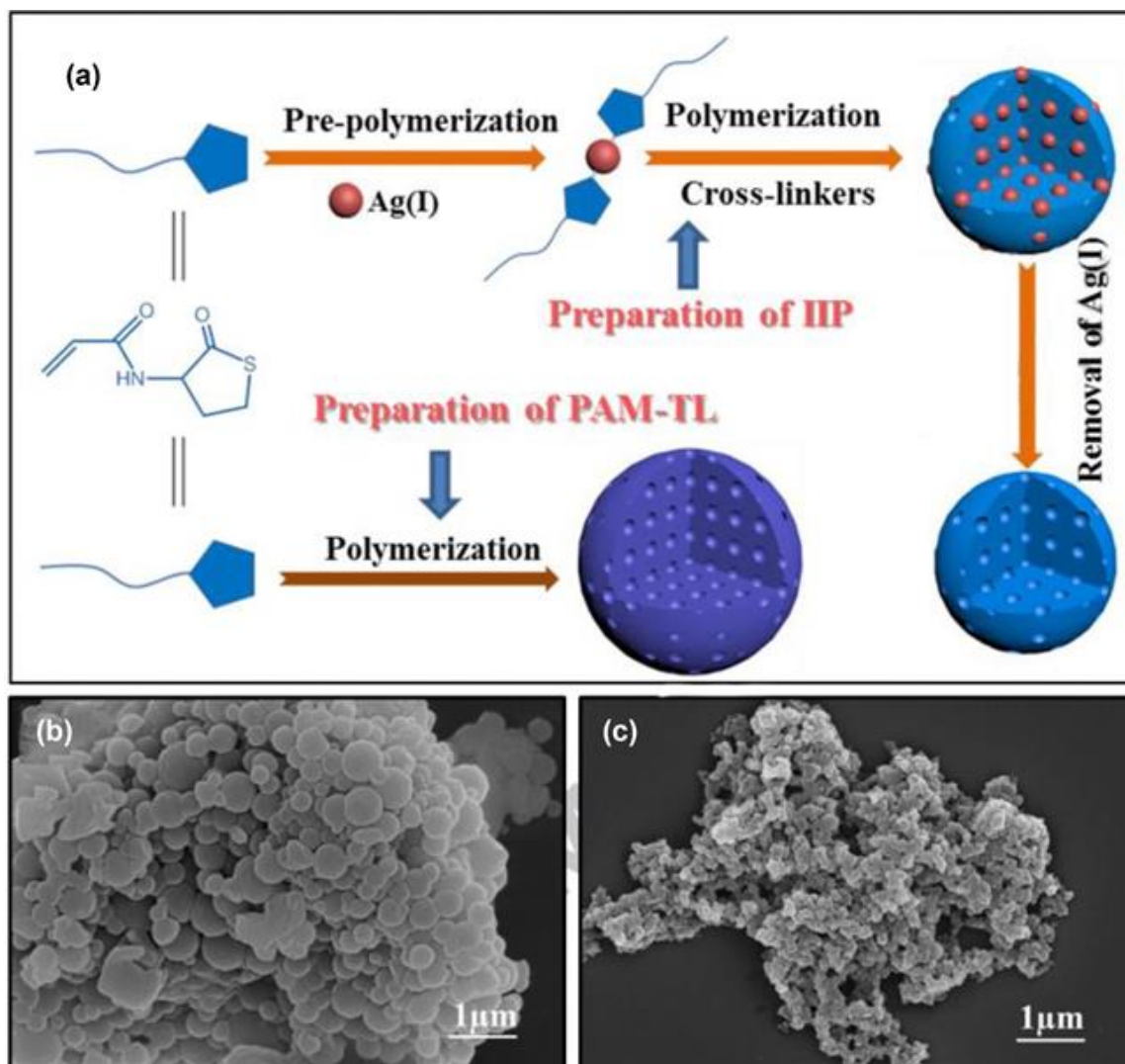


Figure 6.4 (a) Schematic illustration of PAM-TL and IIP; SEM images of PAM-TL (b) and IIP (c). Adapted from ref. ³⁵ with permission from Elsevier, Copyright 2018.

Compared with cationic imprinting, anionic imprinting is more difficult because anionic templates have much smaller species diversity, charge size ratio, and irregular geometry than cationic templates. Xi *et al.*³⁶ prepared anion-imprinted polymers, enhancing phosphate adsorption capacity *via* electrostatic attraction between positive–negative charges (Figure 6.5). The IIP exhibited satisfactory phosphate sorption ability, although the phosphate species varied from H_2PO_4^- to HPO_4^{2-} . The report indicated that the

specific selectivity of cationic imprinted polymers could also remain in anion-imprinted polymers by rational design and construction.

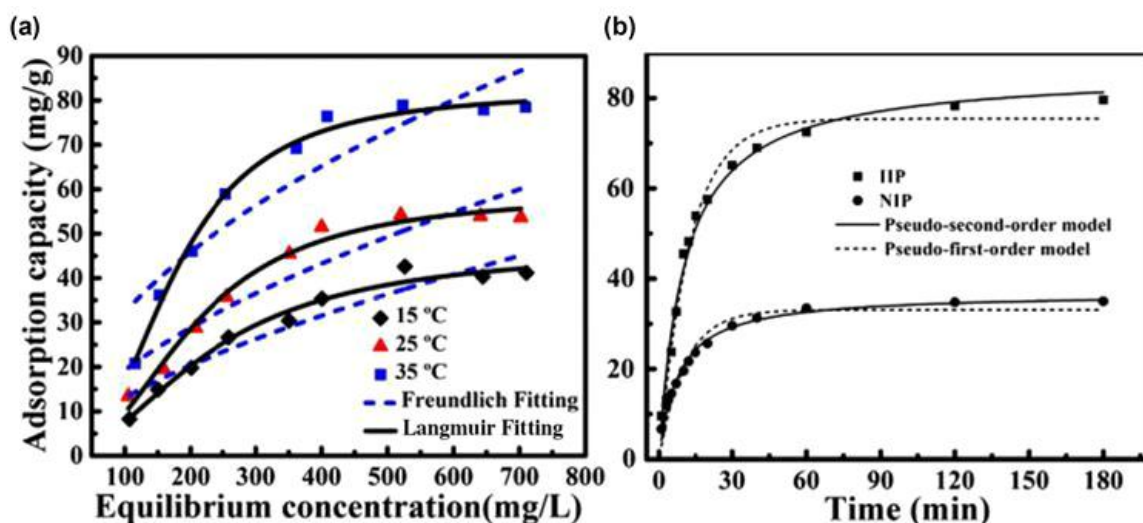


Figure 6.5 Sorption isotherm at different temperatures for $\text{P} [\text{PO}_4^{3-}]$ adsorption on IIP (a), the initial phosphate concentration range from 100 to 700 mg L^{-1} , contact time: 12 h; and sorption kinetics for phosphate adsorption on IIP/NIP (b) with a phosphate concentration of 500 mg L^{-1} at 35 °C, pH: 6.5 ± 0.2 . Adapted from ref. ³⁶ with permission from Elsevier, Copyright 2019.

Zou *et al.*³⁷ reported a method to remove $\text{Cr}(\text{vi})$ using a nanocomposite denoted MOF-rGO using a selective electrochemical process (Figure 6.6). The nanohybrid was synthesized by *in situ* growth of a metal-organic framework (MOF) with Co metal centers, $[\text{Co}_2(\text{btec})-(\text{bipy})(\text{DMF})_2]_n(\text{Co-MOF})$, on the surface of reduced graphene oxide (rGO). rGO purveyed the necessary electric conductivity for constructing an electrode, whereas the Co-MOF provided strongly selective adsorption sites toward CrO_4^{2-} . When employed as an anode in the treatment cycles, the MOF-rGO electrode exhibited high adsorption selectivity toward CrO_4^{2-} over competing ions such as SO_4^{2-} , Cl^- , and $\text{As}(\text{iii})$ and obtained a charge efficiency (CE) of $\sim 100\%$ thanks to the powerful physical-sorption of CrO_4^{2-} onto the Co-MOF. Both the electro and physisorption abilities could be recovered by the

overturn of the applied voltage. The highly toxic Cr(vi) was reduced to the less toxic Cr(iii) species and discharged into brine afterward.

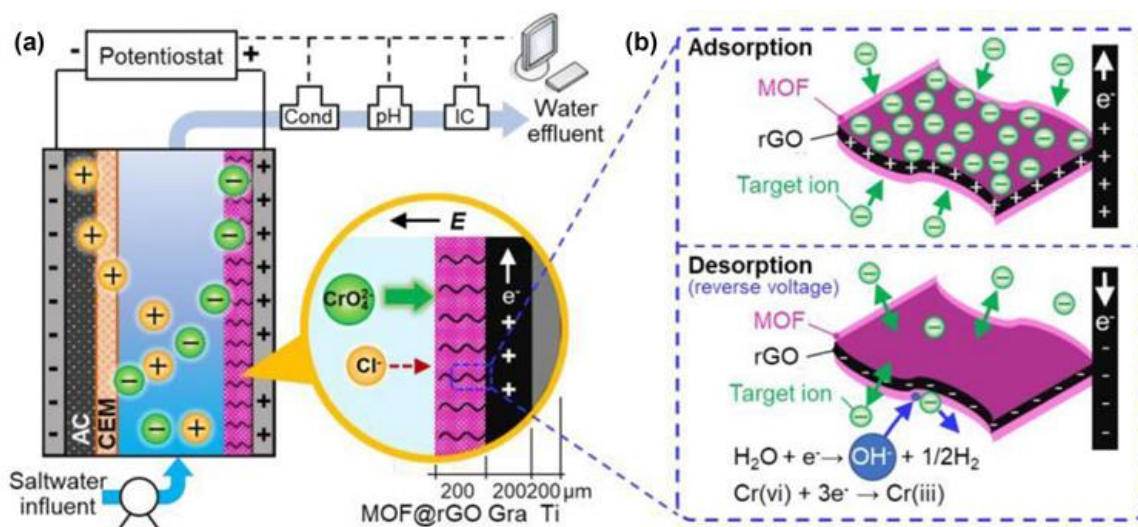


Figure 6.6 Schematic diagram indicating the application of MOF–rGO in an asymmetric electrosorption system for the selective removal of Cr(vi). (a) Schematic of MOF–rGO as a selective electrode in an asymmetric electrosorption system. Gra: graphite sheet. Ti: titanium sheet. (b) Enhanced adsorption and desorption/reduction of Cr(vi) in a charge–reversed voltage cycle. Adapted from ref. ³⁷ with permission from American Chemical Society, Copyright 2020.

In general, three selective mechanisms can be summarized: (i) the selectivity between the functional groups and the target pollutants; (ii) selectivity of the template-directed materials,^{36,38,39} especially in ion-imprinted technology;⁴⁰ (iii) the different electronic field strengths to capture different ions according to the difference of the electrochemical oxidation–reduction potential of the ions.

6.2.2 Regenerable and Separable Nanoadsorbents

Regenerable adsorbents can significantly reduce the cost, so adsorbent regeneration is usually crucial in practical applications. However, the regeneration of adsorbents can be annoying because many concentrated acids, alkalis, salts, or strong chelating agents usually need to be applied. Therefore, many scientific research studies are devoted to adsorbents that

can be regenerated using green or sustainable methods or are self-regenerative.

Some efforts combine photocatalysis with adsorption to design composite systems, which can utilize sunlight to regenerate saturated adsorbents. Suh *et al.*⁴¹ reported a TiO_2 -LDH-based nanomaterial (Figure 6.7), which demonstrated a combined function of adsorption and photocatalysis to improve the decontamination efficiency substantially. It could remove pollutants using adsorption and be subsequently regenerated by photocatalysis. TiO_2 -LDH indicated a significantly high adsorption capacity toward the model contaminant methyl orange ($\sim 1450\text{--}1459\text{ mg g}^{-1}$), which was even higher than most commercial and laboratory-synthesized carbon-based adsorbents. The high adsorption capacity was considered to originate from the delaminated and high temperature-treated LDH. On the other hand, the photocatalytic regeneration performance of the adsorbent after adsorption was increased by the utilization of light-active plasmonic nanoparticles of TiO_2 , and the nanocomposite could regain more than 97% of its original adsorption ability after five cycles.

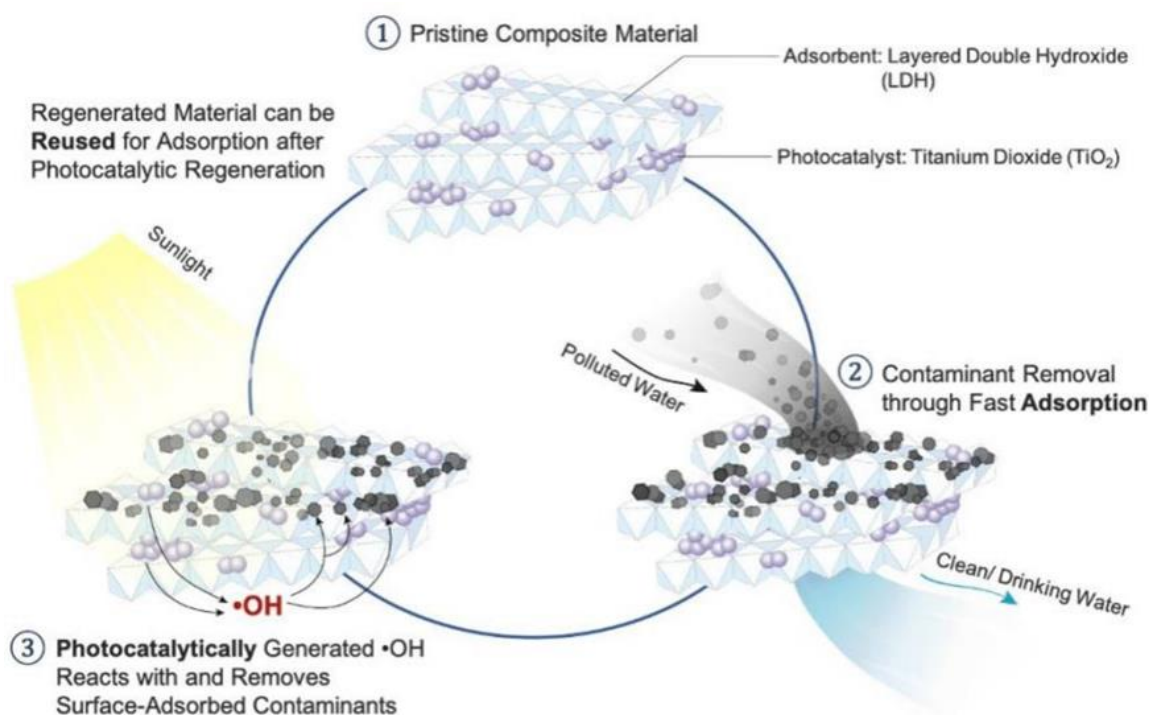


Figure 6.7 Conceptual chart of an adsorption–photocatalysis nanocomposite system. When the TiO₂–LDH nanocomposite was added to contaminated water, decontamination occurred *via* quick sorption. Once the nanocomposite had reached its adsorption balance, the nanocomposite was irradiated using sunlight to experience photocatalytic renewal. Once adequately regenerated, the material could be reused for another adsorption cycle. Adapted from ref. ⁴¹ with permission from American Chemical Society, Copyright 2020.

Bai *et al.*⁴² prepared an octopus-like polymeric adsorbent with CO₂-responsive ability (Figure 6.8). Several heavy metals could be captured with very high Q_e using this adsorbent *via* coordination. Most vitally, the fast and total renewal of the adsorbent and recycling of heavy metal ions could be easily fulfilled by bubbling CO₂ to the adsorbent for a few minutes under mild conditions, *i.e.*, room temperature and atmospheric pressure. The adsorbent could then be renewed to its adsorptive condition and used again when CO₂ was eliminated by merely bubbling another gas.

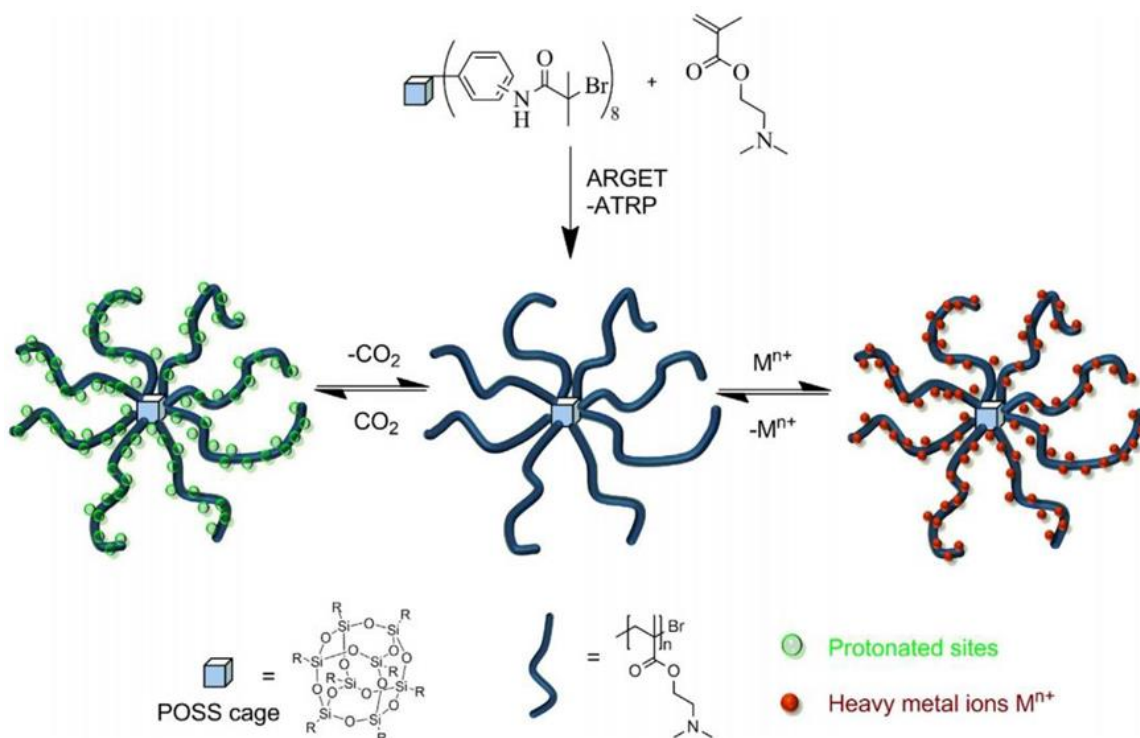


Figure 6.8 Scheme of ARGET-ATRP synthesis of octopus POSS–PDMAEMA and competing CO₂ protonation and metal coordination balances. Adapted from ref. ⁴² with

In addition to the regeneration of adsorbents, the separation of adsorbents is also a major problem in applying adsorption technology. Generally, to obtain a larger specific surface area, adsorbent particles are usually nanosized, making filtration separation difficult. Chen *et al.*⁴³ prepared a novel magnetic nanocomposite of La–Zr using a coprecipitation strategy (Figure 6.9). The magnetic adsorbent showed a maximum adsorption ability of 88.5 mg g⁻¹. Furthermore, the nanoadsorbents used could be readily enriched and recovered using an external magnetic field.

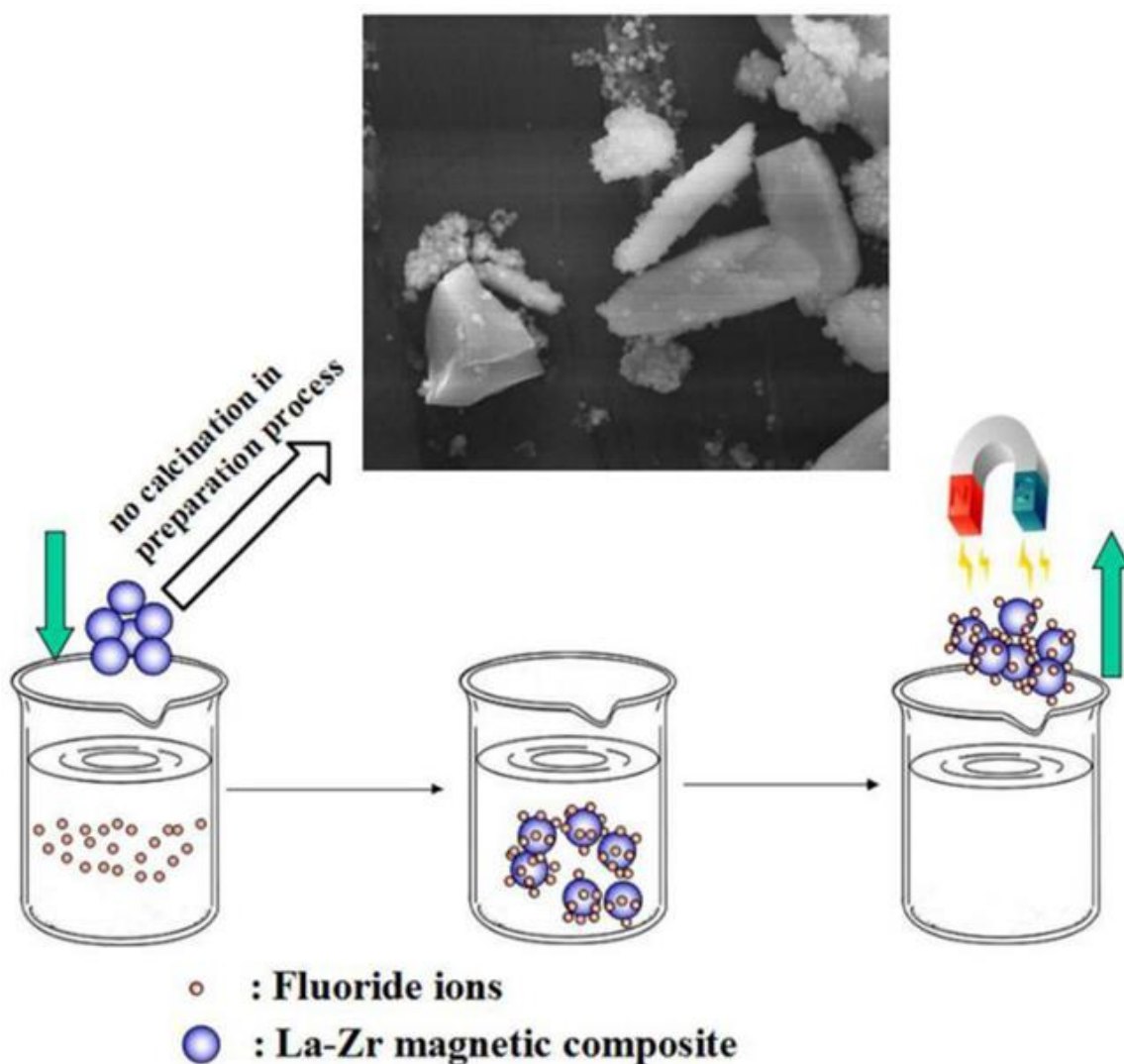


Figure 6.9 Schematic diagram of the La–Zr magnetic composite. Adapted from ref. ⁴³ with permission from the Royal Society of Chemistry.

Wang *et al.*⁴⁴ synthesized a La–Zr–Ce tri-metal adsorbent with regular morphology. There were two morphological shapes in the nanocomposite: the nanoprisms were $\text{La}_2(\text{C}_2\text{O}_4)_3$, and the mesoporous nanospheres were $\text{Fe}_3\text{O}_4\text{--m}(\text{ZrO}_2\text{--CeO}_2)$. The nanoprisms were ornamented with nanospheres to form the nanocomposite. The nanohybrid had a maximum sorption ability of 117.3 mg g^{-1} toward F^- and was applicable in a wide pH range from 2 to 10 with high anti-interference performance. Because of the magnetic component of Fe_3O_4 , the nanoadsorbents could be easily isolated and recycled by applying an external magnetic field.

6.2.3 Nanoadsorbents Equipped with Indicators

Detection is another important treatment for pollutants in addition to removal and is usually the step before the removal step. However, most pollutant treatment studies detected and removed contaminants separately. Combining the detection and removal of pollutants into one treatment reagent can dramatically reduce costs and facilitate operation. For this purpose, several novel nanomaterials that can simultaneously detect and adsorb pollutants in water have been developed in recent years.

Jiang *et al.*⁴⁵ prepared a novel nanocomposite adsorbent that could identify and eliminate heavy metals simultaneously (Figure 6.10). Its adsorption ability rivaled superior conventional sorbents; moreover, it could vary its color to determine the sorbates and their concentrations. The color changes were very readily detected through the naked eye or with a photometer. This nanoadsorbent could not only eliminate a large number of heavy metal ions but also qualitatively and quantitatively measure them.

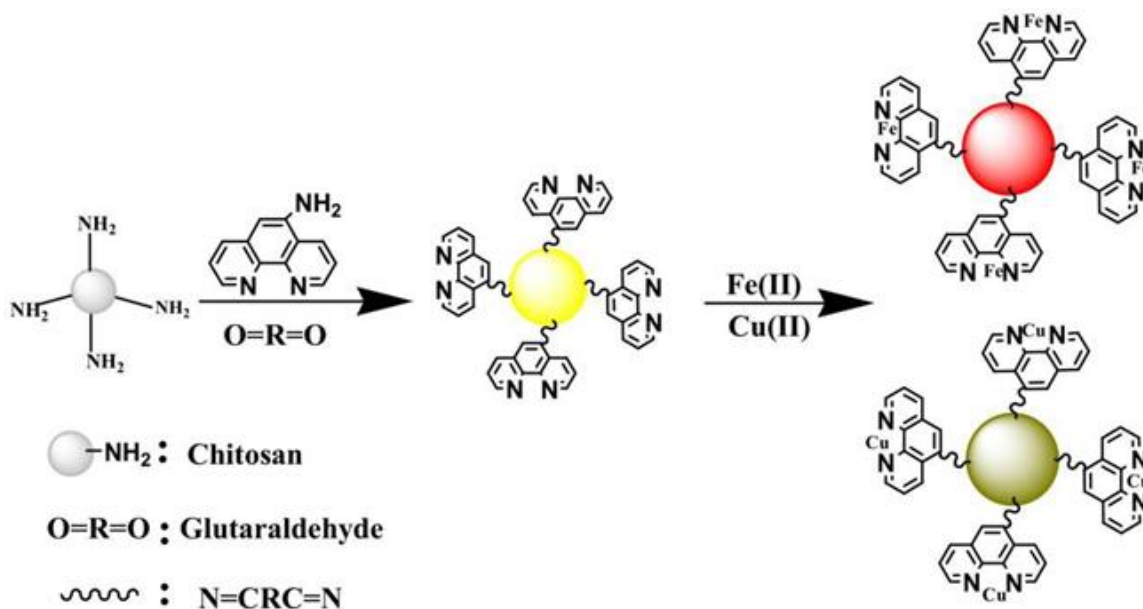


Figure 6.10 Schematic diagram of the composite with detection and removal abilities. Adapted from ref. ⁴⁵ with permission from the Royal Society of Chemistry.

Zhang *et al.*⁴⁶ incorporated thiol-rich ligands (H_2DMBD) with a water-stable $\text{NH}_2\text{-UiO-66}$ (NU66) precursor to prepare a mixed-ligand $\text{NH}_2\text{-UiO-66-SH}$ (NSU66) with a hierarchical pore structure. Unlike conventional adsorbents, this nanoadsorbent could sense and remove Hg^{2+} simultaneously. The as-synthesized NSU66 not only indicated a considerable elimination capacity with a rapid scavenging rate (within 60 min), strong adsorption ability (265.29 mg g^{-1}), and satisfactory selectivity but also possessed a qualified sensing ability, equipped with a low measuring limitation ($3.50 \times 10^{-2} \mu\text{mol L}^{-1}$), wide linear range ($1.00\text{--}99.7 \mu\text{mol L}^{-1}$), strong specificity, and high anti-interference capacity. The sensing function played an important role in exhibiting elimination, and the pre-enrichment effect originating from the adsorption course correspondingly enhanced the sensor sensitivity. Notably, the detection and capture capacities of NSU66 were dramatically enhanced compared to those of NU66, which stemmed from the exquisite design of the mixed ligand and hierarchical pore formation. Moreover, proven outstanding stability and reusability emphasized the viability of NSU66 in practical applications. These outcomes suggested that the smart adsorbent NSU66 could be

employed as a favorable platform for early warning and guided elimination of toxic Hg^{2+} in water.

Du *et al.*⁴⁷ designed a smart adsorbent based on a MOF (Figure 6.11). It could serve as a ratiometric fluorescent probe to precisely monitor the course of Cu^{2+} elimination with a dual-emitting fluorescence signal. Unlike conventional bifunctional materials, this exquisitely designed platform overcame the considerable gap to incorporate two functions into one. This facile platform afforded reliable fluorescent feedback toward Cu^{2+} during the elimination progression, changing linearly according to the sorption course level, which was extremely promising in effectively monitoring sorption progression. The underlying connection between the sorption and fluorescence feedback toward Cu^{2+} was studied *via* density functional theory (DFT) calculations. In particular, due to the favorable ion binding attraction of ZIF-8 and the self-calibrating capability of RhB, the as-synthesized smart nanoadsorbent exhibited a surpassing sorption capability of 608 mg g^{-1} , wide feedback range ($0.05\text{--}200 \text{ mg L}^{-1}$, 2.07×10^{-1} to $8.29 \times 10^{-4} \text{ mol L}^{-1}$), ultrastrong sensitivity (0.04 mg L^{-1} , $1.91 \times 10^{-7} \text{ mol L}^{-1}$) toward copper ions and high anti-interference capability.

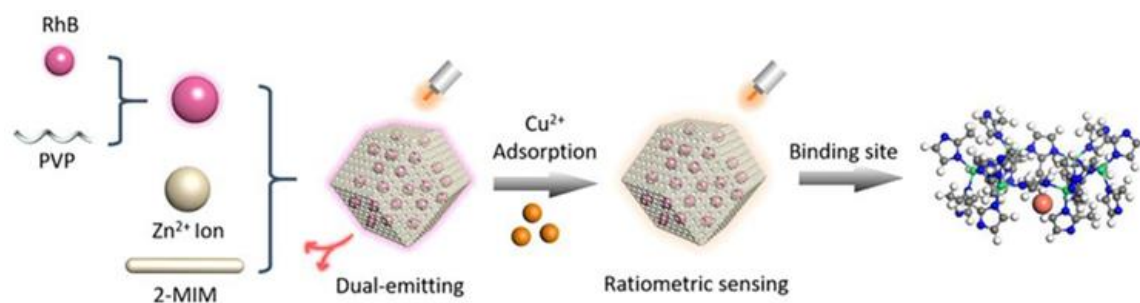


Figure 6.11 Schematic diagram of the preparation of RhB@ZIF-8 as a dual-emission smart sorbent. Adapted from ref. ⁴⁷ with permission from American Chemical Society, Copyright 2020.

These adsorbents equipped with indicators open a promising pathway to boost ample improvements in the areas of environmental detection and contaminant elimination.

6.2.4 Rare Earth Nanoadsorbents

Rare earth elements show high adsorption capacities for various nonmetallic inorganic pollutants, including phosphorus and fluoride. Therefore, adsorbents based on rare earth elements are highly required, but their development is slow due to the high cost of rare earth elements. Recently, some nanoadsorbents containing rare earth elements have attracted much attention. Almost all are nanocomposites, incorporating rare earth elements with cheap metals to dramatically reduce the cost; furthermore, in multimetallic systems, synergistic effects often emerge to improve adsorption performance significantly.

Jiang *et al.*⁴⁸ prepared a novel La–Zr nanocomposite using a one-pot strategy under mild conditions. The adsorbent showed a strong F[−] adsorption capacity of 143 mg g^{−1}. The adsorption mechanism was considered to be chemisorption. Another rare earth-containing nanoadsorbent of the Y–Zr–Al composite was also developed in Jiang's group²⁴ (Figure 6.12). The adsorbent exhibited a laminated morphology with a remarkably high surface area of 256.6 m² g^{−1}. The composite showed outstanding F[−] adsorption performance of high maximum sorption ability (31.0 mg g^{−1}) accompanied by high sorption abilities at low F[−] concentrations, indicating that it was among the top fluoride adsorbents. Moreover, it showed high anti-interference ability coexisting with various competing ions, emphasizing its high feasibility in practical applications.

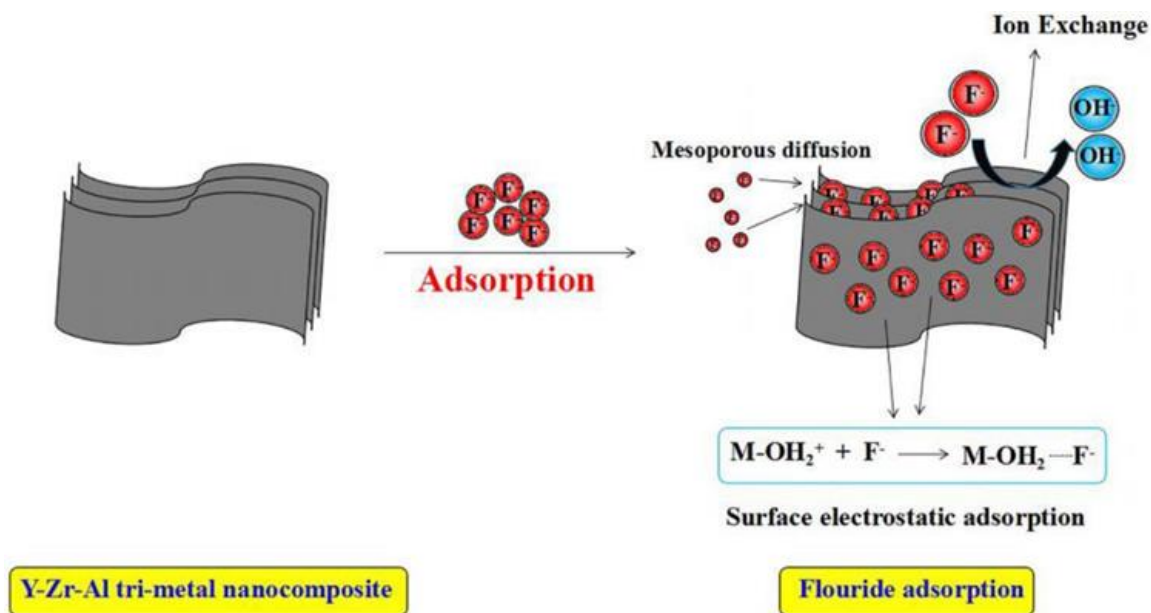


Figure 6.12 Schematic diagram of the feasible defluoridation mechanism over the Y–Zr–Al composite. Adapted from ref. ²⁴ with permission from Elsevier, Copyright 2019.

Chen *et al.*⁴⁹ prepared a novel Fe–Mg–La tri-metal composite *via* a coprecipitation method (Figure 6.13). The function of individual metals in the tri-metal composite was elaborated. Adsorption isotherms of the adsorbent were studied. The results indicated that the adsorption capability toward F⁻ was 13.2 mg g⁻¹ at an equilibrium F⁻ concentration of 1 mg L⁻¹ and the maximum adsorption ability was 47.2 mg g⁻¹, displaying the outstanding defluoridation property of the sorbent. The fluoride-saturated sorbent could be renewed using an alkaline treatment and re-employed.

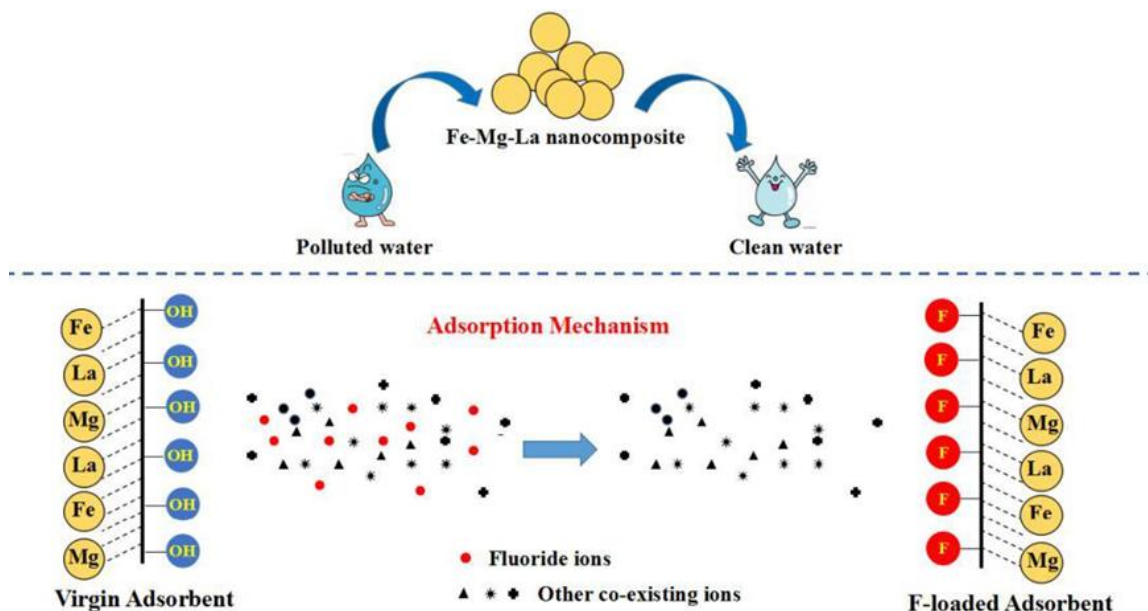


Figure 6.13 The adsorption mechanism of the Fe–Mg–La tri-metal composite. Adapted from ref. 49 with permission from Elsevier, Copyright 2018.

Guo *et al.*⁵⁰ imbedded Fe–La or Al–La nanocomposites into cellulose–graphene hybrids (CG hybrids) to synthesize Fe–La–CG nanohybrids or Al–La–CG nanohybrids for F^- adsorption in the presence of phosphate (Figure 6.14). The results indicated that the Al–La–CG composites were primarily in the amorphous state, whereas the Fe–La–CG composites possessed identical crystalline phases compared to hydrated lanthanum oxides (HLO) and hydrated iron oxides (HFO). The F^- uptake by the Al–La–CG and Fe–La–CG nanocomposites agreed with similar trends as the pH changed; however, the sorption performance of the Al–La–CG nanocomposites was superior to that of the Fe–La–CG hybrids at the same pH values. F^- adsorption onto the Al–La–CG nanocomposites showed high selectivity toward coexisting phosphate compared with the Fe–La–CG nanocomposites, further indicating that the Al–La–CG nanocomposites were more favorable for F^- sorption. The fraction areas of La–F and Al–F in the XPS pattern of the Al–La–CG nanocomposite accounted for 79.1% and 20.9%, respectively, showing that F^- adsorption was mainly based on La species but not Al species. Similarly, the La–F fraction area of the XPS pattern in the F^- saturated Fe–La–CG nanocomposites accounted for

55.6%, higher than that (44.4%) of Fe–F, also indicating the prominent role of La in this hybrid.

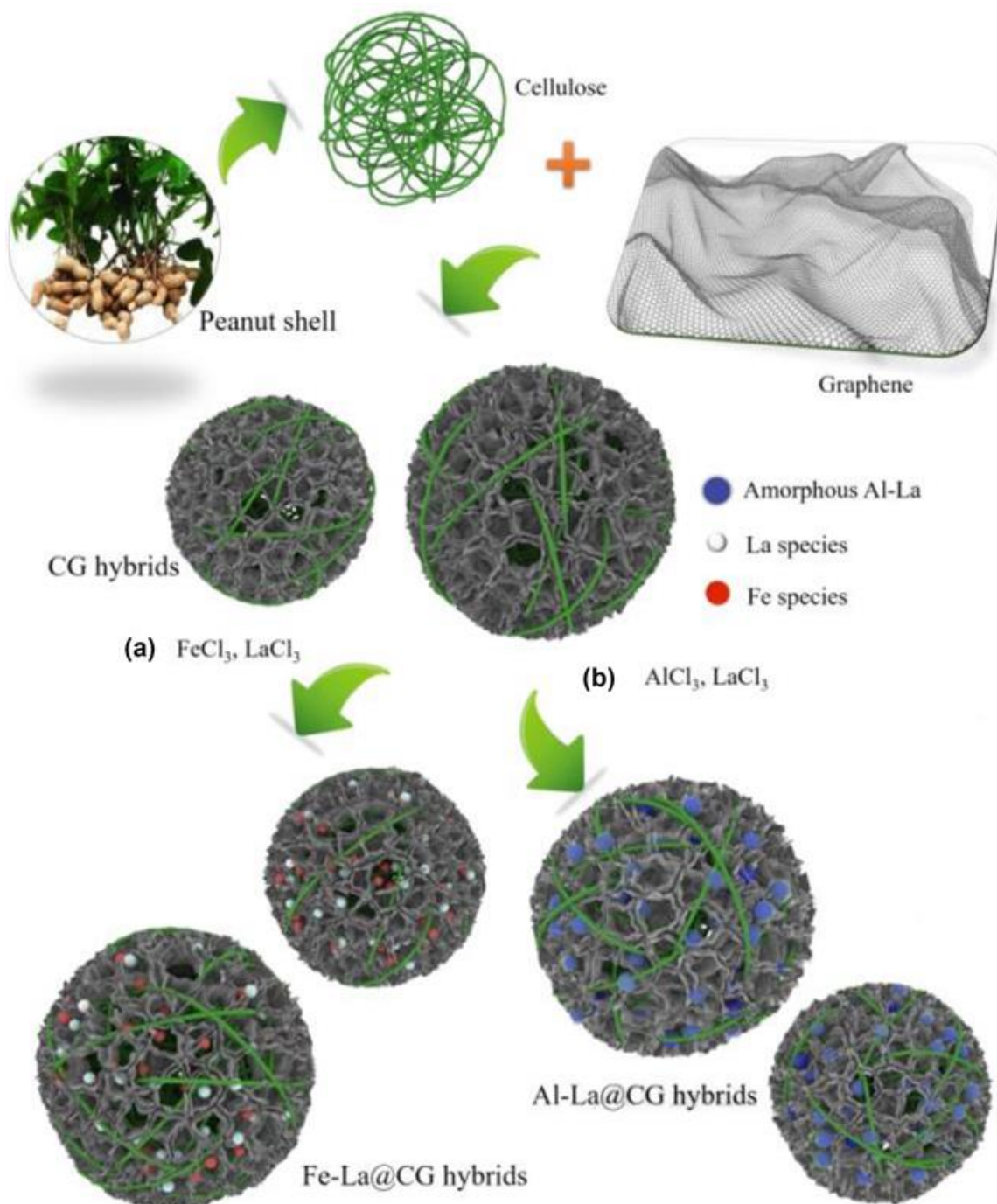


Figure 6.14 Preparation schemes of (a) Fe–La–CG and (b) Al–La–CG composites. Adapted from ref. ⁵⁰ with permission from Elsevier, Copyright 2019.

6.2.5 Broad-spectrum Nanoadsorbents

Pollutants in water usually have many components. Selectivity can solve the problem of removing single component pollutants in a variety of coexisting ions. However, if multiple pollutants coexist and need to be treated simultaneously, broad-spectrum adsorbents are required.

Broad-spectrum adsorbents usually contain multicomponent functional groups. Peng *et al.*⁵¹ incorporated ethylenediaminetetraacetic acid into a robust MOF (MOF-808) to fabricate a broad-spectrum heavy metal ion capturer (Figure 6.15). The trap tested for 22 heavy metal ions in all, including hard, soft, and marginal Lewis metal ions, and showed that the capturer was highly efficient, with elimination rates of more than 99% in single-constituent sorption, multiconstituent sorption, or breakthrough progression. Moreover, the nanomaterial could also be employed as a host for metal ion loading with wide selections for the amount and type of ion with a controllable intake ratio to fabricate well-distributed single- or multiple-metal catalysts.

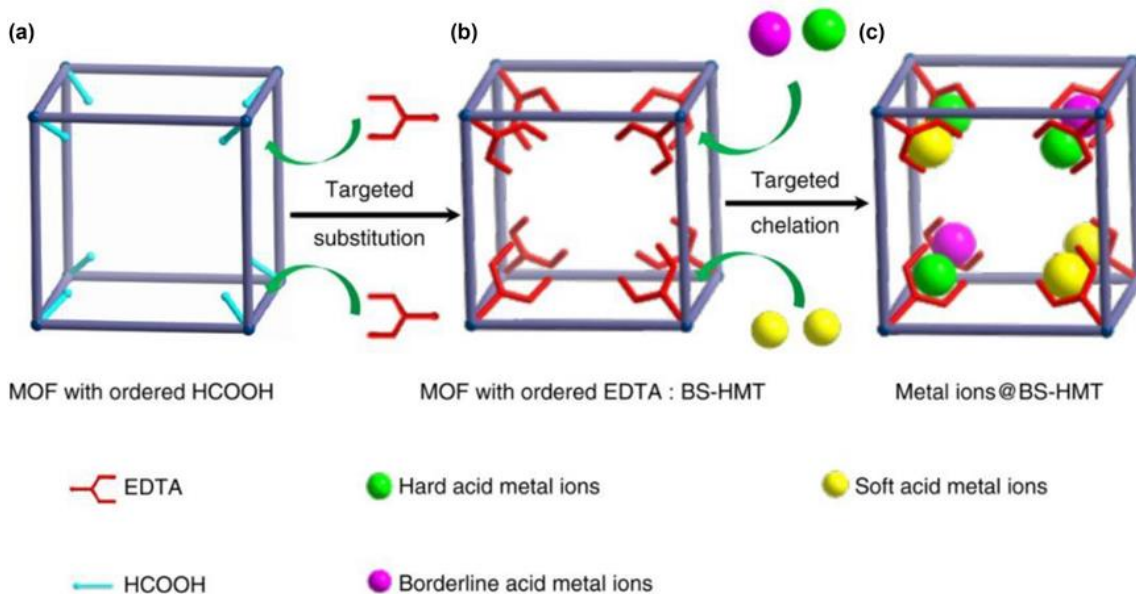


Figure 6.15 Schematic diagram of the BS-HMT concept. (a) The ordered HCOOH in MOF-808 could be replaced by EDTA to obtain (b) MOF-808 with ordered EDTA, which could be employed as (c) a BS-HMT for metal ion trapping. Adapted from ref. ⁵¹,

Coexisting pollutants compete for active adsorption sites of adsorbents, hence decreasing the efficiency of simultaneous adsorption. After multiple adsorbates have been simultaneously adsorbed onto the same adsorbent, sequentially desorbing them can prevent them from being mixed after desorption so that they can be separately recovered with high purity. Under these conditions, Tian *et al.*⁵² prepared a nanohybrid equipped with two functional domains (Figure 6.16). One was the GO domain, which was responsible for the sorption of inorganic metal ions; the other was the PNIPAm domain, responsible for the sorption of organic substances. This two-function-domain sorbent showed excellent simultaneous adsorption performance for both Pb^{2+} and 4-NP. Furthermore, the adsorbed Pb^{2+} and 4-NP could be sequentially desorbed using different conditions and recovered as valuable resources with high purity.

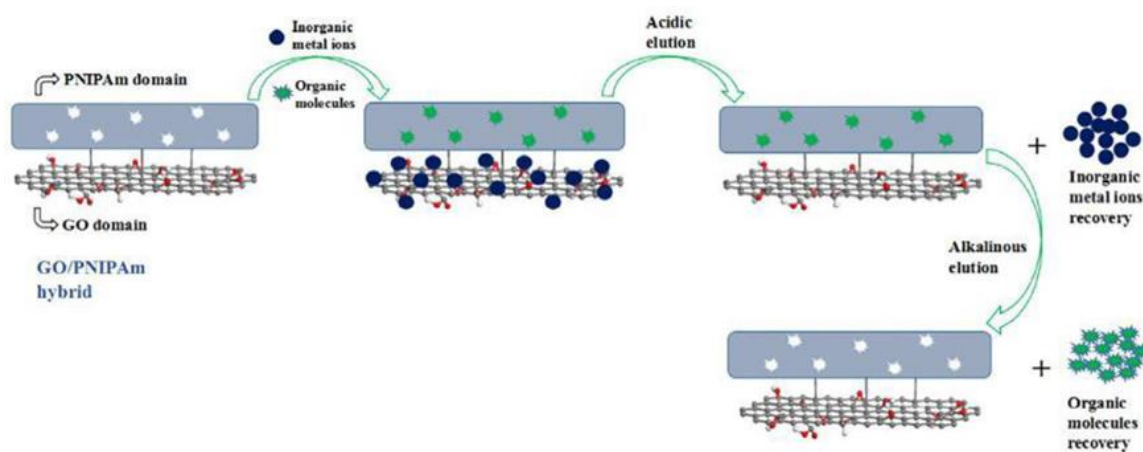


Figure 6.16 Schematic illustration of the simultaneous adsorption toward organic and inorganic targets over GO–PNIPAm. Adapted from ref. ⁵² with permission from Elsevier, copyright 2018.

Chen *et al.*⁵³ reported an environmentally friendly graphene oxide–chitosan (GO–CS) hydrogel as a novel kind of sorbent for water treatment. The GO–CS hydrogels were synthesized *via* self-assembly of GO sheets and CS chains. A 3D network consisting of GO sheets cross-linked by CS

was observed in the GO–CS hydrogels. The GO–CS nanocomposite hydrogels exhibited a strong adsorption capability for various pollutants, including cationic and anionic dyes, in addition to heavy metal ions. The dye sorption mechanism was studied with a spectral strategy, and electrostatic interaction was considered the primary interaction between ionic dyes and the adsorbent.

Yu *et al.*⁵⁴ prepared multifunctional graphene oxide (GO)–chitosan (CS) aerogel microspheres (GCAMs) with honeycomb–cobweb structures and radially directed microchannel formation by incorporating electrospraying with freeze-casting to optimize sorption performances toward heavy metal ions and soluble organic contaminants (Figure 6.17). The GCAMs showed surpassing sorption capabilities toward heavy metal ions such as Cu(ii), Pb(ii), and Cr(vi), cationic dyes such as rhodamine B, methylene blue (MB) and anionic dyes such as eosin Y, methyl orange, and phenol. It took just five mins to arrive at balance sorption capabilities of 82% and 89% toward Cr(vi) (292.8 mg g⁻¹) and MB (584.6 mg g⁻¹), respectively, much faster than the sorption balance time (75 h) of a GO–CS monolith. More vitally, the GCAMs maintained outstanding sorption capability for six cycles of sorption–desorption. The broad-spectrum, fast, and regenerative sorption achievement provided the GCAMs with a high practical potential for water treatment applications.

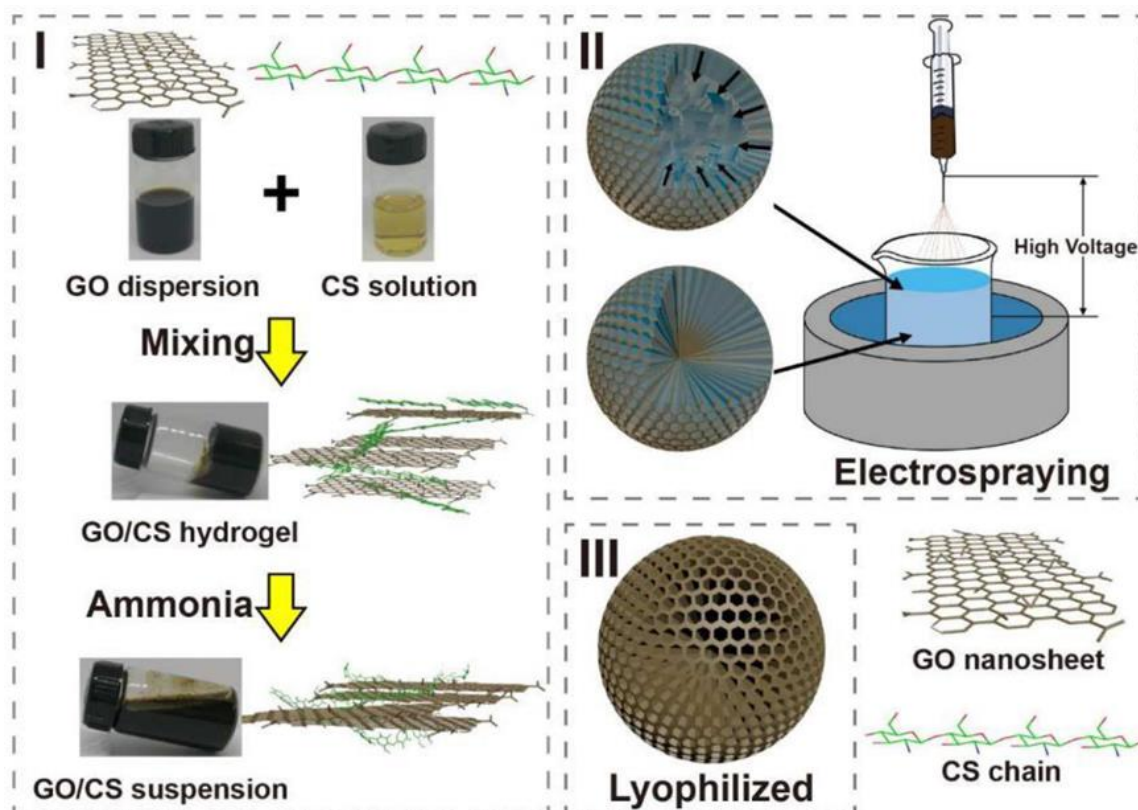


Figure 6.17 The synthesis scheme of GCAMs. Adapted from ref. ⁵⁴ with permission from American Chemical Society, Copyright 2017.

Wang *et al.*⁵⁵ reported a cross-linked β -cyclodextrin (β -CD) polymer capable of removing a broad spectrum of organic pollutants from water using fast sorption (Figure 6.18). A family of β -CD polymers (β -CDPs) was prepared by nucleophilic aromatic substitution of β -CD hydroxyl groups and 4,4'-difluorodiphenylsulfone. The β -CDPs were applied to adsorb various organic pollutants using static or dynamic sorption. It could be seen that >99% of pollutants in water were eliminated by passing the feed water through the column filled with β -CDPs. The results of the static sorption tests showed that the sorption progression was rapid and that the sorption capability was significantly high (the maximal adsorption ability was 113.0 mg of bisphenol A per gram of β -CDP).

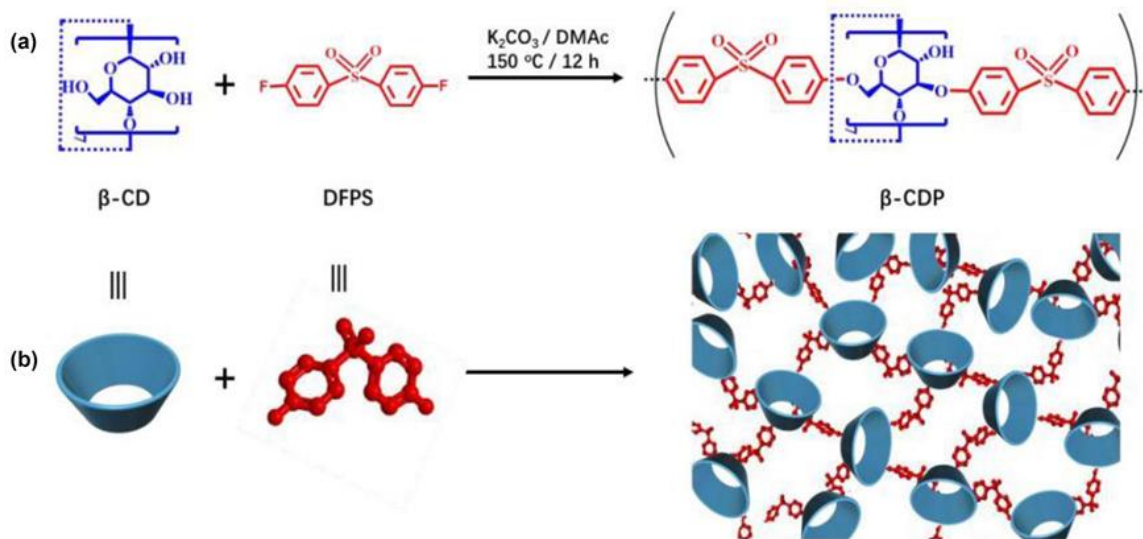


Figure 6.18 (a) Preparation of β -CDP from the nucleophilic aromatic substitution reaction. (b) Schematic illustration of β -CDP structure. Adapted from ref. ⁵⁵ with permission from Elsevier, Copyright 2017.

Xiao *et al.*⁵⁶ prepared environmentally friendly reduced graphene oxide (RGO–Cys) with excellent conjugated formation and dispersing capacity, which exhibited strong sorption abilities toward a dye family with conjugated aromatic structures. The maximum sorption capabilities for anionic indigo carmine (IC) and cationic neutral red (NR) were as high as 1005.7 mg g^{-1} and 1301.8 mg g^{-1} , respectively. The total sorption amount in mixed dye solutions was even higher (more than 3500 mg g^{-1}), and the highest total capacity for the simultaneous sorption of dyes was gained in their mixed solutions. RGO–Cys, after being loaded with IC and NR, could be readily renewed by washing with 0.1 M NaOH and ethanol, respectively. The sorption dominated by π – π interactions could be further employed to remove various other dyes and Cu^{2+} .

6.3 Conclusion

This chapter has summarized the various categories of novel nanoadsorbents that have been developed so far for the separation of hazardous pollutants from water. These materials are versatile, interesting, and promising because they exhibit different pollutant removal properties,

such as high selectivity, regenerable and separable ability, and simultaneous detection and adsorption performance. Some examples of high-impact research with exciting results are present.

Although these nanoadsorbents have great potential in improving pollutant removal performance, there are still some key aspects and limiting challenges that need to be solved.

Taking selective adsorbents as an example, high selectivity and recovery toward pollutants are usually the main advantages, but the adsorption capacity and pH adaptability remain stubborn drawbacks. There must be compatible cavities or specific adsorption groups to recognize the target ions designed in selective adsorbents, but these structures may lower the density of adsorption sites and result in a low adsorption capacity. Additionally, the species of target ions in water may vary with pH, making them difficult to recognize. These may be the main reasons for the stubborn drawbacks of selective adsorbents. However, based on the merits described above, the demand for selective adsorption increases and the number of related studies continues to grow.

With the development of chemical science, materials science, and environmental science, it is anticipated that the performance of nanoadsorbents could keep increasingly outstanding. It is believed that nanoadsorbents are promising for the future of water treatment.

Acknowledgements

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Chapter 7

Application of Titanate Nanotubes for Water Treatment

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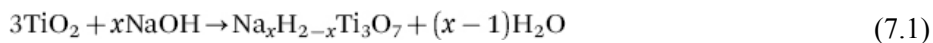
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7.1 Introduction

TiO₂, which is the most widely used photocatalyst, shows high photocatalytic activity due to its excellent chemical and optical properties like quantum size effects and strong adsorption in the ultraviolet (UV) or visible regions.^{1,2} In recent years, titanate nanotubes (TNTs) synthesized through hydrothermal methods *via* TiO₂ and NaOH/KOH have drawn increasing attention. Generally, TNTs have uniform tubular microstructure, large specific surface area, abundant functional groups (–ONa/–OH), good ion-exchange properties, high solution stability and high photoelectric quantum conversion effects,^{3–5} and thus show great application potential in the environmental remediation area.

Hydrothermal treatment of TiO₂ with high concentrations of alkali results in the formation of titanate. Within the large family of TNTs fabricated *via* NaOH treatment, sodium trititanate (Na_xH_{2–x}Ti₃O₇) and hydrogen titanate (H₂Ti₃O₇) are typical compositions for TNTs, which are formed through the reaction shown in eqn (7.1). Figure 7.1 displays a schematic diagram of the H₂Ti₃O₇ formation mechanism,⁶ which includes two steps: a) transformation of the [TiO₆] lattice configuration in TiO₂ to a negative Ti₃O₇^{2–} skeleton; (b) neutralization of the negative charge of the Ti₃O₇^{2–} layer on the side underneath the surface by H⁺ in the interlayer space, and formation of H₂Ti₃O₇ plates, and c) curling of the surface layer at the edge of the H₂Ti₃O₇ plates for the formation of nanotubes.



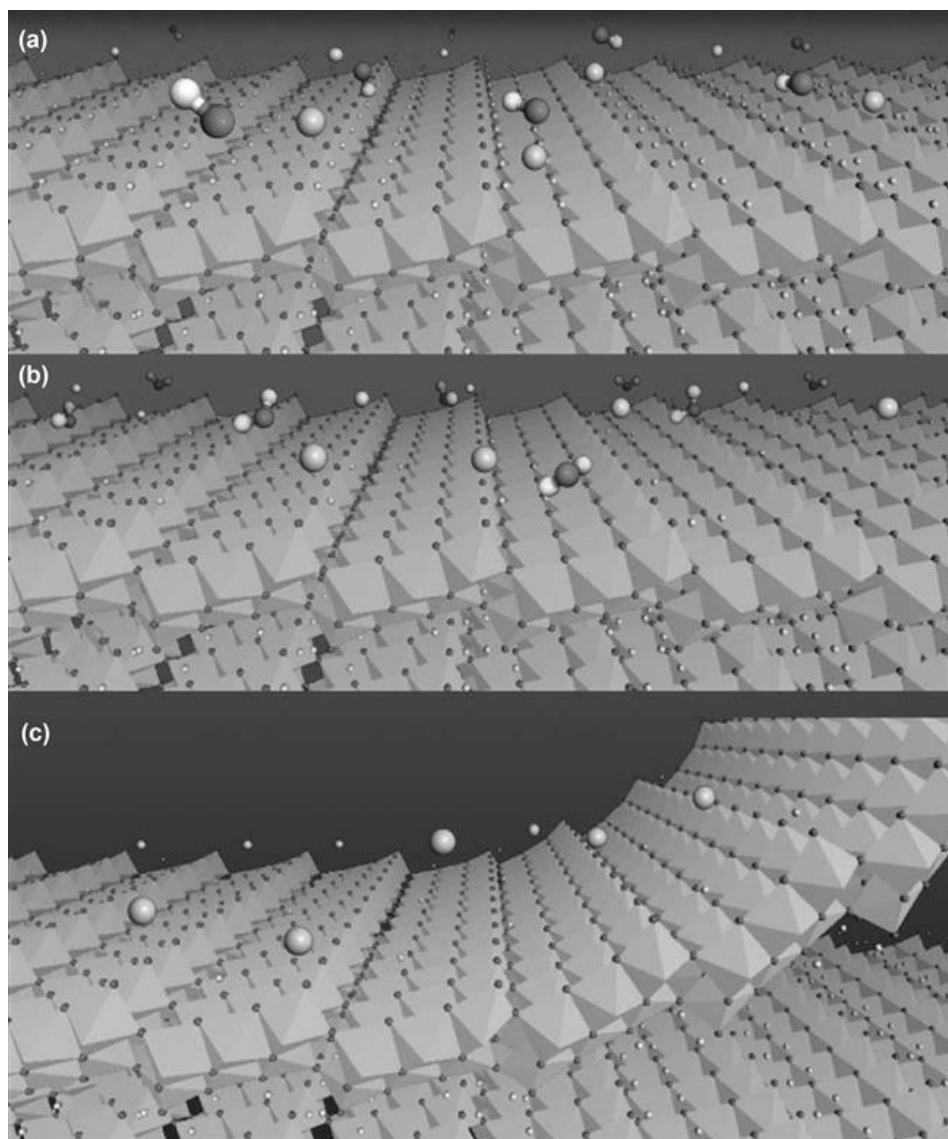


Figure 7.1 Schematic models of the formation of $\text{H}_2\text{Ti}_3\text{O}_7$ in an alkali environment and cleavage of the surface layer due to hydrogen deficiency on the surface.¹ White balls: H; black balls: O; gray balls: Na. (a) A near stoichiometric $\text{H}_2\text{Ti}_3\text{O}_7$ surface in contact with many OH^- and Na^+ ions. (b) Many H^+ on the surface have been carried away by OH^- , forming H_2O . (c) When the surface hydrogen loss exceeds a critical value the surface strain energy becomes so large that the surface layer may overcome the coupling with the layer beneath and peel away from the plate. Reproduced from ref. ⁶ with permission from American Physical Society, Copyright 2003.

The basic structure of TNTs is composed of: a) corrugated ribbons of edge-sharing $[\text{TiO}_6]$ octahedrons as the negatively charged layers, and b) H^+ and Na^+ located in the interlayers (Figure 7.2).⁷⁻⁹ The negatively charged skeleton ($\text{Ti}_3\text{O}_7^{2-}$) captures cationic contaminants through electrostatic attraction, and the interlayered H^+/Na^+ are exchangeable ions for adsorption. Therefore, ion-exchange is the primary property of TNTs, not like TiO_2 , which has high photocatalytic activity as the most important characteristic.

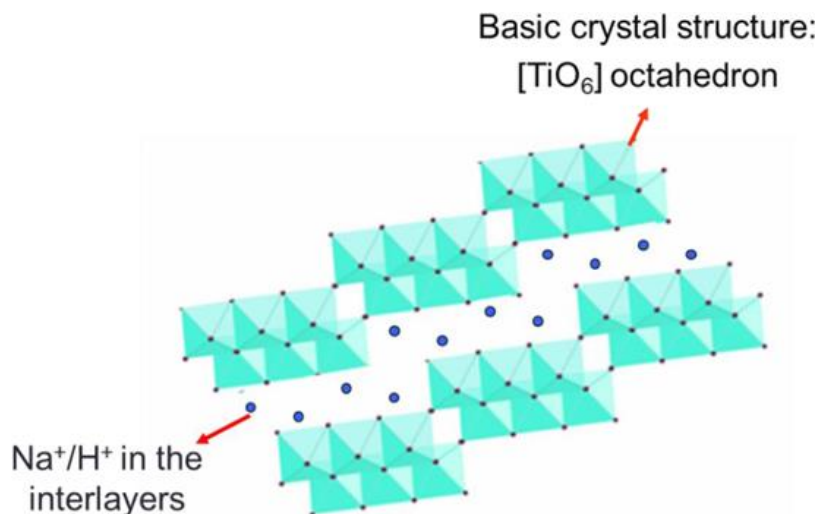


Figure 7.2 Structure and composition of trititanate.

In recent years, TNTs have drawn great interest in the environmental application and research areas due to the following reasons: 1) titanate is the second largest family of titanium-based materials, and study of its environmental behavior and toxicity is of great significance; 2) the structure and composition of TNTs can be easily designed by controlling synthesis conditions; 3) the specific physicochemical properties lead to good adsorptive and photocatalytic performance of TNTs and modified TNTs; 4) the open-ended, multi-layered tubular structure and nanopores/mesopores of TNTs exhibit high nano-confinement effects; 5) good solution stability and separation properties result in great practical application potentials in the water treatment area. The applications of TNTs for water treatment mainly focus on: 1) their use as adsorbents, especially for the removal of heavy metal cations;^{10–12} 2) the use of TNTs and modified TNTs as photocatalysts for the transformation of heavy metals and degradation of organic pollutants;^{13,14} and 3) the use of TNTs and modified TNTs as catalysts to activate peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) for $\text{SO}_4^{\cdot-}$ production and organic pollutant degradation.^{15,16} There is only one study focusing on the environmental implication of TNTs, which reports the aggregation and sedimentation of TNTs, so future studies on the toxicity of TNTs are urgently needed.¹⁷

Overall, the objectives of this chapter are to 1) provide the latest developments of the synthesis of TNTs, 2) illustrate the morphology, crystal structure and composition of TNTs, 3) provide an overview of the environmental applications of TNTs, 4) evaluate the aggregation and sedimentation of TNTs in water, and 5) identify knowledge gaps and future research needs.

7.2 Synthesis and Characterizations of TNTs

7.2.1 Synthesis of TNTs

Hydrothermal treatment using the precursor TiO_2 is the most widely used method to synthesize TNTs, and Table 7.1 summarizes the hydrothermal conditions for TNT preparation. The temperature of hydrothermal reactions is generally $<200\text{ }^\circ\text{C}$, so it is a facile and low-cost process for TNT synthesis. Moreover, long reaction times facilitate the formation of titanate with good crystallinity. TNTs are always prepared under strong alkaline (NaOH or KOH) conditions and a subsequent washing treatment

after the hydrothermal reaction can affect the final chemical composition of TNTs.^{18,19} Hydrogen, sodium and potassium TNTs are labeled H–TNTs, Na–TNTs and K–TNTs in [Table 7.1](#), respectively.

Table 7.1 The hydrothermal conditions for TNT synthesis and the chemical composition of the prepared materials.

Materials	Chemical composition	Hydrothermal conditions					References
Precursor	Alkali and concentration	Temperature	Reaction time	Washing method			
H–TNTs	$\text{H}_2\text{Ti}_3\text{O}_7$	Anatase	10 M NaOH	130 °C	72 h	DI water to pH 7.0	Chen <i>et al.</i> ⁷
H–TNTs	$\text{H}_2\text{Ti}_3\text{O}_7$	Anatase	10 M NaOH	140 °C	22 h	Dilute H_2SO_4 to pH 7.0	Bavykin <i>et al.</i> ⁸
H–TNTs	$\text{H}_2\text{Ti}_3\text{O}_7$	TiO_2	10 M NaOH	150 °C	20 h	Dilute HNO_3 to pH 7.0	Kitano <i>et al.</i> ⁹
H–TNTs	$\text{H}_2\text{Ti}_3\text{O}_7$	TiO_2	10 M NaOH	140 °C	22 h	Dilute H_2SO_4	Bavykin <i>et al.</i> ¹⁰
H–TNTs	$\text{H}_{0.67}\text{TiO}_{2.33}, 0.28\text{H}_2\text{O}_{\text{abs}}$	Rutile	10 M NaOH	150 °C	72 h	DI water to pH 7.0	Thorne <i>et al.</i> ¹¹
H–TNTs	$\text{H}_2\text{Ti}_n\text{O}_{2n+1} \cdot x\text{H}_2\text{O}$ ($3 < n < 6$)	P25 TiO_2	10 M NaOH	150 °C	48 h	DI water to pH 7.0	Lan <i>et al.</i> ¹²
Na–TNTs	$\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$	TiO_2	10 M NaOH	110 °C	20 h	Dilute HCl to pH <7	Kagusu <i>et al.</i> ^{13,14}
Na–TNTs	$\text{Na}_2\text{Ti}_3\text{O}_7$	$(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$	Na_2CO_3	900 °C	5 h	—	Stenina <i>et al.</i> ¹⁵
Na–TNTs	$\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$	TiO_2 sol	10 M NaOH	150 °C	48 h	DI water	Qamar <i>et al.</i> ¹⁶
Na–TNTs	$\text{Na}_{0.92}\text{H}_{1.08}\text{Ti}_3\text{O}_7 \cdot 1.18\text{H}_2\text{O}$	P25 TiO_2	10 M NaOH	130 °C	72 h	DI water to pH 9.0	Liu <i>et al.</i> ¹⁷
Na–TNTs	$\text{Na}_{1.2}\text{H}_{0.8}\text{Ti}_3\text{O}_7 \cdot 0.8\text{H}_2\text{O}$	Anatase	10 M NaOH	120 °C	15–30 h	Dilute HCl to pH 7–8	Morgado <i>et al.</i> ¹⁸
Na–TNTs	$\text{Na}_{0.7}\text{H}_{1.3}\text{Ti}_3\text{O}_7 \cdot 0.5\text{H}_2\text{O}$	Anatase	10 M NaOH	120 °C	15–30 h	Dilute HCl to	Morgado <i>et al.</i> ¹⁸

Na-TNTs	$\text{Na}_{0.1}\text{H}_{1.9}\text{Ti}_3\text{O}_7 \cdot 0.1\text{H}_2\text{O}$	Anatase	10 M NaOH	120 °C	15–30 h	pH 5–7 Dilute HCl to pH <5	Morgado <i>et al.</i> ¹⁸
K-TNTs	$\text{K}_2\text{Ti}_6\text{O}_{13}$	P25 TiO_2	10 M KOH	200 °C	12 h	Dilute HCl to pH 6.0	Yu <i>et al.</i> ¹⁹

7.2.2 Morphology, Crystal Phase and Composition of TNTs

The morphologies of P25-type TiO_2 nanoparticles (NPs) and the prepared TNTs characterized using transmission electron microscopy (TEM) are shown in Figure 7.3. It is observed that the TiO_2 NPs are composed of spherical nanoparticles with a mean diameter of 20–30 nm. The synthesized TNTs exhibit uniform tubular morphologies, and the nanotubes are hollow and open-ended. High-resolution TEM (HRTEM) further indicates that the synthetic nanotubes have highly uniform outer (*ca.* 9 nm) and inner (*ca.* 4.5 nm) diameters and their walls are comprised of 4–5 layers. The interlayer distance is 0.75 nm, which is assigned to the characteristic crystal plane of sodium titanate (200).²⁰ Additionally, they were hundreds of nanometers in length and the length–diameter ratio was 100 or even higher.

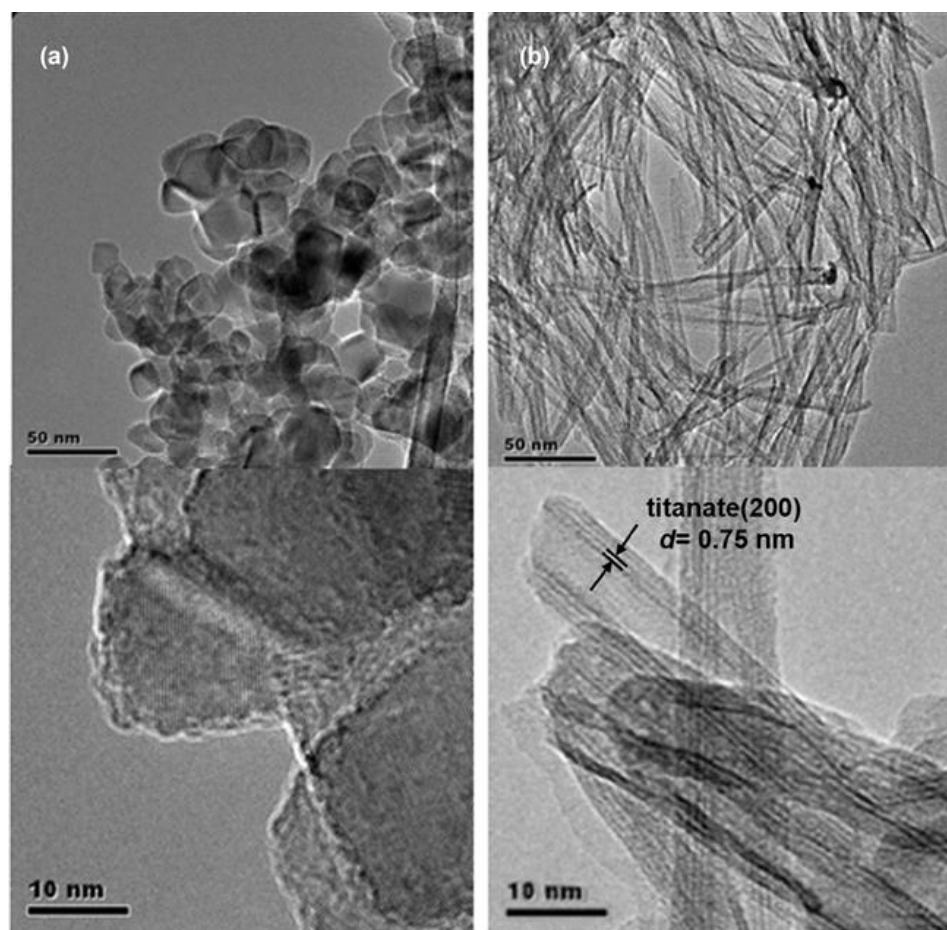


Figure 7.3 TEM and HRTEM images of (a) TiO₂ NPs and (b) TNTs. Reproduced from ref. ¹⁷ with permission from Elsevier, Copyright 2013.

The crystalline phases analyzed using X-ray diffraction are shown in Figure 7.4. The observed peaks at $2\theta \approx 10^\circ$, 24° , 28° , 48° and 62° are all assigned to sodium titanate.⁸ For Na-TNTs, the peaks at 9.8° , 24.3° , 28.4° and 47.8° are consistent with the crystal planes of T(200), T(201), T(111) and T(020) of sodium trititanate (JCPDS No. 31-1329; crystal system: monoclinic, space group: $P2_1/m$). While for H-TNTs, these diffractions correspond to T(020), T(110), T(130) and T(200), respectively.²¹ Further, the observation of H-TNTs at 11.2° , 24.4° , 29.1° and 48.4° can be attributed to the crystal planes of T(100), T(102), T(111) and T(020) (JCPDS No. 36-0654). For Na-TNTs, the peak at *ca.* 10° represents the interlayer distance of the TNTs, which is *ca.* 0.75 nm and is attributed to the sodium titanate (200) crystal plane.²⁰ TNTs synthesized through alkaline-hydrothermal methods are sodium trititanate, with a chemical composition of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ ($x = 0-0.75$, which is related to the remaining Na content).^{8,22} Specifically, the basic skeleton is composed of triple end-shared $[\text{TiO}_6]$ octahedrons linked as Z-shape ribbons with Na^+/H^+ located in the interlayers of the TNTs (Figure 7.2).^{8,22}

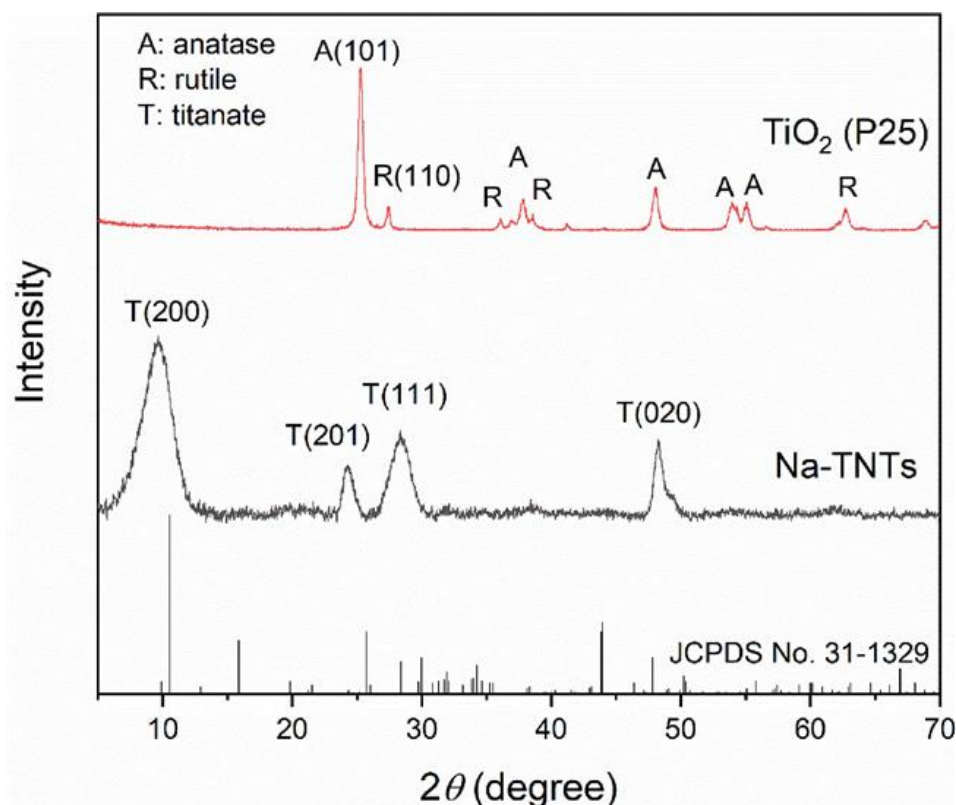


Figure 7.4 XRD patterns of TNTs.

The elemental composition of Na-TNTs analyzed using X-ray photoelectron spectroscopy (XPS), and the main elements of the Na-TNTs displayed in the survey XPS spectra (Figure 7.5a) are Na, Ti, and O. In the high-resolution spectra of O 1s (Figure 7.5b), the peaks at *ca.* 530 and *ca.* 532 eV are attributed to crystal lattice oxygen $[\text{TiO}_6]$ and surface-adsorbed OH (Ti-OH), respectively.^{10,23} In the high-resolution Ti 2p spectra (Figure 7.5c), the doublet level of Ti 2p_{3/2} (458.7 eV) and Ti 2p_{1/2} (464.5 eV) with a ratio of 2 : 1 and a doublet separation of 5.8 eV is in accordance with the $[\text{TiO}_6]$ structure in titanate.²⁴

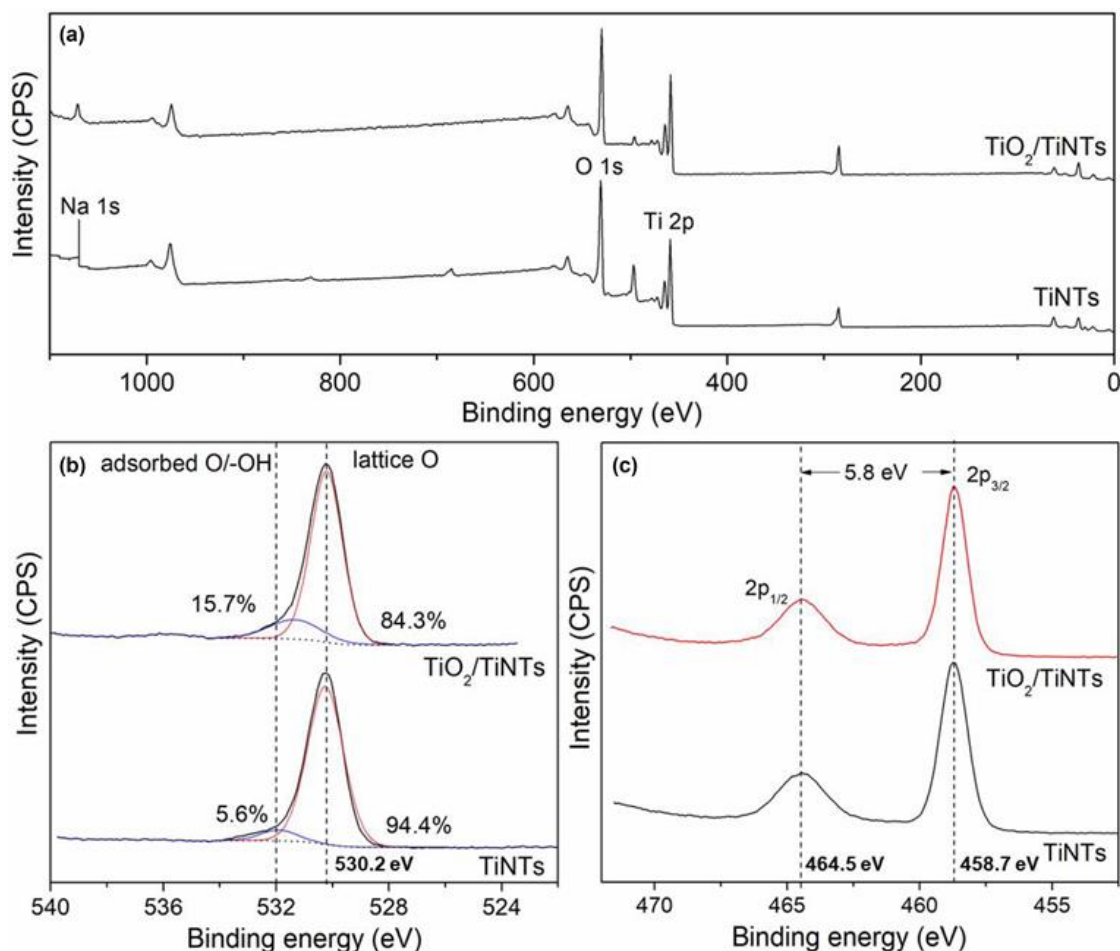


Figure 7.5 (a) XPS survey spectra of Na-TNTs (marked as TiNTs in the figure) and TiO_2 -TiNTs; (b) high-resolution of O 1s, and (c) Ti 2p. Reproduced from ref. ³⁵ with permission from Elsevier, Copyright 2021.

The other key physicochemical parameters of TiO_2 (P25) NPs and TNTs are listed in Table 7.2.²⁵ Compared with TiO_2 , the TNTs have larger specific surface areas ($272.3 \text{ m}^2 \text{ g}^{-1}$) and single point pore volumes ($1.26 \text{ cm}^3 \text{ g}^{-1}$), which is important for adsorption or reaction with contaminants. Besides, the low point of zero charge (pH_{PZC}) value of the TNTs (2.56) suggests the material is negatively charged at neutral pH solution, which is beneficial for cation adsorption.

Table 7.2 Physicochemical parameters of TiO_2 (P25) and TNTs. Reproduced from ref. ¹⁷ with permission from Elsevier, Copyright 2013.

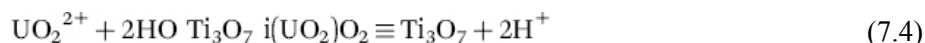
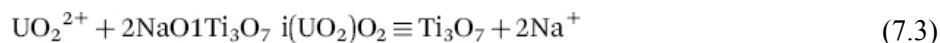
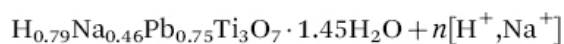
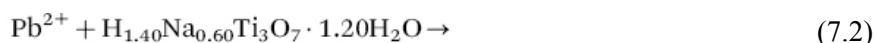
Material	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Single point total pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Average pore diameter (nm)	pH_{PZC}
TiO_2 (P25)	46.9	0.18	15.5	6.67
TNTs	272.3	1.26	18.6	2.56

7.3 Applications of TNTs for Heavy Metal Removal

7.3.1 Adsorption of Heavy Metals in Waters Using TNTs and Modified TNTs

TNTs with abundant –OH and –ONa groups on the surface and low pH_{PZC} values of ~ 2.6 are confirmed to show excellent adsorption performance for metal cations.^{3,4,10} Ion-exchange is widely considered to be the main mechanism for metal cation adsorption, which proceeds between the target metal cations and the exchangeable Na^+/H^+ ions located in the interlayers of the TNTs.^{8,10,26} Therefore, TNTs have been used as adsorbents to remove various heavy metals from waste waters, including common metal cations (*e.g.*, Pb^{2+} and Cd^{2+}),^{10,12,27,28} heavy metal molecules and anions (*e.g.* arsenite and arsenate),^{29–31} radionuclides (*e.g.* $\text{U}(\text{vi})$, Sr^{2+} , Ba^{2+} , Cs^+ and Eu^{3+}),^{11,32–38} and even noble metals (*e.g.* Ag^+ and Pd^{2+}).^{26,39,40}

Our group has systematically studied the adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} and Cr^{3+} from aqueous solution onto TNTs in single and multiple systems.¹⁰ It was found that TNTs show large adsorption capacity for these four heavy metals, with the mechanism of ion-exchange between the metal ions and H^+/Na^+ located in the interlayers of TNTs. Binary or quaternary competitive adsorption indicates that the adsorption capacities of the four heavy metals using TNTs follows the sequence Pb^{2+} (2.64 mmol g^{-1}) $\gg$ Cd^{2+} (2.13 mmol g^{-1}) $>$ Cu^{2+} (1.92 mmol g^{-1}) $\gg$ Cr^{3+} (1.37 mmol g^{-1}), which is consistent with the reverse order of the metal hydration energies. In addition, we proposed that the adsorption mechanism of heavy metal cations on TNTs includes the following three steps (Figure 7.6): (i) hydrated heavy metal ions dissociate to bare ions; (ii) bare metal ions transfer to the negatively-charged surface of TNTs; and (iii) bare metal ions are exchanged with H^+ and Na^+ ions. The adsorption formulas for typical metal cations such as $\text{Pb}(\text{ii})$ and $\text{U}(\text{vi})$ can be written as:^{10,11}



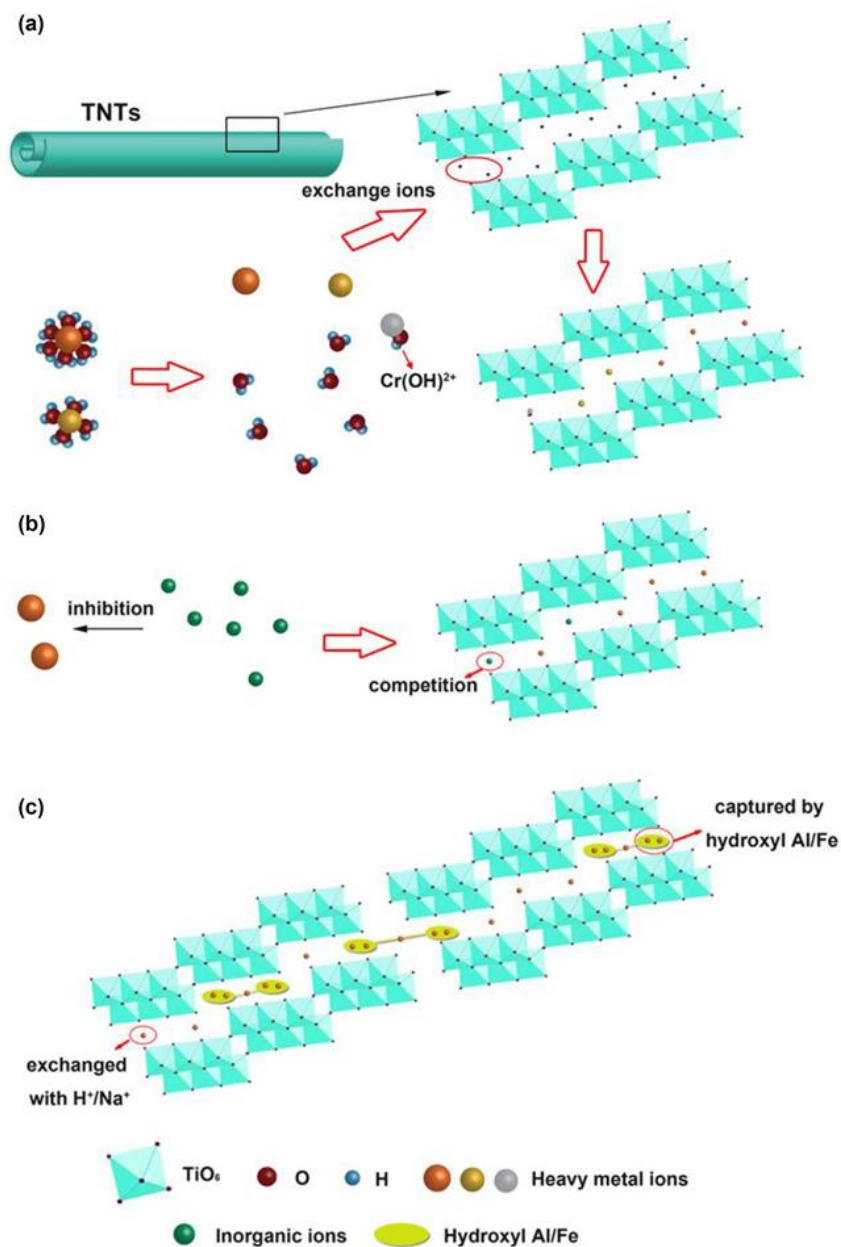


Figure 7.6 Schematic diagram of heavy metal cation adsorption onto TNTs in multiple systems. (a) Ion-exchange process between Cr(OH)_2^+ and H^+/Na^+ located in the interlayer space of TNTs; (b) Competition effect of inorganic ions for adsorption sites with target metal ions; (c) Target ions captured by hydroxyl-Al/Fe intercalated or coated TNTs. Modified based on our previous study. Reproduced from ref. ¹⁰ with permission from Elsevier, Copyright 2013.

Zhang's group also reported that the ion-exchange process of metal cations by titanates ($\text{Na}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$) is selective.²⁶ The valence, hardness, and radius of cations are key factors affecting the selectivity. Cations with higher valence, lower hardness and smaller radii will be preferentially adsorbed. Table 7.3 shows the hardness, valence and radius values of some cations. According to Pearson's hard-soft acid-base (HSAB) principal, hard acids bind strongly to hard bases and soft acids bind strongly to soft bases.^{41–43} Metal cations in solution serve as Lewis acids, while sodium titanate can

be regarded as strong alkali–weak acid salt ($\text{Na}_2\text{Ti}_3\text{O}_7$). Based on the hardness values, the metals can be classed into three groups: hard (*e.g.*, H^+ , Li^+ , Na^+ and K^+), soft (*e.g.*, Ag^+ , Pd^{2+} and Au^+) and borderline (*e.g.*, Cu^{2+} , Pb^{2+} and Ni^{2+}). As a hard base, H_2O binds tightly to Na^+ in the interlayers of titanate, leading to collapse of the layered structure. The possibility and selectivity of ion-exchange by titanate can be explained and predicted by comparing the values of the two cations. This is important for the application of TNTs and titanate nanomaterials in practical wastewaters with coexisting metals. For example, hard cations such as Na^+ , Mg^{2+} and Ca^{2+} are usually present in contaminated wastewater at greater levels, resulting in the inefficiency of traditional treatment technologies. Ag^+ , Cu^{2+} , Hg^{2+} and Pb^{2+} are much softer than Na^+ , Mg^{2+} and Ca^{2+} , thus possess higher priority in the ion-exchange process.

Table 7.3 The values of absolute hardness and radius of metal cations. Reproduced from ref. ²⁶ with permission from John Wiley & Sons, Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Cation	Absolute hardness ^a	Radius ^b (Å)
H^+	∞ (hard)	– 0.18
Li^+	35.1 (hard)	0.76
Na^+	21.1 (hard)	1.02
K^+	13.6 (hard)	1.38
Ag^+	6.9 (soft)	1.15
Rb^+	11.7 (hard)	1.52
Au^+	5.7 (soft)	1.37
Mg^{2+}	32.5 (hard)	0.72
Ca^{2+}	19.7 (hard)	1
Mn^{2+}	9.3 (hard)	0.83
Fe^{2+}	7.3 (borderline)	0.78
Ni^{2+}	8.5 (borderline)	0.69
Cu^{2+}	8.3 (borderline)	0.73
Hg^{2+}	7.7 (soft)	1.02
Sr^{2+}	16.3 (hard)	1.18
Pb^{2+}	8.5 (borderline)	1.19
Ba^{2+}	12.8 (hard)	1.38
Pd^{2+}	6.8 (soft)	0.86
Al^{3+}	45.8 (hard)	0.535
Sc^{3+}	24.6 (hard)	0.745
Fe^{3+}	13.1 (hard)	0.645
La^{3+}	15.4 (hard)	1.032
Eu^{3+}	—	0.947

^a Absolute hardness equals the one half the difference between the ionization energy and the electron affinity.

^b The distance between the nucleus and the electron in the outermost shell of an cation (an atom loses electron).

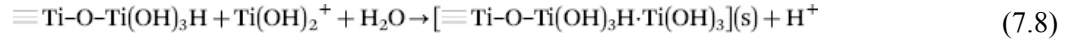
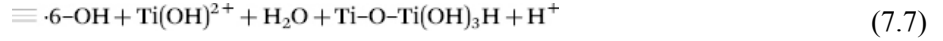
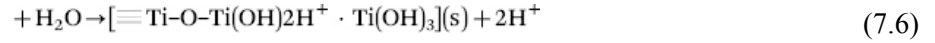
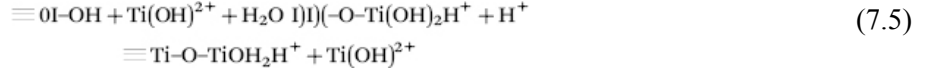
Water chemistry conditions usually affect the adsorption of heavy metals using TNTs. The solution pH is the most important factor as it dominates the species of metal ion that exists in the aqueous phase.^{10,27} In our previous studies, we found the inorganic ions Na^+ , K^+ , Mg^{2+} and Ca^{2+} inhibited metal cations using TNTs, and claimed that the effects of inorganic ions (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) included: (1) competition for adsorption sites with target metal ions because of the ion-exchange properties of

TNTs; (2) reduction in the activities of metal ions, thus limiting their transfer to the surface of the TNTs; and (3) enhancement of TNT aggregation but a less effective specific surface area of the electrolyte ions due to the electric double layer compression effect (Figure 7.6b).¹⁰ However, the presence of Al^{3+} and Fe^{3+} promotes metal cation adsorption by TNTs because hydrolysis of Al^{3+} and Fe^{3+} widely occurs at high concentrations and pH, and the formed hydrolyzates such as $\text{M}(\text{OH})^{2+}$, $\text{M}(\text{OH})_2^+$, and $\text{M}(\text{OH})_3$ ($\text{M} = \text{Fe}$ or Al) bond with the TNTs to capture target heavy metals, which is like a flocculation process on the material (Figure 7.6c). We also carefully studied the effects of inorganic cations, carbonate and natural organic matter on the adsorption of $\text{U}(\text{vi})$ using TNTs.¹¹ It was found that the presence of Ca^{2+} and CO_3^{2-} inhibited $\text{U}(\text{vi})$ adsorption due to competitive adsorption effects and the formation of anionic/electro-neutral complexes. However, humic acid (HA) promoted $\text{U}(\text{vi})$ adsorption because the adsorbed HA facilitated the complexation of $\text{U}(\text{vi})$ with titanate. In addition, HA also greatly compressed the inhibition effects of Ca^{2+} and CO_3^{2-} on $\text{U}(\text{vi})$ adsorption.

Negatively charged TNTs cannot capture metal anions through electrostatic attraction and subsequent ion-exchange.^{30,31,44} We found that TNTs only exhibited a small adsorption capacity for $\text{Cr}(\text{vi})$ (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) at low pH values (≤ 2), due to the electrostatic attraction from the positively charged surfaces of the adsorbents. When the pH increased, the adsorption of $\text{Cr}(\text{vi})$ was greatly inhibited and the adsorption capacity almost decreased to 0 at high pH values (≥ 4), due to drastic repulsion of $\text{Cr}(\text{vi})$ anions by the negatively charged TNTs at high pH values.⁴⁴ Therefore, modification of TNTs to promote the anion adsorption performance is necessary. Protonation to fabricate hydrogen TNTs (H-TNTs), cationic functional groups coating and metal oxide deposition are the most commonly applied methods to promote the adsorption capacity of TNTs for metal anions. H-TNTs have higher pH_{PZC} values than Na-TNTs, and thus possess higher adsorption capacity for metal anions. For example, Niu *et al.* reported that protonated TNTs exhibited fast uptake rates and high adsorption capacities for inorganic As(iii) (existing as $\text{As}(\text{OH})_3$) and As(v) (existing as H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$).²⁹ Moreover, surface complexation, rather than electrostatic interaction was the primary adsorption mechanism of such metal molecules and anions in neutral and alkaline conditions. After TNTs was modified by amino groups ($-\text{NH}_2$) using 2-bromoethylamine hydrobromide through $\text{S}_\text{N}2$ reactions, the new material, TNTs- RNH_2 , showed a maximum enhanced Langmuir adsorption capacity of 69.1 mg g^{-1} for $\text{Cr}(\text{vi})$ at pH 2, which was almost five times larger than that of the fresh TNTs.⁴⁵ Similarly, after the protonated titanate nanotubes were modified by amino groups by covalently grafting [1-(2-amino-ethyl)-3-aminopropyl]trimethoxysilane (AAPTMS), the synthesized amino-functionalized titanate nanotubes (NH_2 -TNTs) had a maximum $\text{Cr}(\text{vi})$ adsorption capacity of 153.85 mg g^{-1} , calculated using the Langmuir model, even at a near neutral pH of 5.4 and was much larger than that of the H-TNTs (26.60 mg g^{-1}).⁴⁶ Our group developed a new composite material, iron oxide nanoparticle-grafted titanate nanotubes (Fe-TNTs), which were synthesized using a facile, one-step water-ethanol hydrothermal method and applied for As(v) removal from water.³⁰ The Fe-TNTs showed a large As(v) adsorption capacity of 90.96 mg g^{-1} determined using the two-site Langmuir model, which was almost three times that of the original TNTs. Due to the coexistence of titanate and Fe_2O_3 phases in the composite material, electrostatic interactions followed by complexation were confirmed to be the primary adsorption mechanism.³⁰

For metal ions to easily hydrolyze at specific water chemistry conditions, the adsorption mechanism is co-precipitation with ion-exchange. Previously, we studied the adsorption of $\text{Ti}(\text{i})$ and $\text{Ti}(\text{iii})$ using TNTs and found ion-exchange between Ti and Na^+ in the interlayers of TNTs was the primary mechanism for $\text{Ti}(\text{i})$ adsorption. However, the adsorption mechanism is different for $\text{Ti}(\text{iii})$, which involves either ion-exchange with Na^+ at low $\text{Ti}(\text{iii})$ concentrations or co-precipitation in the form of $\text{Ti}(\text{OH})_3$ with TNTs at

high Ti(III) concentrations.⁴⁷ The co-precipitation of Ti(III) on the surface of the TNTs can be described by eqn (7.5)–(7.8).⁴⁷ Kochkar's group also reported that the adsorption isotherms of Pd(II) on HNTs ($H_xNa_{2-x}Ti_2O_5 \cdot H_2O$ with $x = 1.61$ or 1.65) occurred in two stages: (1) an initial stage of cationic exchange and (2) precipitation of different Pd salts at high concentrations of Pd(II).⁴⁰



7.3.2 Photocatalytic Transformation of Heavy Metals Using TNTs and Modified TNTs

For metals that can achieve species transformation, reduction and oxidation treatments may greatly reduce their toxicity, and then subsequently adsorption or precipitation are applied. Therefore, a combined oxidation–reduction and adsorption is recommended for the removal of such metals. For example, As(III) exhibits much higher toxicity than As(V) because of its high affinity to thiols, which are active sites of many important enzymes in the human body.^{48,49} Therefore, a common technique for As removal from aqueous solution is the oxidation of As(III) to As(V) to reduce toxicity first, followed by further treatment to achieve complete removal.⁵⁰ Cr(VI) exhibits a higher toxicity and mobility than Cr(III) in the environment and the human body, the reduction of Cr(VI) to Cr(III) is usually chosen as an effective remediation method for Cr-polluted waters.^{51,52} U(VI), which usually exists as UO_2^{2+} cations, is soluble and much more mobile in the environment.⁵³ In contrast, U(IV), which mainly exists as UO_2 , is only sparingly soluble ($K_{sp} = -52.0$) and much less mobile. Therefore, the reductive transformation of U(VI) to U(IV) precipitate is considered more viable as the reduced form of U(IV) is much more resistant to remobilization than adsorbed U(VI).^{54–56} In recent years, TNTs and modified TNTs have been significantly developed for the photocatalytic transformation of heavy metals. It is well known that TNTs are good heavy metal cations adsorbents due to their excellent ion-exchange characteristics, large surface area, and abundant functional groups. However, unlike the precursor, TiO_2 , neat TNTs only show weak photocatalytic activity due to the rapid recombination of excited electrons and holes after irradiation.^{31,57–60} In addition, the light absorption edge of TNTs is ~ 360 nm with a band gap energy (E_g) of 3.4 eV,³¹ so TNTs can only utilize UV light for photocatalysis. Metal doping and heterojunction architectures have been applied to promote the photocatalytic activity of TNTs, so as to remove heavy metals *via* integrated photocatalysis and adsorption.^{31,61–63}

We fabricated iron-deposited titanate nanotubes (Fe–TNTs) with both high photocatalytic activity and adsorptive performance through a one-step hydrothermal method and applied them for the simultaneous removal of As(III) and As(V) *via* initial As(III) oxidation followed by As(V) adsorption.³¹ At a high Fe–TNTs dosage of 0.6 g L^{-1} under UV light irradiation at pH 3.0, 99.6% of As(III) was photo-oxidized within 30 min, and >99% of the total As removal was achieved within 70 min (Figure 7.7b). The Fe in the composite material played a dual role: (1) the Fe^{3+} located in the interlayers of the TNTs acted as temporary electron- or hole-trapping sites; and (2) the attached $\alpha\text{-Fe}_2\text{O}_3$ NPs played the role of a charge carrier for electrons transferred from the TNTs (Figure 7.7a). These two effects restarted the electron–hole pair recombination thus promoting photocatalysis.

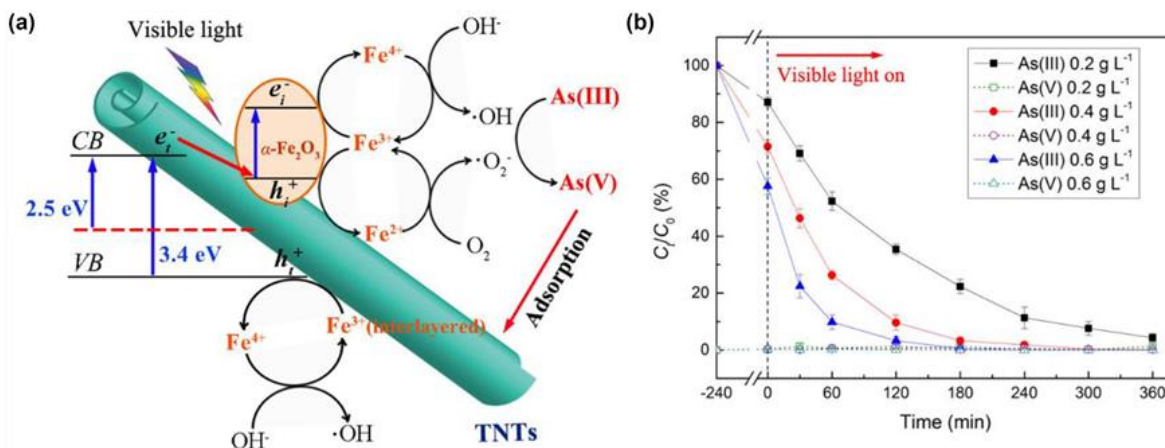


Figure 7.7 (a) Schematic diagram and (b) experimental kinetics of photocatalysis–adsorption of As(III) and As(V) using Fe–TNTs at different initial dosages under UV light. Reproduced from ref. 42 with permission from American Chemical Society, Copyright 1968.

For metal photocatalytic reduction using TNTs and modified TNTs, we prepared a niobate–titanate nanoflake (Nb–TiNFs) composite, which exhibited a heterojunction structure of trititanate ($\text{Na}_{1.6}\text{H}_{0.4}\text{Ti}_3\text{O}_7 \cdot 1.7\text{H}_2\text{O}$) and sodium niobate ($\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$).⁶³ The Nb–TiNFs exhibited rapid adsorption kinetics and large adsorption capacities for U(VI) (Langmuir $Q_{\text{max}} = 298.5 \text{ mg g}^{-1}$) at pH 5.0 via ion-exchange and surface complexation. More importantly, the Nb–TiNFs were able to convert U(VI) into immobile $\text{UO}_2(\text{s})$ under solar light through photocatalytic reduction. In addition, the uranium was trapped in the tunnel lattice of the titanate and niobate heterojunction after adsorption and reduction, which prevented re-oxidation of U(IV) to U(VI) , thus achieving long-term immobilization of uranium. Remobilization tests indicated that only 18.7% of U(IV) was re-oxidized to U(VI) and almost no uranium dissolved into the aqueous phase when exposed to air for a period of 90 days.

We also proposed an interesting, combined one-step system for the simultaneous removal of Cr(VI) and Cr(III) in coexistence with TiO_2 NPs and TNTs.²⁵ In the one-step system (Figure 7.8), Cr removal was substantially promoted because of the synergistic effect of photocatalysis and adsorption. In this system with coexisting TiO_2 and TNTs, the Cr(VI) accumulated on the surface of the TiO_2 nanoparticles is reduced to Cr(III) by photoexcited electrons, and Cr(III) is immediately adsorbed by the TNTs owing to their large adsorption capacity and quick kinetics. The transfer of Cr(III) from TiO_2 to TNTs results in the continuous release of the photocatalytic TiO_2 sites and then exposure to Cr(VI) , thus enhancing photocatalysis. However, in the absence of TNTs, Cr(III) have nowhere to escape to and accumulate around the TiO_2 nanoparticles, which inhibits the interfacial contact of Cr(VI) and photocatalytic sites. Therefore, close collaboration between TiO_2 and TNTs in the chromium removal process makes it possible to promote the photocatalytic reduction of Cr(VI) using the ideal receiver mechanism for Cr(III) of adsorption on TNTs.

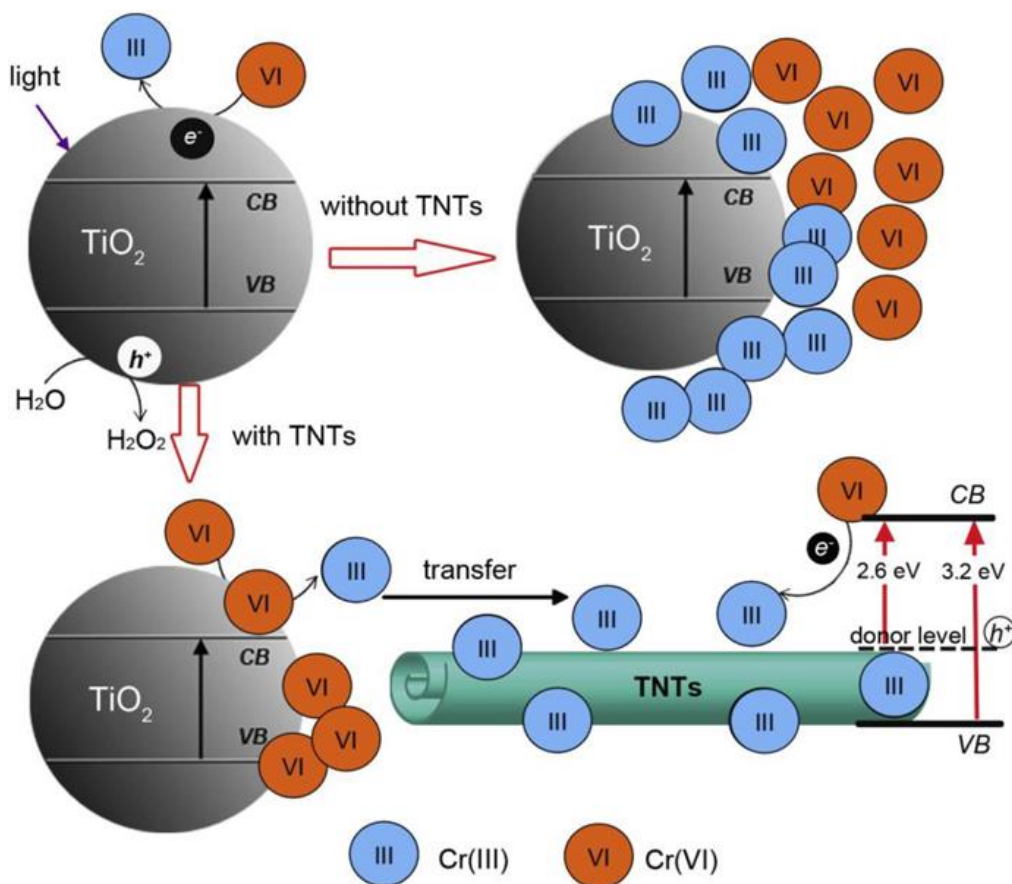


Figure 7.8 Schematic diagram of the synergistic mechanism of photocatalysis and adsorption with TiO_2 and TNTs. Reproduced from ref. ²⁵ with permission from Elsevier, Copyright 2014.

7.3.3 Reductive and Oxidative Immobilization of Heavy Metals Using Modified TNTs

Considering the large specific surface area of TNTs, grafting of oxidizing/reducing materials onto TNTs also can achieve the reductive and oxidative immobilization of heavy metals. Moreover, pre-accumulation of target metal ions onto TNTs can enhance the subsequent reduction or oxidation process. Kang *et al.* synthesized a composite material with iron monosulfide nanoparticles (FeS NPs) deposited onto TNTs, and an efficient total Cr removal was reported through the reduction of $\text{Cr}(\text{vi})$ to $\text{Cr}(\text{iii})$ on FeS and the subsequent adsorption of $\text{Cr}(\text{iii})$ on the TNTs. Our group reported a composite material of amorphous MnO_2 nanoparticles decorated on TNTs ($\text{MnO}_2\text{-TNTs}$, $0.4\text{MnO}_2 \cdot \text{Na}_{1.1}\text{H}_{0.9}\text{Ti}_3\text{O}_7$).⁶⁴ The MnO_2 fraction oxidized the contaminant and promoted its removal. Although the material was not used for the oxidation and immobilization of heavy metals, it has high potential for the removal of some pollutants, such as $\text{As}(\text{iii})$.

7.4 Applications of TNTs for Organic Pollutant Removal

7.4.1 Adsorption of Organic Pollutants in Waters Using TNTs and Modified TNTs

In the early stages of the application of TNTs as adsorbents, the application of TNTs for organic pollutant adsorption mainly focused on organic dye removal. Moreover, due to the cationic ion-

exchange properties and low pH_{PZC} of TNTs, only cationic dyes (*e.g.*, methylene blue, Basic Green 5, and Basic Violet 10) were reported to be efficiently removed.^{9,65–67} Xiong *et al.* reported that the Langmuir maximum adsorption capacity of methylene blue (MB) could reach 133.33 mg g^{-1} at pH 7.0, and chemical sorption through ion-exchange was the primary mechanism.⁹

Existing species and dissociated forms significantly affect the adsorption of organics using TNTs. Therefore, the following scientific and theoretical challenges facing TNTs for organic pollutant adsorption must be considered: (1) the effectiveness of TNTs for the adsorption of organics with various speciations; (2) the underlying adsorption mechanism of organics with various molecular structures using TNTs; (3) the application of theoretical calculations such density functional theory (DFT) to deeply reveal the adsorption mechanism; and (4) quantitation of the structure–activity relationship between organic adsorption capacity and structure/quantum parameters (*e.g.*, molecular orbital distribution, electrostatic potential, polarity constant, electronegativity, molecular dipole moment, and *etc.*); (5) the practical application of TNTs in complicated situations (*e.g.*, at different pH values, in the presence of natural organic matter and inorganic ions) for organic pollutant removal. We have carefully investigated the adsorption behaviors and mechanisms of ciprofloxacin (CIP, a model pharmaceuticals and personal care product) with different dissociated species using TNTs through both experimental and theoretical calculations.⁶⁸ The CIP species including CIP^+ , $\text{CIP}^\pm$, CIP^- at various pH values exhibit significantly different adsorption favorability (Figure 7.9a). DFT calculations indicate that variation of pH affects the protonated/deprotonated forms of CIP (Figure 7.9b), and then changes the distribution of molecular orbitals (highest occupied molecular orbitals, HOMO and lowest unoccupied molecular orbitals, LUMO) and the electrostatic potential (ESP) energy of CIP (Figure 7.10). The ESP of CIP species follows the trend: CIP^+ ($180.57 \text{ kcal mol}^{-1}$) > $\text{CIP}^\pm$ ($146.78 \text{ kcal mol}^{-1}$) > CIP^- ($12.30 \text{ kcal mol}^{-1}$), indicating the side of the piperazine ring in CIP oriented toward the TNTs dominates CIP adsorption. The integration of experimental and theoretical results, revealed, for the first time, that ESP energy serves as the indicator and predictor of adsorption ability for organic molecules with various dissociated forms, and helps to describe the adsorption mechanism of organic pollutants. The theoretical method proposed in this study provided deep insight into similar research on the adsorption of organics using titanate nanomaterials.

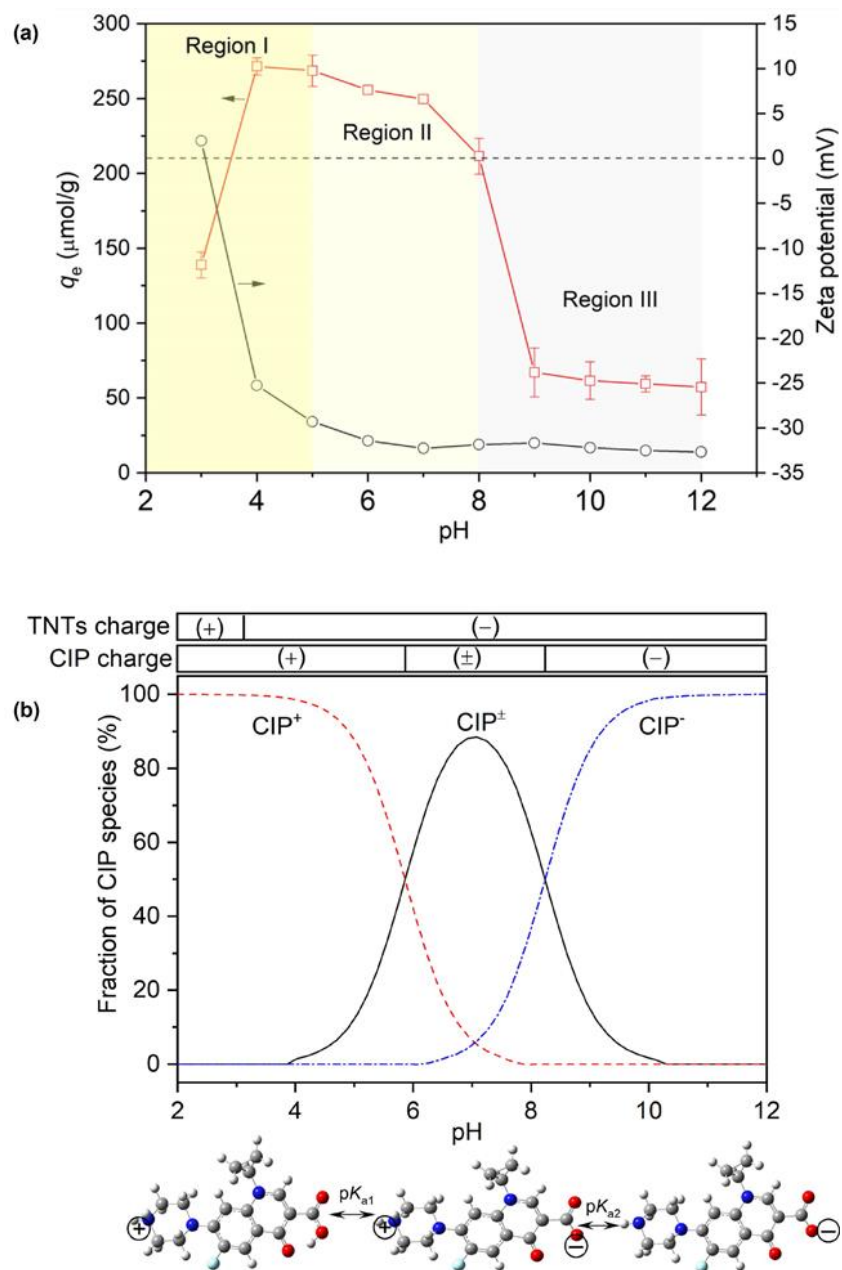


Figure 7.9 (a) Equilibrium adsorption capacity of CIP using TNTs as a function of pH with the zeta potential of TNTs; (b) distribution of CIP species as a function of pH. Reproduced from ref. ⁶⁸ with permission from Elsevier, Copyright 2020.

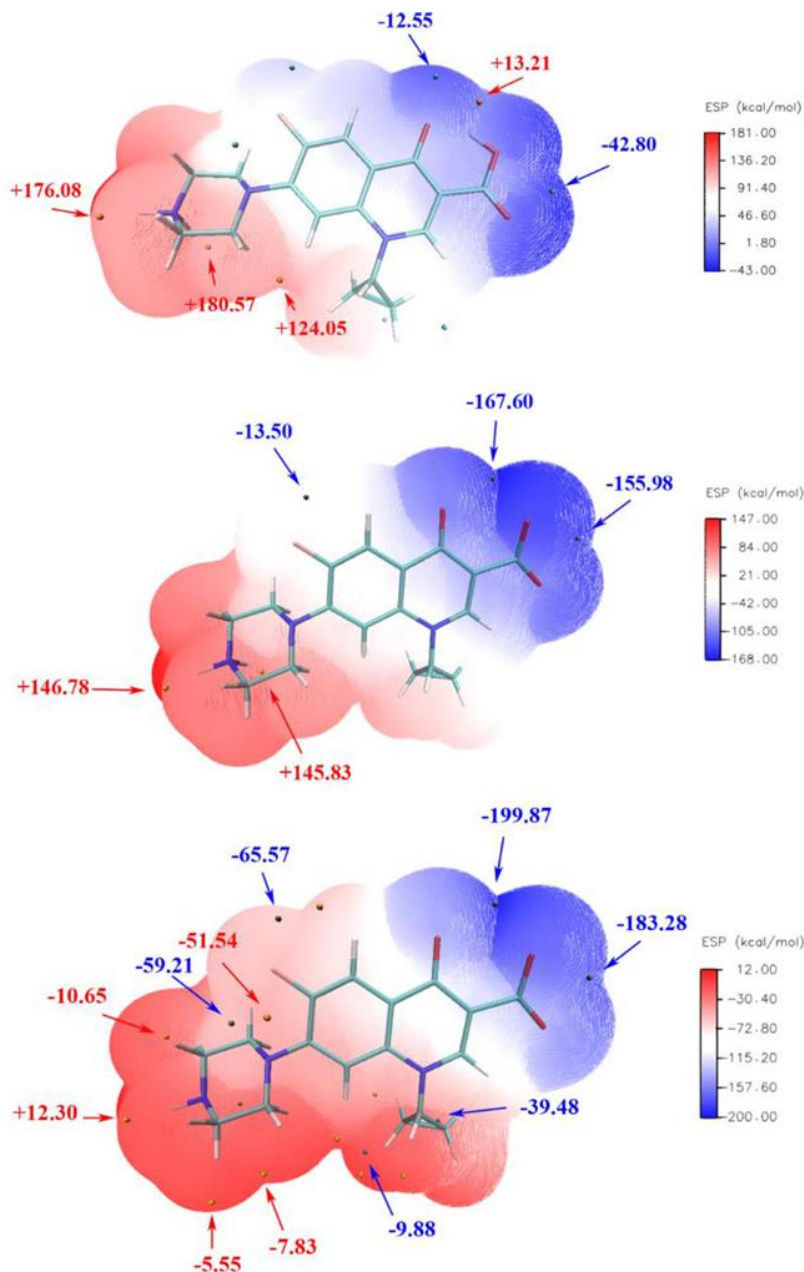


Figure 7.10 Electrostatic potential map of CIP⁺, CIP[±], and CIP⁻. Reproduced from ref. ⁶⁸ with permission from Elsevier, Copyright 2020.

Unlike the adsorption properties for heavy metal cations, the organic pollutant adsorption performance of neat TNTs is weak owing to: (1) the inorganic structure of titanate; (2) no π - π interactions between titanate and organic molecules with benzene rings, and (3) titanates with hydrophilic surfaces cannot capture hydrophobic organic molecules such as polycyclic aromatic hydrocarbons (PAHs).^{13,17,69} To enhance the adsorption property of TNTs for organics, carbon materials are widely applied as skeletons to support TNTs and fabricate new composite materials, as carbon materials generally have high adsorption capacities for organics. In recent years, a series of activated carbon (AC) and activated carbon fiber (ACF)-supported TNTs have been developed by our group and

used for organics adsorption.^{69–73} The AC–TNTs and ACF–TNTs composites show broad-spectrum adsorption properties for the removal of organic pollutants, including PAHs, pharmaceutical and personal care products (PPCPs), organic dyes, chlorophenols and per- and polyfluoroalkyl substances (PFAS).^{69–74} The mechanism of enhanced adsorption performance of the TNTs after carbon modification is explained using capillary condensation.⁶⁹ As displayed in Figure 7.11a, although micro-carbon is grafted on both the interior and exterior walls of the nanotubes, more micro-carbon accumulated at the entrance of the tubes, forming a narrow throat at the open ends of the nanotubes and a relatively larger, ellipsoidal cavity inside the nanotubes mimicking the ink-bottle pore geometry. The carbon coating reduced most of the interior tube diameters to <4 nm (*ca.* 1–2 nm), which is conducive to capillary condensation. Four steps can be discerned during the transition from adsorption to capillary-condensation. At low concentrations, the organic molecule (phenanthrene as a model) is adsorbed on the pore and slit walls following the classical Langmuir mode (Step I in Figure 7.11a). With increasing matrix potential, the adsorbed layer thickens to a point where the slits are filled with liquid due to capillary condensation (Step II in Figure 7.11a). Further increasing the matrix potential fills the “belly” of the pore, resulting in a reduction in the radius of curvature of the liquid–vapor interfaces and forming a circle or elongated oval-shaped interface (Step III in Figure 7.11a). Subsequently, the pore is completely filled (Step IV in Figure 7.11a). The TNTs–AC showed an extremely high adsorption capacity for phenanthrene of 12.1 mg g^{−1} calculated using the Langmuir isotherm model, which was about 11 and 575 times higher than those of AC (1.1 mg g^{−1}) and TNTs (0.021 mg g^{−1}), respectively (Figure 7.11b).⁶⁹

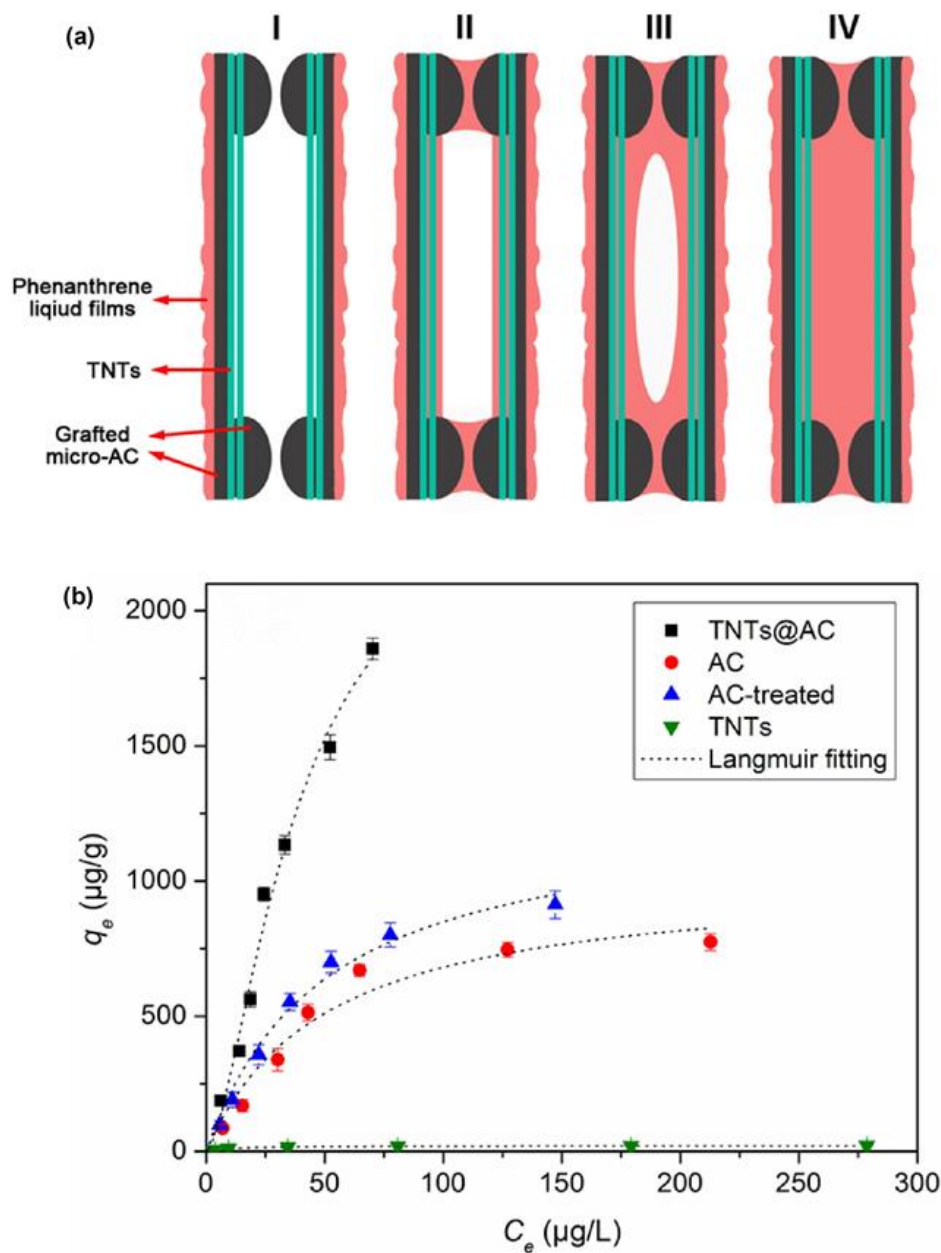


Figure 7.11 (a) A conceptualized representation of the bottle-filling mechanism and transition from adsorption to capillary condensation for carbon modified TNTs; (b) adsorption isotherms of phenanthrene using various materials. Reproduced from ref. ⁶⁹ with permission from American Chemical Society, Copyright 2016.

7.4.2 Photocatalytic Degradation of Organic Pollutants in Waters using TNTs and Modified TNTs

To degrade and even mineralize organic pollutants, great efforts have been made to promote the photocatalytic activity of TNTs. As a one-dimensional (1D) tubular nanomaterial, TNTs derived from TiO_2 have great advantages when applied as photocatalyst for organics removal: (1) the uniform tubular structure with large specific area is a good skeleton to support various photoactive materials; (2) the 1D tubular structure exhibits high nano-confinement effects, which is beneficial to the transfer of

photoexcited electrons, and thus high photoelectric conversion rates can be obtained; (3) the structure and composition of titanate can be controlled by hydrothermal treatment conditions in the preparation process, and different TiO_2 crystalline phases can be transformed *in situ* from titanate, (4) the excellent ion-exchange property facilitates the procedure for doping or deposition of metals, (5) the good stability in aqueous solution can achieve easy separation after application. In addition, composite materials based on TNTs with integrated adsorptive performance and photocatalytic activity are also experiencing a boom in development for organics removal through pre-accumulation of organics and subsequent photocatalytic degradation. We propose that these materials are expected to show the following synergistic effects on organics removal: (1) the high adsorption capacity of non-titanate components (e.g., AC and ACF) can concentrate the target organic pollutants onto the surface of the composite material, facilitating the subsequent photocatalytic degradation; (2) the high photocatalytic activity of modified TNTs leads to effective degradation of the adsorbed pollutants, which also regenerates the spent material; (3) the doped/deposited components on TNTs can enhance both the adsorption capacity and kinetics of TNTs; and (4) the doped/deposited components may serve as electron shuttles and prevent the recombination of excited holes and electrons, and thus enhance the photodegradation efficiency.⁶⁹

Methods used to modify TNTs to promote the photocatalytic activity and applied for organic pollutant degradation are summarized in detail below.

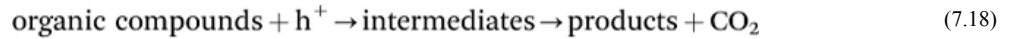
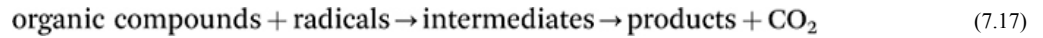
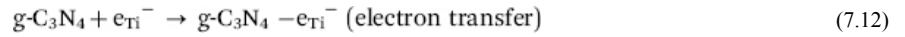
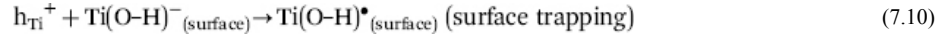
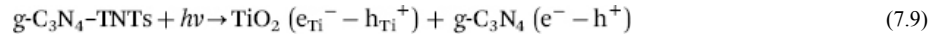
i) **Calcination:** Calcination can induce transformation of titanate to TiO_2 phases (anatase and rutile), thus promoting *in situ* heterojunction architectures of titanate and TiO_2 .^{14,65,75–77} Generally, the calcination temperature and sodium content greatly affect the crystalline phases of the formed titanium material, and thus the photocatalytic activity.^{65,67,77} Generally, H-TNTs tend to form TiO_2 phases after calcination, while Na-TNTs (sodium trititanate) are inclined to form hexa-titanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$).^{65,67,75,77} Lee *et al.* reported that the photocatalytic activity of as-synthesized and heat-treated TNTs follows the order: M-TNT (medium Na content, 1.21 wt% Na) > L-TNT (low Na content, 0 wt% Na) > H-TNT (high Na content, 7.23 wt% Na) and the reaction rate constants of M-TNT are comparable to that of P25 TiO_2 (especially at 200 °C) before 600 °C (Figure 7.12).⁶⁷

ii) **Metal doping:** Various metals (e.g., Fe, Co, Pt, *etc.*) and non-metallic elements (e.g., C, N, B, *etc.*) have been applied as doping agents to promote the photocatalytic activity of TNTs.^{78–82} Zaki and Lee synthesized a series of metal-doped sodium TNTs after ion-exchange of various cations including Mg^{2+} , Ca^{2+} , Zn^{2+} , K^+ , Cr^{3+} , Ce^{3+} , Ce^{4+} , Mo^{5+} , and La^{3+} .⁸³ They found that the prepared metal-doped materials had E_g values in the range 2.02–2.8 eV, which facilitated their application as photocatalysts under the irradiation of solar or visible light to degrade organic compounds. Peng's group prepared Fe-incorporated hydrogen nanotubes ($\text{H}_2\text{Ti}_3\text{O}_7$) and found the new material had a greatly improved photon absorption efficiency in the visible region compared with pure H-TNTs.^{84,85} DFT calculations based on first principles further revealed that a stable structure forms after Fe-doping of the $\text{H}_2\text{Ti}_3\text{O}_7$ structure, with the formula $\text{FeHTi}_6\text{O}_{14}$. The intercalated Fe atoms in the interlayers of $\text{FeHTi}_6\text{O}_{14}$ form a 1D Fe chain along the [010] plane, and the overlapping Fe-3d_{z^2} orbitals along the channel result in a delocalized 1D band below the Fermi level extending the absorption edge of $\text{FeHTi}_6\text{O}_{14}$ well into the visible region (Figure 7.13).^{84,85}

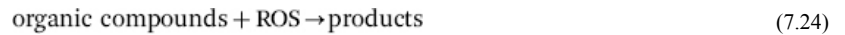
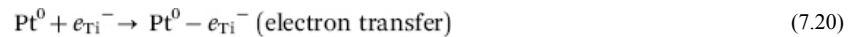
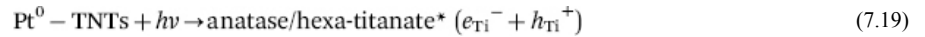
iii) **Architecture of heterojunction:** Semiconductor composition to fabricate heterojunctions efficiently promotes the photocatalytic property of each phase. For photocatalysts with heterojunction structures, photoexcited electrons (e^-) on the conduction band (CB) or holes (h^+) on the valence band (VB) of the composite semiconductor migrate to the CB or VB of titanate due to their band offsets, thus inhibiting recombination of electron-hole pairs and an enhanced photocatalytic activity. Recently, we have clearly illustrated the photoexcited electron transfer chain on titanium materials. Specifically, “hot spots” at rutile–anatase–titanate interfaces form and then facilitate electron transfer (Figure 7.14a). Firstly, the small rutile crystallites act as an antenna to accept the photons under light irradiation, and rapid excited electron transfer occurs to form a donor level of the rutile phase to lower

the energy of the anatase lattice trapping sites, resulting in a more stable charge separation. More efficient and stable electron transfer exists at the rutile–anatase–titanate interfaces, because a subsequent transfer further moves electrons from the anatase trapping sites to the titanate trapping sites, and then to the surface trapping sites. In the meantime, transfer of the photogenerated electrons also retards recombination with holes. Therefore, the stabilization of charge separation is a rutile-originating and third-order subsequent transfer process, which greatly promotes the photocatalytic activity.

The developed titanium photocatalyst with rutile–anatase–titanate interfaces can further composite with other semiconductors (e.g., g-C₃N₄) to develop new visible light-driven photocatalysts. Figure 7.14b describes the mechanism of the enhanced photocatalytic activity of two-dimensional/one-dimensional (2D/1D) g-C₃N₄–TNTs heterojunctions.¹⁴ The architecture of “rutile–anatase–titanate” and g-C₃N₄ enhances the donor–acceptor charge carrier separation and transfer mechanism of the direct Z-scheme but not the type I heterojunction. Upon solar irradiation, the titanium “hot spots” interface and g-C₃N₄ generate a conduction band (e[−], electrons) and remain as a valence band (h⁺, holes) (eqn (7.9)). The two types of phases have different roles: 1) the titanium “hot spots” interface has a high number of photoactive sites, and some of the generated electrons and holes are trapped at the surface of the material; moreover, in the presence of water and oxygen molecules, surface trapping of holes (Ti(O–H)[•] and [•]O[−]) also occurs (eqn (7.10) and (7.11)).^{86,87} 2) g-C₃N₄ can utilize visible light for photocatalytic reactions and production [•]O₂[−] at the CB (eqn (7.13)). More importantly, the heterojunction structure of g-C₃N₄–TNTs leads to an energy level difference between the titanium materials and g-C₃N₄, thus g-C₃N₄ acts as a new electron acceptor to transfer the photo-excited electrons *via* the titanium “hot spots” (eqn (7.12)). In the meantime, oxidation of H₂O or OH[−] occurs at the VB of the titanium materials to produce [•]OH (eqn (7.14) and (7.15)). In addition, [•]OH is also transformed from [•]O₂[−] according to eqn (7.16). The produced radicals and h⁺ are responsible for organic compound degradation (eqn (7.17) and (7.18)).



iv) **Noble metal deposition:** Deposited noble metals (e.g., Pt, Ag and Au) act as photoexcited electron mediators due to their good electroconductivity, thus retarding the recombination of electron–hole pairs.^{75,88,89} Figure 7.15 shows the role of deposited Pt⁰ in the enhanced photocatalytic activity of TNTs.⁷⁵ Under solar irradiation, the TNTs (hexa-titanate) generate electrons (e[−]) in the CB and holes (h⁺) in the VB (eqn (7.19)). However, the pristine titanate is not photoactive under visible light due to its relatively large E_g value. The electrons are immediately transferred to the deposited Pt⁰ after excitation (eqn (7.20)), thus inhibiting electron–hole recombination. The migrated electrons are then captured by electron acceptors such as O₂ to form superoxide radicals ([•]O₂[−]) (eqn (7.21)). The holes oxidize water molecules and oxygen into reactive oxygen species (ROS) such as [•]OH and H₂O₂ (eqn (7.22) and (7.23)). These ROS are responsible for the degradation of organic compounds (eqn (7.24)). Meanwhile, the organic compounds are also directly attacked by holes to produce degraded intermediates and products *via* eqn (7.25).



v) **Carbon material compositing:** The grafting and compositing of carbon materials on titanate promotes the removal of organic pollutants, and generally plays two roles: (1) carbon materials can pre-adsorb target organic pollutants onto TNTs to facilitate the subsequent degradation, and (2) carbon materials can transfer photoexcited electrons to inhibit the rapid recombination of electron-hole pairs.^{69,70,90–92} AC, ACF and carbon nanotubes (CNTs) are usually selected as the skeleton materials to support TNTs, while graphene and carbon quantum dots (CQDs) are often applied as grafting components in small fractions. For example, the photocatalytic performance of CQD-modified potassium titanate nanotubes (CQDs– $K_2Ti_6O_{13}$) composites was remarkably enhanced compared with the neat and calcined $K_2Ti_6O_{13}$ nanotubes.⁹² CQDs– $K_2Ti_6O_{13}$ could efficiently degrade amoxicillin under the irradiation of visible light and a broad spectrum of light sources (365–630 nm). The narrowed E_g value and transfer of photo-excited electrons by the CQDs inhibited the immediate combination of electron-hole pairs, thus promoting photocatalytic activity.

vi) **Surface oxidation:** Surface oxidation of titanate by chemical oxidants like H_2O_2 changes the composition of titanate and leads to surface defects, thus promoting photocatalytic activity.^{93–95} After treatment using H_2O_2 , the peroxo titanium functional group (Ti–O–O) is formed between the interlayers of the titanate crystal lattice ($[TiO_6]$ octahedral skeleton), resulting in an increased interlayer distance from 7.5 to 10.02 Å. The formation of the peroxo functional groups reduces the electron density adjacent to the Ti atom, raising the valence band to 1.35 eV and forming a band gap of 2.50 eV, which is much lower than that of TNTs (~ 3.2 eV in this work). Thus, the peroxo-functionalized TNTs more efficiently utilized visible light for organic pollutant degradation.⁹³

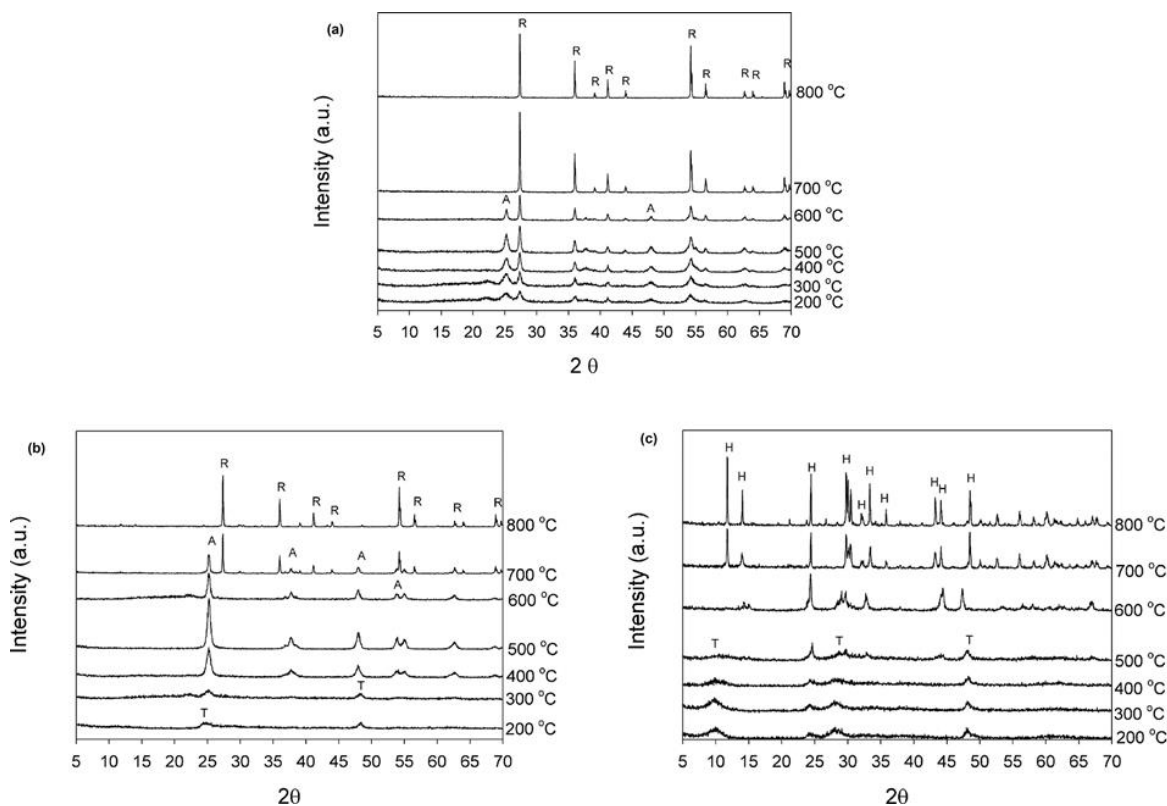


Figure 7.12 XRD patterns of heat-treated TNTs ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$) materials: (a) L-TNT (0 wt% Na), (b) M-TNT (1.21 wt% Na), and (c) H-TNT (7.23 wt% Na). Legend: H = sodium hexatitanate, T = sodium trititanate, A = anatase, and R = rutile. Reproduced/Adapted from ref. ⁷⁷ with permission from Elsevier, Copyright 2007.

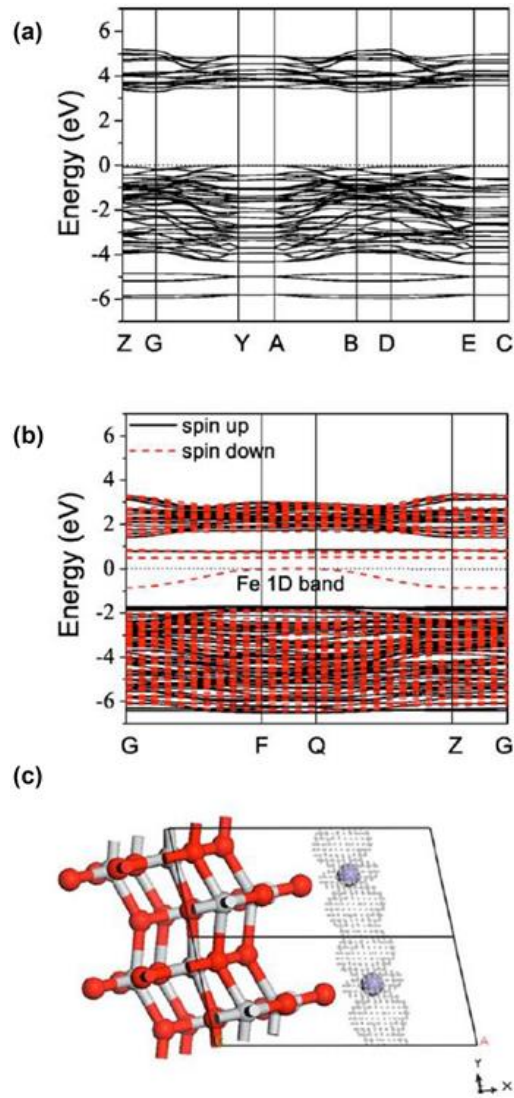


Figure 7.13 Electronic band structure of (a) $\text{H}_2\text{Ti}_3\text{O}_7$ and (b) $\text{HFeTi}_6\text{O}_{14}$. (c) Real-space orbital map of the 1D Fe band of (b) viewing along the $[100]$ plane. The d_{z^2} orbitals of Fe overlap along the $[010]$ plane. Reproduced from ref. ⁹⁵ with permission from American Physical Society, Copyright 2006.

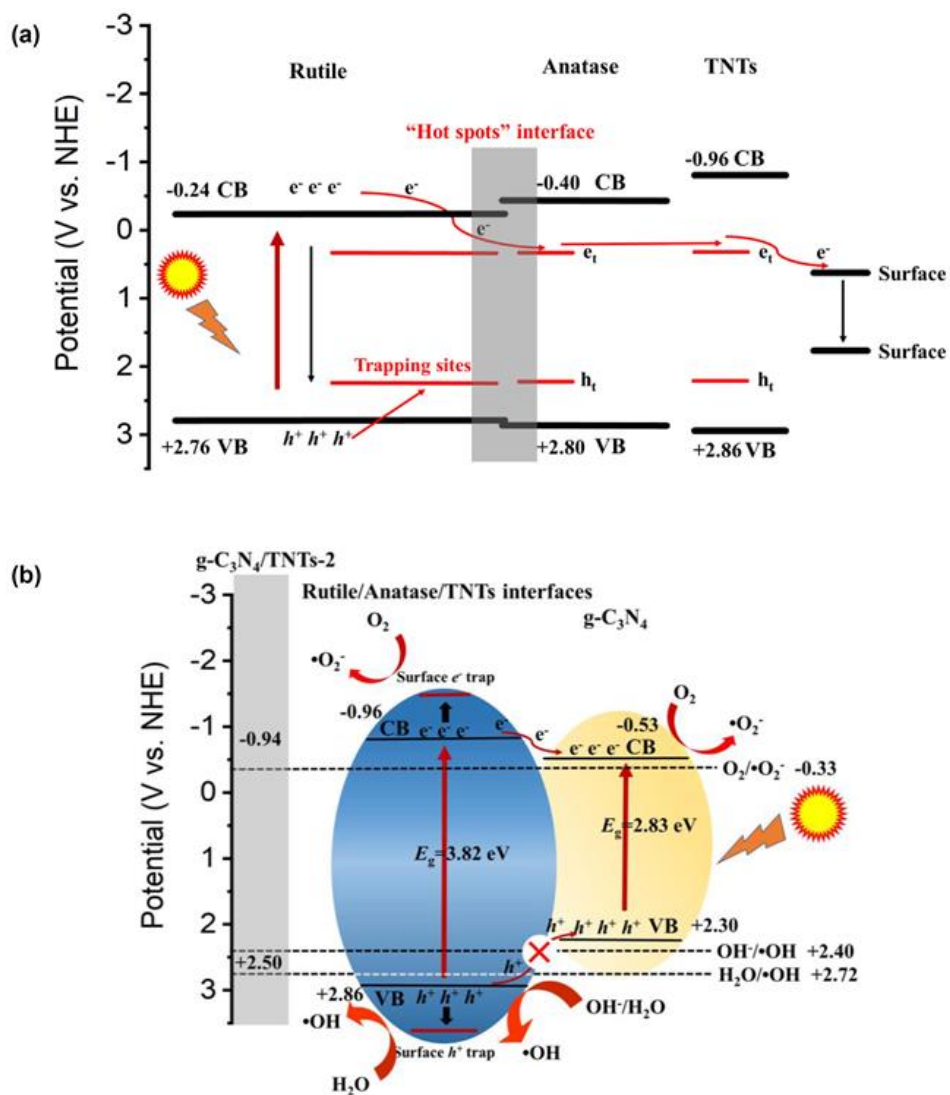
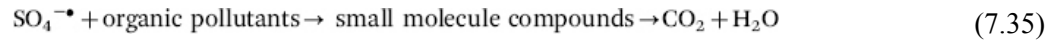
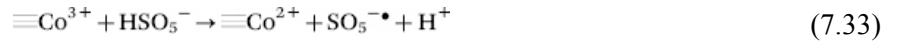
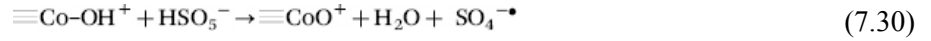


Figure 7.14 (a) Schematic illustration of mechanism of catalytic “hot spots” at the rutile–anatase–titanate interface and (b) heterojunction structure of 2D/1D g-C₃N₄–TNTs. Reproduced from ref. ¹⁴ with permission from Elsevier, Copyright 2021.

When transition metal–TNTs composite materials are applied for PMS/PDS activation and organic degradation, the transition metal (*e.g.*, Co(ii)) component is the primary active site (Figure 7.16b), and reactions for PMS activation and organic compound degradation include:¹⁵



where “ $\equiv\text{TiOH}^-$ ” represents TNTs with surface –OH groups; “ $\text{Ti}\equiv(\text{OH})\text{Co}^+$ ” and “ $\equiv\text{Co-OH}^+$ ” represent material-bound Co(ii) species (Co linked with [Ti–O]); “ $\equiv\text{CoO}^+$ ”, “ $\equiv\text{Co}^{3+}$ ” and “ $\equiv\text{Co}^{2+}$ ” are Co species bound with titanate.

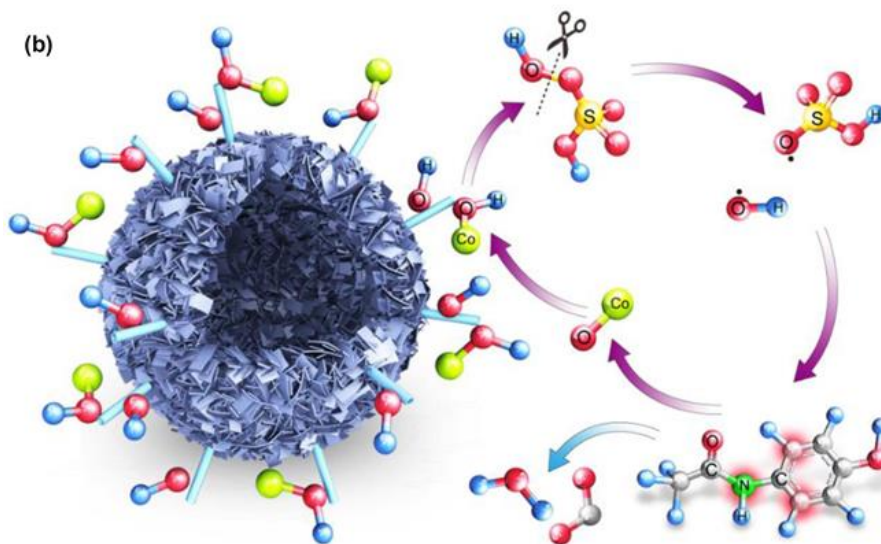
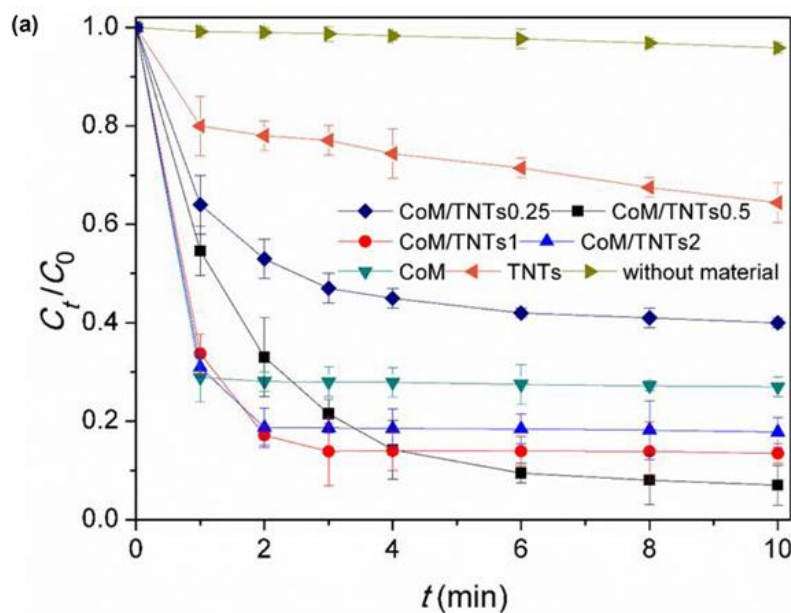


Figure 7.16 (a) Acetaminophen degradation in various catalytic PMS systems (experimental conditions: initial acetaminophen concentration = 50 μM , PMS dosage = 0.2 mM, material dosage = 0.1 g L^{-1} , and pH = 5.0); (b) schematic diagram of PMS activation and organic pollutant (acetaminophen as a model) degradation using $\text{Co}(\text{OH})_2$ hollow microsphere-supported TNT composites. Reproduced from ref. ¹⁵ with permission from Elsevier, Copyright 2020.

A class of $\text{Co}(\text{OH})_2$ hollow microsphere-supported TNT composites (CoM–TNTs) were synthesized and exhibited enhanced acetaminophen (ACE) degradation efficiency after PMS activation through heterogeneous catalysis (Figure 7.16).¹⁵ The role of the TNT fraction in the composite material for PMS activation includes: (1) TNTs have abundant $-\text{OH}$ groups on the surface, so a large number of material-bound $\square\text{Co}-\text{OH}$ complexes (linked with $[\text{Ti}-\text{O}]$) are formed during reaction, leading to efficient PMS activation; (2) TNTs with a good ion-exchange properties retain the formed cobalt cations (*e.g.*, CoO^+ ,

Co³⁺ and Co²⁺), thus, promoting the Co-induced PMS catalysis cycle (eqn (7.28)–(7.34)). Dionysiou and his group of researchers found that the application of TiO₂ as a skeleton to support cobalt-based materials promotes the formation of Co–OH complexes, because surface –OH groups are easily formed due to the ability of TiO₂ to dissociate H₂O. Therefore, TiO₂-supported cobalt materials show a high reactivity for PMS activation and organic contaminant degradation.¹⁰³ Compared with TiO₂, the nanoscale TNTs with abundant –OH hybridized with Co(OH)₂ significantly promote the formation of Co–OH complexes and subsequent PMS activation for organic compound degradation.⁶⁴ Ma's group also reported a titanate nanotube-supported magnetic CoFe₂O₄ nanoparticle material (CoFe₂O₄–TNTs), which could efficiently activate PMS for the degradation of organic pollutants. The CoFe₂O₄–TNTs realized higher total organic carbon (TOC) removal but less cobalt leaching compared with the neat CoFe₂O₄.¹⁰⁴

An amorphous MnO₂ nanoparticle *in situ*-anchored onto titanate nanotubes composite material (AMnTi) with a chemical composition of (0.3MnO₂) · (Na_{1.22}H_{0.78}Ti₃O₇) was developed for PMS activation and carbamazepine (CBZ) degradation.¹⁶ It was indicated that AMnTi had a three- and 21-fold higher CBZ degradation rate compared with the pristine TNTs and MnO₂, respectively. Efficient charge transfer and catalytic activation through Mn–O–Ti linkages occurred, and a Mn–Ti cycle that mediated the catalytic PMS activation was the key mechanism.

7.4.4 Co-removal of Heavy Metals and Organic Pollutants in Waters Using TNTs and Modified TNTs

TNTs and modified TNTs can also be applied to solve the problems of combined pollution with coexisting heavy metals and organic pollutants in wastewater. On one hand, TNTs with excellent ion-exchange properties can simultaneously adsorb metal cations and cationic organics. For example, TNTs could achieve co-adsorption of Cu and CIP, with large adsorption capacities of 234.5 μmol g^{−1} for Cu(II) and 237.0 μmol g^{−1} for CIP at pH 4 in a binary system.¹⁰⁵ The Cu(II)–CIP complexes dominate the adsorption capacity and mechanism. It is interesting that adsorption of CIP was promoted by high concentration of Cu(II) at pH 3–8 due to formation of abundant Cu(CIP[±])²⁺, while inhibited by low concentrations of Cu(II) because of competitive adsorption. In addition, the adsorption affinity of CIP species to TNTs was ranked as: Cu(CIP[±])²⁺ > CIP⁺ > CIP[±] > Cu(CIP[±])₂⁺ > Cu(CIP[−] · CIP[±])⁺ > CIP[−].¹⁰⁵

On the other hand, TNTs derived composite materials have been developed to simultaneously remove heavy metals and organic pollutants, and the material design concepts include: (1) the materials have high adsorption capacities for both heavy metals (especially metal molecules and anions) and organics, (2) the materials can achieve adsorptive removal of heavy metals and photocatalytic degradation of organics, and (3) the materials can reduce heavy metal toxicity by means of species transformation through photocatalysis, and can degrade organics at the same time. Simultaneous adsorption of U(VI) and 2-chlorophenol (2-CP) using TNTs–ACF was achieved in a binary system.⁷² The adsorption mechanism of U(VI) was ion-exchange at the –O[−] functional sites in the interlayers of TNTs, while 2-CP was adsorbed *via* hydrophobic interactions with ACF and capillary condensation. Moreover, the adsorption synergy of U(VI) and 2-CP in the binary system led to formation of complexes between U(VI) ions and phenolic groups of 2-CP through cation–π interactions, which promoted the respective contaminant adsorption onto TNTs–ACF.⁷² A series of TiO₂–TNTs composites were prepared through initial hydrothermal treatment and subsequent wet chemical reaction, and the materials simultaneously removed heavy metal and organic pollutants *via* combined adsorption and photocatalysis.^{24,106} The optimum TiO₂–TNTs composite (TiNTs-120-2) could effectively remove four coexisting contaminants from solution, with high removal efficiencies of 89.8% for methyl orange (MO), 96.5% for MB, 93.5%

for Pb^{2+} and 95.5% for phenol, respectively.¹⁰⁶ In addition, the TiO_2 -TNTs composite also exhibited both good adsorptive performance for $\text{Cu}(\text{II})$ and high photocatalytic activity for phenanthrene degradation (Figure 7.17). The maximum $\text{Cu}(\text{II})$ Langmuir adsorption capacity on TiO_2 -TNTs reached 115.0 mg g^{-1} at pH 5, and >95% of phenanthrene was degraded within 4 h under UV light (Figure 7.17a). More importantly, the coexistence of $\text{Cu}(\text{II})$ in the water system promoted the photocatalytic degradation of phenanthrene, as the $\text{Cu}(\text{II})$ incorporated in the lattice of titanate trapped photoexcited electrons and thus inhibited electron-hole recombination (Figure 7.17b).⁷⁵

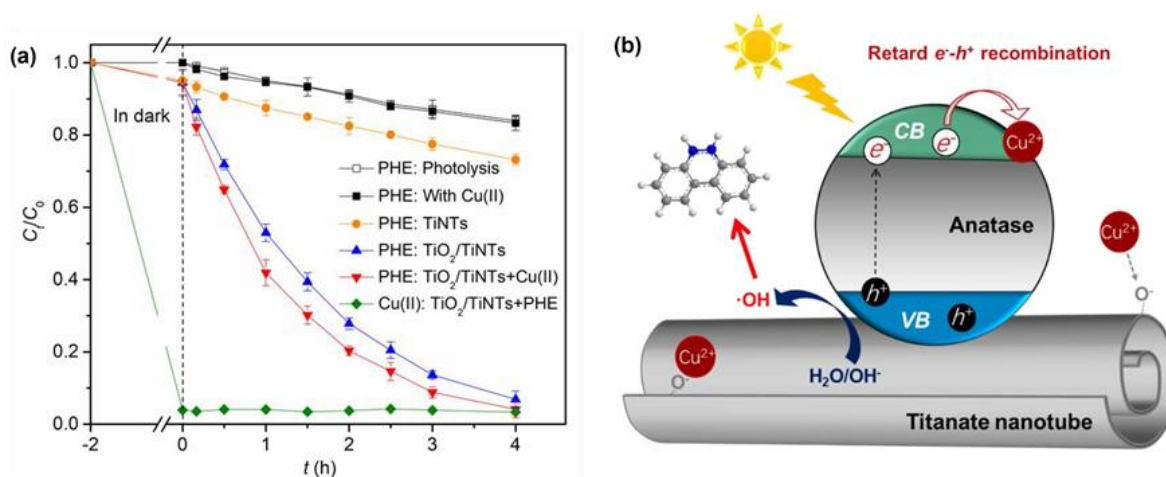


Figure 7.17 (a) Schematic illustration of $\text{Cu}(\text{II})$ adsorption and the synergistic effect on enhanced photocatalytic degradation of phenanthrene using TiO_2 -TNTs; (b) simultaneous adsorptive removal of $\text{Cu}(\text{II})$ and photocatalysis of phenanthrene (PHE) also using TiO_2 -TNTs. (Initial $\text{Cu}(\text{II})$ concentration = 20 mg L^{-1} , phenanthrene = $200 \text{ } \mu\text{g L}^{-1}$, TiO_2 -TNTs dosage = 0.5 g L^{-1} , pH = 5, temperature = 25°C , UV light irradiation.) Reproduced from ref. ²⁴ with permission from Elsevier, Copyright 2018.

7.5 Implications of TNTs in Aqueous Systems

TiO_2 nanoparticles are widely used in industry as anti-scratch additives, photocatalysts, color additives, and sun screens, so a large amount of TiO_2 NPs are released into the aquatic environment.^{107,108} With the increasing application of TNTs, it is inevitable that these nanomaterials will be released into the environment particularly *via* ground and surface water. Moreover, it is also believed that such possible contamination could pose toxicological risks to the ecosystem and public health,^{109–111} or influence the bioavailability of other toxic pollutants.¹¹² During both storage and later transportation, aggregation and sedimentation of nanomaterials occur. The physico-chemical properties (*i.e.*, crystallinity, microstructure, surface area, chemical composition) of the nanomaterials will affect their aggregation and sedimentation. Therefore, study of the environmental behavior (aggregation and sedimentation) in aqueous solution of TNTs is very important. However, unlike the precursor TiO_2 nanoparticles, there are quite a few researchers studying the environmental behavior of TNTs in aqueous system. In addition, until now, there has been no study related to the toxicity of TNTs.

Only one research study has focused on the aggregation and sedimentation of TNTs under typical water chemistry conditions (pH, ionic strength and natural organic matters (NOMs) in comparison with TiO_2 NPs.¹⁷ It was indicated that small-sized TiO_2 aggregate particles ($< 1000 \text{ nm}$) do not settle in solution, however, larger particle sizes ($>1000 \text{ nm}$) result in poor stability for TNTs (Figure 7.18a). In

addition, the sedimentation rates of TNTs (5.0×10^{-4} to $1.48 \times 10^{-2} \text{ min}^{-1}$) were much higher than that of TiO_2 NPs (ranging from 5.0×10^{-5} to $1.78 \times 10^{-3} \text{ min}^{-1}$) (Figure 7.18b), and other conventional nanoparticles, such as ZnO and CeO_2 . Moreover, large particle sizes contribute to a high sedimentation rate as shown in Figure 7.18.

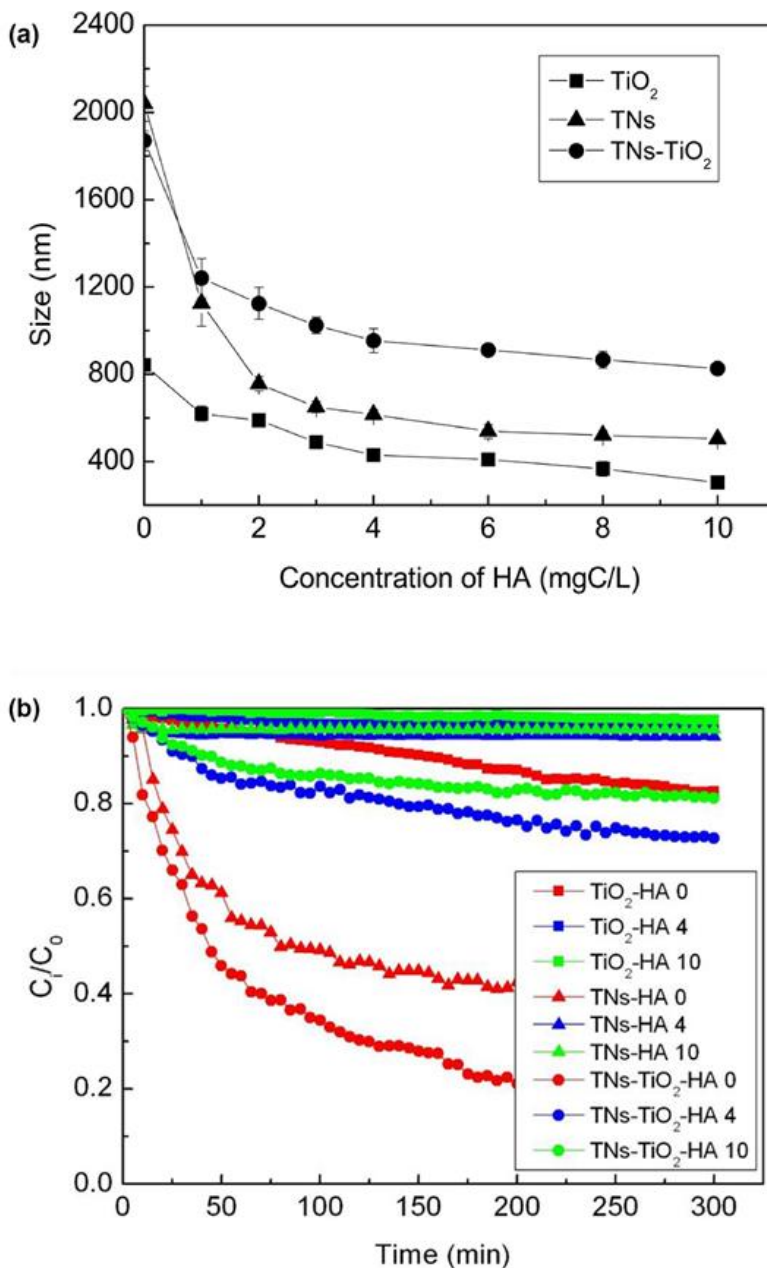


Figure 7.18 (a) Effect of HA on the average Z-size of different nanomaterials in the presence of 10 mM Na^+ ; (b) sedimentation kinetics of the nanomaterials as a function of HA. Reproduced from ref. 17 with permission from Elsevier, Copyright 2021.

These differences are highly related to the nanostructure and chemical composition of the materials: the spherical-particle structure of TiO_2 leads to the formation of small aggregate sizes, while the tubular structure of TNTs with high surface area and excellent ion-exchange properties result in larger sizes

(Figure 7.19a). Moreover, solution pH, ionic strength and HA had a major influence on the aggregation and sedimentation of the nanomaterials. When solution pH was close to pH_{PZC} , the nanomaterials have a large, aggregated size and high sedimentation rate. The presence of inorganic ions especially Ca^{2+} promotes aggregation, and this effect is more significant for TNTs because of their negatively charged surfaces (Figure 7.19b). NOMs such as HA coated on the nanomaterials effectively inhibits aggregation and reduces the size of the aggregated particles (Figure 7.19c). In addition, a stronger affinity of HA to TNTs results in the enhancement of HA density on the material. When the nanomaterials are exposed to both Ca^{2+} and HA conditions, the following two effects are observed: (1) energy barriers and steric hindrance caused by HA lead to inhibition of aggregation; (2) electrical double layer compression and an ion bridge effect between nanomaterials coated with HA by Ca^{2+} resulted in the promotion of aggregation (Figure 7.19d).

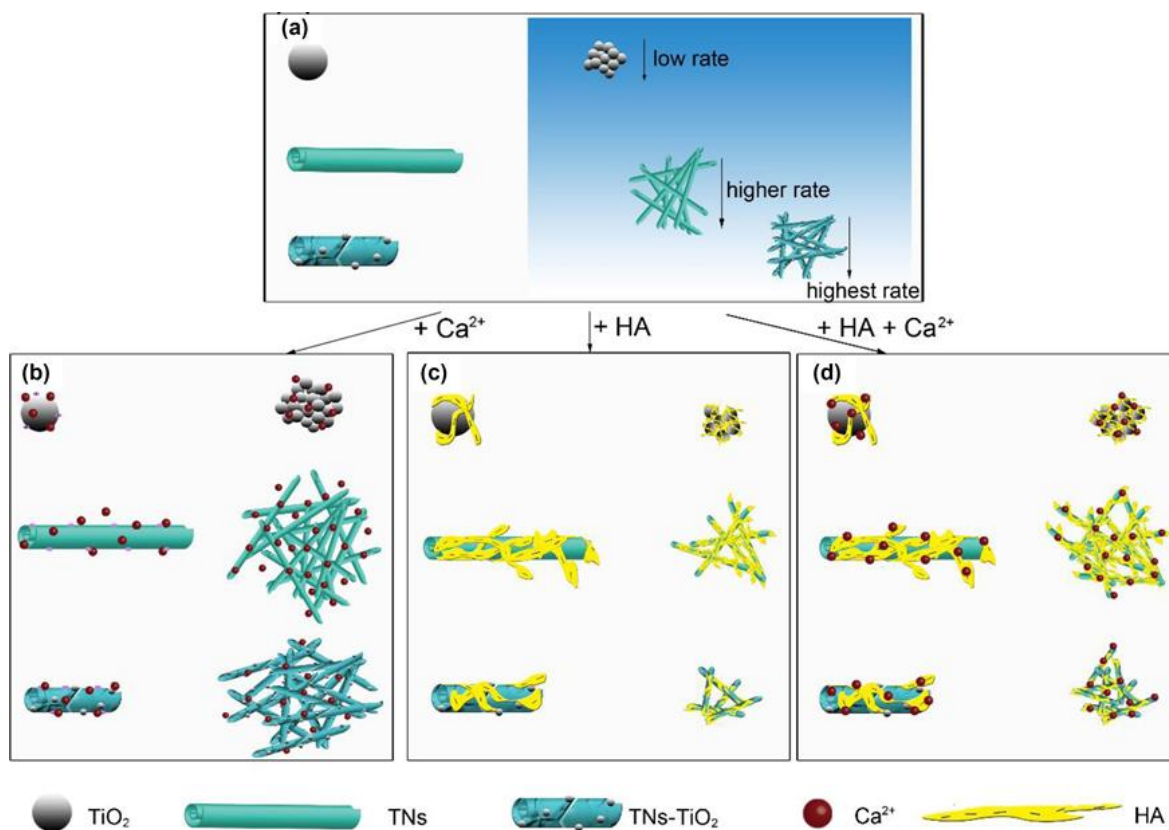


Figure 7.19 Schematic of interactions between inorganic ions, HA and titanium nanomaterials. (a) Structure of nanomaterials, (b) interaction with Ca^{2+} , (c) interaction with HA, (d) interaction with Ca^{2+} and HA. Reproduced from ref. ¹⁷ with permission from Elsevier, Copyright 2013.

7.6 Conclusions and Outlook

In conclusion, TNTs with specific physicochemical properties have been widely applied in the environmental remediation and clean-up areas, which are summarized as:

- (1) TNTs show uniform tubular structure with open-ended and multi-layered nanotubes, which have large specific surface area and low point of zero charge.

(2) Ion-exchange is the primary property for TNTs, so TNTs are good adsorbents for metal cations. The adsorption behaviors and mechanisms are highly related to the species of metals in water. Ion-exchange, electrostatic attraction, co-precipitation and surface complexation are found to be the four primary adsorption mechanisms for metal adsorption by TNTs.

(3) The photocatalytic activity of pure TNTs is weak due to the rapid recombination of photoexcited hole–electron pairs, as well as the wide band gap energy of ~ 3.4 eV. Various techniques including calcination, metal doping, heterojunction architecture, noble metal deposition, carbon material compositing and surface oxidation have been applied to modify TNTs to promote photocatalytic properties.

(4) TNTs are ideal skeletons to support transition metal materials for composite material fabrication, which efficiently activates PMS/PS to produce $\text{SO}_4^{\cdot-}$ for organic pollutant degradation. The role of TNTs is: a) the tubular structure with large surface area stabilizes the coated metal material for increased interfacial reactions, and b) TNTs with abundant $-\text{OH}$ groups facilitate the formation of metal–OH complexes, which is the key species for PMS/PS activation.

(5) TNTs with tubular structures and high length : diameter ratios tend to form aggregates of larger sizes, and thus exhibit high sedimentation rates in solution. The large hydraulic size and high sedimentation rate are important for the separation of materials after application.

In the future, the following knowledge gaps and further research needs should be considered:

(1) For metal adsorption, clear adsorption mechanisms for different metal species (*i.e.* cations, anions and molecules) are needed, and quantitative structure–activity relationship (QSAR) between metal species and adsorption capacity on TNTs should be explored.

(2) For adsorption of metal cations *via* ion-exchange, the order of cations, *i.e.* affinity to titanate, is to be investigated. Moreover, the primary parameters of cations in relation to their adsorption capacity using TNTs also need to be explored.

(3) For photocatalysis, how to design photocatalyst using TNTs as the skeleton in order to integrate the advantages of specific structure and composition is an important topic. In addition, QSAR on the composition of TNTs (*e.g.*, the content of Na, crystal lattice composition and interlayered ions) and photocatalytic activity should be clearly studied.

(4) Besides PMS/PS activation for $\text{SO}_4^{\cdot-}$ production, there is no information on the application of TNTs for the activation of other oxidants (such as H_2O_2 and peroxy acids). The activation and radical attack mechanisms should also be illustrated.

(5) Reactors based on adsorption and photocatalysis for the practical application of TNTs should be developed, and separation methods should be proposed for the reuse of TNTs.

(6) Information on the toxicity of TNTs is urgently needed, including the toxicity of specific microorganisms and organisms, population communities, important biogeochemical cycles, and even eco-systems.

Abbreviations

2D/1D	two-dimensional/one-dimensional
AC	activated carbon
ACF	activated carbon fiber
AOPs	advanced oxidation processes
CB	conduction band
CNTs	carbon nanotubes
E_g	band gap energy

FeS	iron monosulfide
HRTEM	high-resolution TEM
HSAB	hard–soft acid–base
MB	methylene blue
MO	methyl orange
NPs	nanoparticles
PAHs	polycyclic aromatic hydrocarbons
PDS	peroxydisulfate
PFAS	per- and polyfluoroalkyl substances
PMS	peroxymonosulfate
PPCPs	pharmaceutical and personal care products
TEM	transmission electron microscopy
TNTs	titanate nanotubes
UV	ultraviolet
VB	valence band

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Chapter 8

Control of Disinfection Byproduct (DBP) Formation by Advanced Oxidation Processes (AOPs)

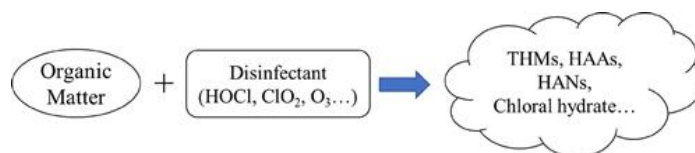
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8.1 Introduction

Water-borne diseases associated with poor water sanitation have posed significant health risks to humans for a long history. Starting in the early 20th century, drinking water disinfection during water treatment aiming at deactivating microbial pathogens has become a common practice especially in developed countries. To date, the most commonly used disinfectants or approaches are chlorine, chloramine, chlorine dioxide, ozone, and ultraviolet (UV).¹ Chlorination, as one of the most widely used approaches, has been considered as one of the greatest achievements in public health before the development of vaccines and antibiotics.² As an unintended consequence of disinfection, the formation of disinfection byproducts (DBPs), however, has raised significant health concerns. Over 600 DBPs have been identified since the 1970s, and most are low molecular weight volatile or semi-volatile compounds.³ DBPs are formed during the reaction (oxidation, addition, and substitution) of disinfectants with organic matter (either natural or anthropogenic) in water, as shown in [Scheme 8.1](#). Previous studies have reported that most of these DBPs are potentially teratogenic, carcinogenic, and mutagenic.³



Scheme 8.1 Illustration of DBP formation. THMs: trihalomethanes; HAAs: haloacetic acids; HANs: haloacetonitriles.

In general, DBP precursors can be grouped into two categories, *i.e.*, halides and organics. Halides are mainly bromide and iodide, while organics include natural organic matter (NOM) and emerging contaminants (ECs), among others. The increase in anthropogenic occurrence of these precursors has been the major reason for the regulatory noncompliance of DBPs in finished water. Although bromine- or iodine-related oxidants (*e.g.*, HOBr or HOI) are not used as disinfectants, bromide and iodide ions can be readily oxidized by HOCl forming HOBr and HOI, which can further react with organic precursors to form brominated and iodinated DBPs. Due to the significantly larger molecular weights of bromide (79.90 g mol⁻¹) and iodide (126.90 g mol⁻¹) than that of chloride (35.45 g mol⁻¹), even slight incorporation of bromide and/or iodide can substantially increase the overall mass concentration of DBPs. In addition, brominated and iodinated DBPs have been widely reported to have significantly higher mammalian cell cytotoxicity and genotoxicity than

their chlorinated analogs.⁴ Therefore, the removal of bromide and iodide before chlorination has become an important task to decrease the formation of DBPs.

For organic precursors, despite most studies focusing on NOM, ECs such as pesticides, dyes, antibiotics, and microorganism-associated compounds (*e.g.*, algal toxins during algal blooms)^{2,5,6} have received more and more attention in recent years because of their increasing abundance and diversity in drinking water sources. In addition to their own risks, they can serve as emerging DBP precursors for the generation of a wide range of DBPs, including both regulated and unregulated species. Therefore, their removal is a critical task in water treatment.

Advanced oxidation processes (AOPs) are a general term for reactions that form radicals (*e.g.*, hydroxyl or sulfate radicals) as the major reactive oxygen species (ROS) for pollutant destruction. Applications of AOPs have grown rapidly in recent years with a large selection of oxidants, such as H₂O₂, O₃, peroxymonosulfate (PMS), and peroxydisulfate (PDS). As most of these oxidants are not reactive enough to oxidize organics on their own, different activation approaches have been introduced to activate the oxidants for the formation of radicals, mainly including energy input and catalytic approaches. Although AOPs have been extensively reviewed in recent years,^{7–13} there is a lack of review on their applications to DBP control.

As discussed in detail in Section 8.2.2, DBP control is usually achieved by two major approaches, the direct removal of DBPs after their formation and the removal of DBP precursors before the disinfection process. Some of the most common techniques are reverse osmosis, nanofiltration, electrolysis, coagulation, and carbon and hydrous oxides adsorption, most of which have been reviewed previously.¹⁴ However, those related to AOPs have not been comprehensively reviewed, especially for direct DBP oxidation and the removal of halides and emerging organic precursors. Given the rapid advance of AOPs in recent years regarding the types of oxidants, oxidant activation approaches, and reaction mechanisms, such a review on using AOPs for DBP control purposes becomes very desirable. This chapter intends to fill the gap and document the most recent advances on such topics.

8.2 Brief Introduction to DBPs

8.2.1 DBPs and Regulations

DBPs are categorized into different groups based on their physicochemical properties, such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). Generally, different disinfection approaches and/or precursors can lead to different DBPs, as shown in Table 8.1.¹ Newly identified precursors such as ECs have been reported to potentially alter the DBP speciation. For example, studies reported that the disinfection of waters impacted by the effluent of wastewater treatment plants (WWTPs) or algal blooms tends to form less THMs but more nitrogen-based DBPs due to the lower aromaticity and higher organic nitrogen content in such waters.^{15,16}

Table 8.1 Groups of DBPs formed from different disinfectants.

Class of DBPs	Chlorine	Ozone	ClO ₂	Chloramine
Trihalomethanes (THMs)	×	×		×
Haloacetic acids (HAAs)	×			×
Haloacetonitriles (HANs)	×	×		
Other haloalkanes	×			
Haloalkenes	×			
Haloaromatic acids	×			
Halodicarboxylic acids	×			×
Halotricarboxylic acids	×			
Mutagen X (MX) and analogs	×		×	×
Haloketones	×	×	×	
Haloaldehyde	×			×

Haloalcohols	×			×
Phenols	×	×		
Halonitromethane	×			
Inorganic compounds		×	×	
Aliphatic aldehyde	×	×	×	
Ketones (aliphatic and aromatic)	×	×	×	
Carboxylic acids	×	×	×	
Aromatic acids	×	×	×	
Aldo and ketoacids		×	×	
Hydroxy acids	×	×		
Others	×	×	×	×

The US EPA has issued regulations on the occurrence of DBPs to reduce their risk to consumers. The THM group contains chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (commonly called THM4). It was first regulated at a maximum annual average level of 100 $\mu\text{g L}^{-1}$ in 1978 and then lowered to 60 $\mu\text{g L}^{-1}$ in 1998 during the issuance of the Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) Rule. This rule also expanded to other groups, including five HAAs (HAA5) (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA)), at 80 $\mu\text{g L}^{-1}$, chlorite at 1.0 mg L^{-1} , and bromate at 10 $\mu\text{g L}^{-1}$. The Stage 2 D/DBP Rule issued in 2006 did not change the standard levels of DBPs, but required all monitoring locations in a distribution system to comply with the regulation so that no consumers are exposed to higher risks than expected.

As drinking water disinfection and the formation of DBPs have been well studied in the past few decades, and many review papers and books have been published on such topics, this section only provides a very brief introduction. More details can be found elsewhere.^{2,3,17–23}

8.2.2 Current DBP Control Approaches and Their Limitations

DBP formation control is usually achieved by two major approaches, one targeting the removal of DBPs and the other focusing on the removal of DBP precursors before the disinfection process. Three major techniques have been widely adopted, *i.e.*, adsorption, electrochemical, and membrane, with additional common ones being enhanced coagulation, carbon and hydrous oxides adsorption, electrolysis, (membrane) capacitive deionization (CDI, MCDI), reverse osmosis, nanofiltration, air stripping, and disinfectant switching.^{10,24–31} As most of these techniques have been reviewed already,^{14,17–19,32,33} this section mainly summarizes the applicability, advantages and disadvantages of some popular techniques so they can be later compared with AOPs.

Generally, all the current approaches have pros and cons, and would only be effective under suitable circumstances.¹⁰ For example, although enhanced coagulation can be effective for NOM removal and has been adopted in many water treatment plants, a high coagulant dosage (*e.g.*, up to 0.3 mM)³⁴ can introduce a large amount of ions resulting in elevated salinity of finished water.²⁹ Besides, enhanced coagulation may primarily remove the hydrophobic portion of NOM that generally consists of humic acid, while the remaining hydrophilic portion contains aliphatic carbons and nitrogenous compounds that can still lead to DBP formation upon chlorination.¹⁰ The application of granular activated carbon for NOM adsorption, on the other hand, can be effective for removing relatively small molecular weight species but can barely handle larger ones, which is likely due to the easier access of small species into the internal pores of the granular activated carbon.³⁵ Membrane-based systems such as microfiltration and ultrafiltration may be able to effectively remove a variety of DBP precursors; however, high energy consumption is a major drawback, which makes them less practical in conventional water treatment. Air stripping has been very well studied and documented by the EPA for volatile DBP removal.²⁴ It also has disadvantages such as high energy consumption and residual chlorine loss; it only targets volatile species such that non-volatile ones like HAAs would not be removed. In addition to these well-studied approaches, some emerging techniques have been applied for DBP

control purposes. For example, as a desalination approach, CDI has been employed to remove bromide and NOM from water.^{36–38}

Other than the approaches for both DBP and precursor removal, switching disinfectants from the most commonly used chlorine to others including ClO₂, chloramine, ozone, or their combinations has been another attractive approach.^{24,39,40} According to Table 8.1, different disinfectants typically produce different groups of DBPs. Therefore, switching to other disinfectants can effectively minimize the formation of THM4 and HAA5, ensuring regulatory compliance. However, the formation of other groups of DBPs may become much more significant in those cases. For instance, studies have found that chloramination considerably enhanced the formation of nitrosamines and iodinated DBPs, while ozonation produced bromate, haloacetaldehydes, and halonitromethanes, although both approaches effectively reduced THM4 and HAA5 formation.² It is important to note that THM4 and HAA5 were initially regulated not only because they were the most abundant groups in chlorinated systems, but as they also positively correlated with many other DBPs such that they can represent the overall risk of the finished water. Switching disinfectants, therefore, would make such an assumption no longer true if there are other groups of DBPs with higher toxicities. For example, a calculation of the toxicity of finished waters containing different groups of DBPs showed that the water with more THM4 and HAA5 actually demonstrated lower toxicity than the water containing less THM4 and HAA5 but slightly more HANs and haloacetaldehydes, even though the total mass of DBPs of the former was higher.² Therefore, switching disinfectants may only resolve the issue of regulatory incompliance for specific DBP groups but may not be able to reduce the risks associated with the water.

8.3 Advanced Oxidation Processes (AOPs)

Compared to other approaches for DBP control, AOPs have seen a surge in activities related to research and development in recent years due to their substantial advantages. Different from air stripping, adsorption, and membrane techniques, AOPs permanently destruct DBPs or their precursors instead of transferring them from one media to another. Another major advantage is that the systems of AOPs are extremely diversified due to a large selection of oxidants, oxidant activation approaches, and reaction mechanisms, thanks to the contributions from a large research community. One can develop a variety of strategies for most water treatment scenarios facing different water quality parameters, target compounds, and co-existing species. Although AOPs have not been primarily studied for DBP control purposes, their applications to EC removal during water treatment can help with DBP control because many ECs are reportedly precursors of either traditional or emerging DBPs.^{6,41} Because a large number of review papers and books have been published on AOPs regarding the type of oxidants, reaction mechanisms, and real-world applications,^{7–13} this section only presents a brief but highly relevant introduction.

8.3.1 H₂O₂, PMS, PDS and Their Activation

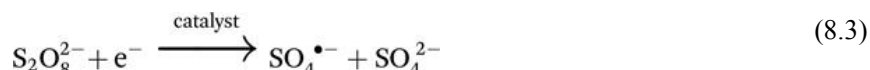
Traditionally used oxidants/approaches include hydrogen peroxide (H₂O₂), ozone (O₃), and UV for photo- or Fenton-related processes for the generation of reactive hydroxyl radicals ([•]OH) (redox potential at 1.8–2.7 VNHE). UV or catalyst (*e.g.*, Fe²⁺)-based activation approaches have been very widely studied for decades and can sometimes be powerful and efficient for the rapid oxidation of a wide range of ECs. The H₂O₂ activation details are summarized in Table 8.2. In addition to laboratory studies, UV–H₂O₂ has been successfully applied in engineering applications in both water and wastewater treatment.

Table 8.2 Common oxidant activation mechanisms in AOPs.

Oxidant	#	Example condition	Reaction mechanism	References
H ₂ O ₂	1	Fe ²⁺ (Fenton reaction)	H ₂ O ₂ + e [−] → OH [−] + [•] OH	55
	2	UV	H ₂ O ₂ → 2 [•] OH	56
PMS	3	Co ²⁺ , Co ₃ O ₄	HSO ₅ [−] + e [−] → SO ₄ ^{•−} + OH [−]	57

	4	UV	$\text{HSO}_5^- \rightarrow \text{SO}_4^{\bullet-} + \cdot\text{OH}$	58
	5	CNT, FeMnO (DET)	$\text{HSO}_5^- + 2\text{e}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^-$	48,49
6	UV, heat	$\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{\bullet-}$	56	
PDS	7	DET (e.g., CuO)	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	46
8	UV	$\text{HOX} \rightarrow \cdot\text{OH} + \text{X}^\cdot$	52,53	
Others	9	UV	$\text{X}^- \rightarrow \text{X}^\cdot + \text{e}^-$ (subsequent: $\text{X}^\cdot + \text{X}^- \rightarrow \text{X}_2^{\bullet-}$)	53

In recent years, the activation of PMS and PDS has gained increasing attention for the generation of sulfate radicals ($\text{SO}_4^{\bullet-}$), which have a higher redox potential (2.5–3.1 V/NHE) and longer half-life (30–40 μs vs. 20 ns) than $\cdot\text{OH}$.⁴² The activation process usually requires the participation of catalysts such as carbon materials and transition metals, or energy input including UV, gamma ray/electron beam, ultrasound, and heat irradiation.^{12,42,43} Generally, the activation by catalysts results in one radical (*i.e.*, $\text{SO}_4^{\bullet-}$) formation while energy input can lead to the formation of two radicals (one $\text{SO}_4^{\bullet-}$ and one $\cdot\text{OH}$ for PMS, or two $\text{SO}_4^{\bullet-}$ for PDS), as shown in the eqn (8.1)–(8.4). More details of some specific activation scenarios can be found in Table 8.2.



Studies have also reported the important roles of other ROS for EC oxidation, such as superoxide radicals ($\text{O}_2^{\bullet-}$), hydroperoxyl radicals ($\text{HO}_2^\cdot$), peroxymonosulfate radicals ($\text{SO}_5^{\bullet-}$), hydrogen radicals ($\text{H}^\cdot$), and hydrated electrons (e_{aq}^-).¹² The redox potentials of these species are lower than those of $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$, but they can still oxidize a variety of ECs, especially those with electron-rich properties.¹² In addition, non-radical and direct electron transfer (DET) pathways have been increasingly recognized for effective EC oxidation.⁷ Please note that although only radical-based systems are generally considered AOPs, we still include non-radical systems in this category given their similar system setups. For instance, recent studies unveiled the role of singlet oxygen ($^1\text{O}_2$) in some PMS activation cases, which has higher selectivity than $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$, and is generally more reactive toward electron-rich compounds due to its electrophilic nature.⁷ Therefore, $^1\text{O}_2$ has been applied for the selective oxidation of target compounds, such as pharmaceutical removal in the presence of NOM,⁷ where NOM is generally more electrophobic and hardly reacts with $^1\text{O}_2$.^{44,45}

8.3.2 Direct Electron Transfer Processes for PMS and PDS Activation

In addition to ROS-based systems, a few studies have demonstrated the DET mechanism for EC oxidation in PMS and PDS systems (*e.g.*, CNT–PMS, CuO–PDS),^{46–48} where ECs can lose electrons to PMS/PDS under the mediation of heterogeneous catalysts resulting in EC oxidation and PMS/PDS decomposition, as illustrated in Figure 8.1. A few examples are also listed in Table 8.2. In most cases, such catalysts tend to have high conductivity and strong interactions (*e.g.*, inner-sphere complexation) with the oxidant for highly efficient electron transfer.^{46,48–50}

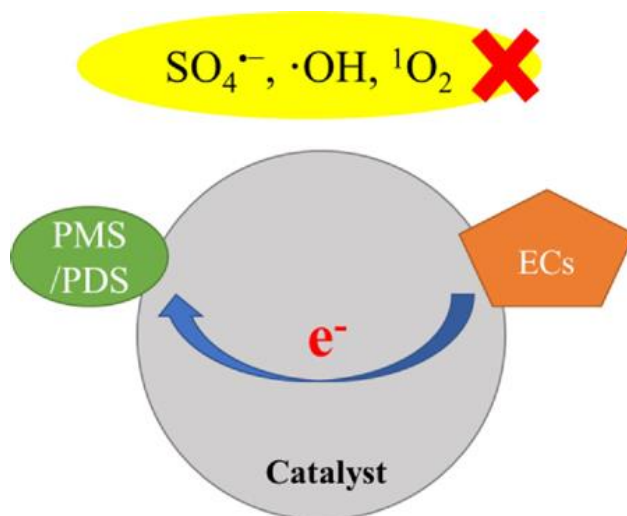


Figure 8.1 Illustration of the direct electron transfer (DET) mechanism in PMS/PDS activation.

Furthermore, an innovative electrochemical system called ‘galvanic oxidation process’ (GOP) was developed by coating a catalyst onto graphite sheets to work as the electrode and separating BPA (bisphenol A) and PMS in two separate containers. BPA was oxidized even when it was physically separated from PMS.⁵¹ As an innovative PMS activation system, GOP not only confirmed the DET mechanism but also demonstrated a number of advantages compared with traditional PMS/PDS-based systems. For example, it is capable of dealing with complex water matrices such as hypersaline wastewater containing high concentrations of radical scavengers such as Cl^- and HCO_3^- . By using GOP, no chemical addition is required and no secondary contamination to the source water would be expected. Lastly, there would be no difficulty in catalyst recovery.

8.3.3 UV–HOX Systems

The photolysis of chlorine or bromine for the formation of $\cdot\text{OH}$ and $\text{Cl}\cdot$ or $\text{Br}\cdot$ has also achieved large progress as emerging AOPs in recent years.^{52,53} The reaction mechanisms are illustrated in Table 8.2. When UV/chlorine was applied to degrade ibuprofen,⁵⁴ the observed ibuprofen degradation rate was more than three times higher than that of the UV– H_2O_2 system under similar experimental conditions. Chlorine-related radicals including $\text{Cl}\cdot$, $\text{Cl}_2^{\cdot-}$, and $\text{ClO}\cdot$ were observed to contribute to 22% to 30% of the ibuprofen removal depending on the pH conditions. A few studies have also reported the formation of halogen radicals during the photolysis of halide ions in environmental aquatic systems, such as $\text{X}\cdot$, $\text{X}_2^{\cdot-}$, and $\text{XY}^{\cdot-}$, where X and Y represent Cl, Br, or I.⁵³ These radicals can play significant roles in EC oxidation in water under sunlit irradiation especially in water that is rich in halides, such as that from oceans, estuaries, and brines. Due to their relatively low redox potentials, similar to $^1\text{O}_2$ and DET, they tend to selectively oxidize contaminants that have electron-rich properties.⁵³ As NOM is generally less reactive than many ECs, such selectivity makes it even more efficient for the self-remediation of the aquatic environment under sunlit irradiation.

8.4 The Application of AOPs or Related Oxidants to DBP Control

8.4.1 Removal of DBP Precursors—NOM

The removal of NOM by AOPs is important for DBP control and has been extensively reviewed.^{10,55–57} Even though most studies on NOM removal using AOPs reported positive effects of AOPs on DBP formation

control, one should still be aware that sometimes it could substantially increase DBP formation.⁵⁸ Such diverse effects are largely related to the inherent properties of NOM, where NOM originally resistant to halogenation could be induced to form more DBPs after AOP treatment, while those originally with higher reactivity toward halogenation tend to have less DBP formation upon AOP treatment.⁵⁸ This might be due to the different stages of destruction of the NOM structures, where the early stages generally involved the breakage of large molecules to smaller ones, resulting in an increased potential of halogenation, while the later stages involved higher extents of mineralization of small molecules. This is also supported by the report that high dosages of radicals from AOPs led to reduced DBP formation regardless of the original properties of the NOM, due to the extensive NOM mineralization.⁵⁸

Compared to halides and many ECs, NOM is relatively less redox reactive. In such cases, only radical-based systems are suitable. This significantly limits the applicability of AOPs because non-radical and DET systems were proved to be substantially advantageous in some circumstances. Therefore, AOPs might be more suitable for the removal of precursors including halides and ECs, and even DBPs themselves, due to their relatively lower concentrations and higher reactivity compared to NOM.

8.4.2 Removal of DBP Precursors—Halides

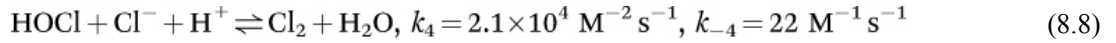
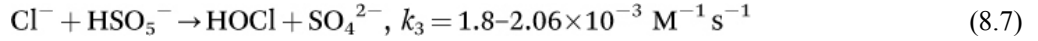
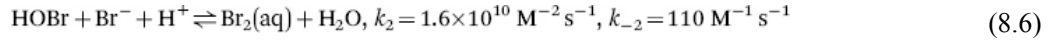
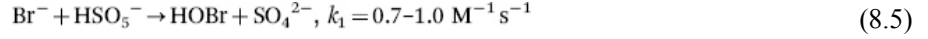
Many studies have focused on the removal of halides including bromide and iodide to reduce the formation of brominated and iodinated DBPs. As mentioned in Section 8.1, bromide and iodide have molecular weights of 79.90 and 126.90 g mol⁻¹, more than two-fold higher than that of chloride (35.5 g mol⁻¹). Minor substitution of chloride with bromide or iodide can considerably increase the weight (mass concentration) of DBPs, resulting in regulatory noncompliance issues. These brominated and iodinated DBPs were also reported to have much higher toxicities than the chlorinated species, as mentioned in Section 8.1. Bromate as an inorganic DBP species can also form during the ozonation process if bromide is present ($\text{Br}^- \rightarrow \text{HOBr} \rightarrow \text{BrO}_2^- \rightarrow \text{BrO}_3^-$). Various strategies have been formulated for bromide and iodide removal in drinking water treatment before disinfection.

8.4.2.1 Halide Removal Using PMS Without Activation

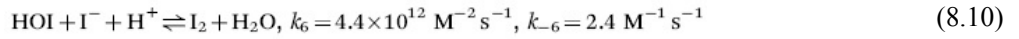
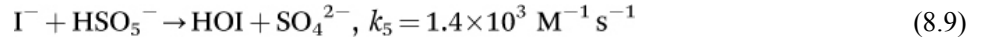
Anthropogenic introduction of halides into drinking water sources can sometimes raise significant concerns due to enhanced DBP formation in water supplies. For example, a study reported that the bromide introduced by two human activities made up 82% of the total bromide in Allegheny River in Pennsylvania at the time of study (2016),⁵⁹ one of which was shale gas production. Due to the recent advances of horizontal drilling and hydraulic fracturing, shale gas production has been rapidly expanding in many countries as an important alternative to the traditional oil/gas production. However, this process continuously produces wastewater containing high concentrations of bromide, with the median of 1.2 g L⁻¹.⁶⁰ In comparison, the median bromide concentration in US surface waters is around 35 µg L⁻¹.¹⁴ The current treatment of such waters generally does not focus on bromide removal.⁶¹ Therefore, the discharge of the effluent could potentially increase the bromide level in surface waters, resulting in increased DBP formation in downstream water supplies.^{59,62,63}

Different techniques have been reported for halide removal for DBP control purposes, including those using AOPs or AOP-related oxidants.^{64,65} For example, one study reported that the addition of PMS into an iodide-containing water efficiently converted iodide to iodate as a safe sink of iodide.⁶⁵ This process considerably reduced iodinated aromatic compound formation during permanganate oxidation. Like chlorination, permanganate oxidation can efficiently oxidize iodide to form HOI, which reacts with organics to form iodinated DBPs. Therefore, during traditional chlorination process, such an iodide removal strategy can effectively help to reduce the formation of iodinated DBPs. In another more comprehensive study, Huang and Zhang proposed a cost-effective approach for bromide and iodide removal from synthetic shale gas produced water using PMS (no activation) coupled with air stripping.⁶⁴ Because of the relatively high second-order rate constant,^{66,67} bromide was rapidly oxidized and then stripped out from water (eqn (8.5)–(8.6)). Due to the considerably lower reaction rate constant of chloride with PMS (eqn (8.7)) and chloride with HOCl

(eqn (8.8)),⁶⁶⁻⁶⁹ this approach was found to have very high selectivity toward bromide even when the concentration of chloride was more than two orders of magnitude higher. Compared to other studies using approaches like aerated electrolysis,^{70,71} this approach removed more than 95% of 15 mM bromide in less than 10 min with a stoichiometric amount of PMS, whereas it took more than 6.5 h using the electrolysis approach.^{70,71} The treated and untreated produced water demonstrated 6% and 200% increases in THM formation, respectively, during the chlorination of affected water.⁴⁹



Iodide has also been frequently found in shale gas produced water at rather high levels, the discharge of which could potentially increase the formation of iodinated DBPs in downstream water supplies. Compared to their chlorinated and brominated analogs, iodinated DBPs were reported to have even higher mammalian cell toxicities.^{72,73} In the same study, Huang and Zhang also investigated the removal of iodide from produced water using PMS following a similar oxidation and air stripping procedure mentioned above.⁶⁴ Upon the formation of I_2 (eqn (8.10)),^{66,74} I_2 was also quickly stripped out of the solution due to its low solubility. However, HOI can be further oxidized by PMS forming IO_3^- at a slightly lower rate, as shown in eqn (8.11).⁷⁵ The study concluded that using a low PMS dosage to target iodide in the presence of bromide can easily remove most of the iodide through air stripping.



8.4.2.2 Halide Removal Using O_3 , H_2O_2 , and PDS

Bromide and iodide can also be oxidized by ozone to form HOBr and HOI. If air stripping is performed properly, these intermediates would be easily stripped out instead of being further oxidized to bromate and iodate.⁷⁶ For example, Huang *et al.* employed ozone aeration for the treatment of a synthetic shale gas produced water and reported an almost complete removal of bromide.⁷⁷ The resulting produced water showed negligible effects on DBP formation in the affected surface water upon chlorination. Similarly, H_2O_2 and PDS can also be used to oxidize I^- forming HOI, although the reaction rates might be much lower than those with PMS.⁷⁸⁻⁸⁰ For example, Wang *et al.* utilized the reaction between PDS and I^- to form HOI to substitute the direct addition of HOI for gold extraction.⁸¹ To improve the reaction efficiency, Guan *et al.* proposed a DET-based PDS activation system using a commercial multiwalled CNT for I^- oxidation.^{82,83} Upon the activation of PDS, I^- was quickly and almost completely oxidized to HOI with negligible formation of iodate in a pH range of 5–9. Complexes formed between PDS and CNT, which achieved fast electron transfer with I^- resulting in PDS decomposition and HOI formation. Although this study was not designed for I^- removal, it can be readily adopted by coupling with air stripping for DBP control.

8.4.2.3 Discussion

The above studies are summarized in Table 8.3. Overall, the removal of bromide and iodide in water supplies before disinfection has become an important task to reduce DBP formation and comply with regulations. Although studies have reported that traditional aluminum coagulation and flocculation processes can remove up to 90% of bromide from raw water, the efficiencies are highly dependent on the coagulant dosages and affected by coexisting species such as DOM, HCO_3^- , SO_4^{2-} , and Cl^- .^{84,85} These processes can usually handle naturally occurring bromide and iodide. However, with an increasing amount of anthropogenic halides introduced into source waters, regular water treatment processes may not be sufficient to ensure DBP regulatory compliance, even with enhanced coagulation with higher doses of coagulants.⁵⁹ In addition to shale gas extraction, other industries such as coal-fired plants, chemical industries, and municipal waste incinerators are also reported to release a significant amount of halides into the environment,^{59,86} to which these approaches may be effectively applied.

Table 8.3 Summary of different studies on halide removal using AOP or AOP-related oxidants.

Target halide	Halide concentration	Approach	pH	Major findings	References
Iodide	N/A	PMS only	5, 7, 9	Iodide was converted to iodate. Reduced iodinated aromatic compounds formed during permanganate oxidation.	69
Bromide	1.2 g L ⁻¹ (15 mM)	PMS with air stripping	5	Bromide was rapidly oxidized and then stripped out from water. High selectivity toward bromide against chloride. Extremely efficient compared to aerated electrolysis (10 min vs. 6.5 h). Significantly reduced DBP formation.	49
Iodide	0.06 g L ⁻¹ (0.5 mM)	PMS with air stripping	5	Iodide was rapidly oxidized and then stripped out from water. The formation of iodate is possible but highly dependent on PMS dosage.	49
Bromide	0.74 g L ⁻¹ (9.3 mM)	Aeration with O ₃	7	Bromide was almost completely oxidized by ozonation. DBP formation was substantially reduced.	81
Iodide	0.1 M	PDS only	5, 7	Iodide was efficiently oxidized to form HOI.	85
Iodide	10 μM	PDS–CNT	5–9	Iodide was quickly and almost completely oxidized to HOI through the electron exchange between iodide and PMS under the mediation of CNT. The formation of iodate was negligible.	95, 96

8.4.3 Removal of DBP Precursors—ECs

8.4.3.1 Why Are ECs Relevant in DBP Formation?

Many ECs, such as pesticides, dyes, and antibiotics, are released into the environment and could potentially pose threats to the environment. Chemicals such as chlordane and dieldrin have been removed from the market due to their persistence, bioaccumulation, and toxicity (PBT); in the meantime, regulations have been made to restrict the introduction of PBT substances to the market.⁸⁷ Among PBT's properties, persistence is usually the leading cause for the accumulation of certain ECs in the environment, which could be potentially harmful due to continuous exposure and increasing concentrations in the surroundings.⁸⁸

In addition to their toxicities to humans, ECs have been reported to be important DBP precursors especially during chlorination and chloramination processes. These ECs include industrial contaminants, municipal wastewater treatment discharged organic matter, and microorganism-associated compounds (*e.g.*, algal toxins

during algal blooms).^{2,5,6} For example, amino acids, short oligopeptides, and the antibiotic chloramphenicol have been reported to be important precursors of THMs and HANs during chlorination and chloramination.^{6,89,90} Studies found that the algal organic matters extracted from *Microcystis aeruginosa* (cyanobacteria), *Scenedesmus quadricauda* (chlorella) and *Nitzschia palea* (diatom) contain proteins, carbohydrates, and amino acids, and contribute to significant amounts of chloroacetamides during chlorination and chloramination.⁵ Such precursors have been reported to have the characteristics of low molecular weight and low hydrophobicity.⁶ Another study evaluated raw water samples from a reservoir and found that the major precursors of dichloroacetamide were protein-like substances made up of amino acids.⁹¹ Different from NOM, however, the removal efficiencies of these organics by traditional water treatment processes (*i.e.*, coagulation, flocculation, sedimentation, and filtration) are very low.^{91,92} Therefore, the application of other approaches has become desirable to lower the toxicities of finished waters in water supplies.

8.4.3.2 Limitations of Traditional Approaches for EC Removal

Traditional methods for water and wastewater treatment are only capable of removing some ECs, as summarized in Table 8.4.^{97,98} As ECs in the effluent of WWTPs can also serve as DBP precursors in downstream water supplies, their removal from wastewater effluents is also important. Conventional wastewater treatment with the activated sludge approach can achieve a removal efficiency of 0 to 90%, which is largely dependent on the physicochemical properties of the specific compound.^{104,105} During drinking water treatment methods such as coagulation and flocculation, lime softening, powder activated carbon adsorption, and membrane filtration can also remove contaminants at least partially, but they have disadvantages such as low efficiencies, strict conditions, long duration, or high energy input.^{93,94} These methods were also mainly designed to concentrate or transport contaminants from one media to another instead of focusing on their destruction. Therefore, further treatment is still needed to ultimately eliminate them from the environment. The applications of UV irradiation or ozonation alone for EC oxidation are limited due to the high dose of UV and low ozone production efficiency, which leads to high energy consumption,^{93,94} even though ozonation can sometimes be powerful due to the formation of $\cdot\text{OH}$.

Table 8.4 Different approaches for EC removal.

Treatment process	Removal efficiency	Notes
Activated sludge	0–90%, highly dependent on the compound physicochemical properties	No destruction
Coagulation–flocculation	< 20%	
Lime softening	< 20% at pH 9–10	
Powder activated carbon adsorption	40–90%, 4 h, depending on the compound polarity	
Membrane filtration (<i>e.g.</i> , reverse osmosis, nano filtration)	> 90%, high energy input	High energy consumption
UV	50–80%, high dose	
Ozonation	> 90%, low ozone production efficiency	
AOPs (utilizing H_2O_2 , PDS, or PMS)	Can easily reach >90% removal in a short time (<i>e.g.</i> , depending on the specific conditions, the $t_{1/2}$ can be as short as 1 min)	

8.4.3.3 AOPs for EC Removal

8.4.3.3.1 Radical-based Systems for EC Removal

Primarily relying on the oxidation power of radicals, AOPs have been widely demonstrated to be efficient for EC removal. For ECs with electron-rich properties, non-radical-based systems were also reported to be effective,⁷ which therefore provide substantial opportunity for one to formulate suitable water treatment strategies. For example, a study applied the UV–chlorine system to the removal of multiple ECs, such as desethylatrazine, sulfamethoxazole, carbamazepine, diclofenac, and benzotriazole, at the pilot scale with a 250 L h⁻¹ flow rate.⁹⁵ All the ECs were effectively oxidized at the initial concentration of 1 µg L⁻¹, and the co-existing DOC of up to 46 mg L⁻¹ did not considerably reduce the EC oxidation efficiencies. The side reactions between chlorine and these organics (as well as their degradation products) led to a negligible formation of DBPs including THMs and *N*-nitrosodimethylamine. Compared to the state-of-the-art UV–H₂O₂, UV–chlorine demonstrated 30–75% energy savings, which made it more suitable for large-scale applications.

Chu *et al.* reported the use of UV–PDS to remove the organic nitrogen precursors of haloacetamides and minimize the formation of other nitrogenous DBPs upon chlorination.⁶ The water samples were collected from three drinking water treatment plants right before disinfection. Although UV or PDS alone did not make any noticeable difference on N-DBP formation, the coupled UV–PDS system substantially decreased haloacetamide formation and bromine incorporation. Similar to traditional DBPs, brominated acetamides also have higher risks than their chlorinated analogs.²³ The precursors of other N-DBPs including HANs and halonitromethanes were also partially removed. The authors believed that such systems could be incorporated into water supplies receiving organic nitrogen-rich waters such as WWTP effluents or waters experiencing algal blooms.

Another study reported the treatment of free amino acids and short oligopeptides using UV–PDS and UV–H₂O₂ for controlling the formation of THMs and HANs during chlorination.⁸⁹ UV–PDS was found to better limit the formation of HANs and brominated DBPs compared to UV–H₂O₂, although it also increased the formation of chloroform from the chlorination of amino acid. This is likely due to the low extent of mineralization of amino acids and short oligopeptides. As mentioned in Section 8.4.1, AOP treatment can easily transform organic precursors with low halogenation potentials to chemicals with high halogenation potentials, or *vice versa*, depending on the physicochemical properties of the organics.⁵⁸ Another study reported the effect of PDS alone and UV–PDS treatment on the subsequent formation of THMs, HANs, and halonitromethanes during the chlorination and chloramination of antibiotics chloramphenicol, thiamphenicol, and florfenicol.⁹⁰ The PDS oxidation alone achieved a statistically significant decrease of THMs during chlorination, or HANs and halonitromethanes during chloramination. UV–PDS, on the other hand, increased the dichloroacetonitrile formation during the subsequent chloramination, but substantially reduced the formation of dichloronitromethane and trichloronitromethane. The authors concluded that such methods can be applied for DBP control in water supplies suffering heavy impact from upstream WWTP effluents.

The above studies are summarized in Table 8.5. In addition, there are many other studies applying AOPs for EC removal, although most of them were not directly used for DBP control purposes.^{7–13} These studies can usually be readily applied if the removal of ECs as the DBP precursors becomes desirable in water supplies.

Table 8.5 Summary of different studies on EC removal using AOPs for DBP control.

ECs	Approach	Disinfection approach	Target DBPs	Major findings	References
Desethylatrazine, sulfamethoxazole, carbamazepine, diclofenac, benzotriazole, tolyltriazole, iopamidole and	UV–Chlorine	N/A	THMs and <i>N</i> -nitrosodimethylamine	The co-existence DOC up to 46 mg L ⁻¹ did not considerably reduce the EC oxidation efficiencies. Negligible formation of DBPs. Compared to the state-of-art UV–	95

17a-ethinylestradiol (EE2)				H ₂ O ₂ , UV–chlorine had 30–75% energy savings.	
Organic nitrogen precursors	UV–PDS	Chlorination	Haloacetamides, HANs and halonitromethanes	Substantially decreased haloacetamide formation and bromine incorporation. The precursors of other N-DBPs including HANs and halonitromethanes were also partially removed.	6
Free amino acids and short oligopeptides	UV–PDS and UV–H ₂ O ₂	Chlorination	THMs and HANs	UV–PDS reduced the formation of HANs and brominated DBPs more than UV–H ₂ O ₂ did. UV–PDS increased the formation of chloroform from the chlorination of amino acids.	89
Chloramphenicol, thiamphenicol, and florfenicol	PDS alone and UV–PDS	Chlorination, chloramination	THMs, HANs, and halonitromethanes	PDS alone decreased THM during chlorination, and decreased HANs and halonitromethanes during chloramination. UV–PDS increased dichloroacetonitrile during chloramination, but reduced dichloronitromethane and trichloronitromethane. These approaches can be used for water supplies suffering heavy impact from WWTP effluents.	90

8.4.3.3.2 Issues Associated with Radicals and Outlook on Non-radical Systems

One drawback of the above radical-based systems is that bromide can be easily oxidized by radicals (especially $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$) to form bromate causing regulatory compliance challenges. In fact, such reactions may always occur whenever $\text{SO}_4^{\cdot-}$ and/or $\cdot\text{OH}$ are generated in the presence of bromide. Therefore, bromide has to be evaluated in advance and be removed if necessary. In addition, non-excessive $\text{SO}_4^{\cdot-}$ dosages could also cause property changes of NOM due to the low extent of mineralization resulting in potentially increased formation of other traditional DBPs, as mentioned in Section 8.4.1.

Although most of the studies on EC removal by AOPs are based on radical formation, the newly discovered non-radical and DET pathways can be beneficial in a number of ways, overcoming the drawbacks of radical-based systems such as quenching of radicals by anions and formation of byproducts (*e.g.*, bromate

and chlorate), which lead to reduced treatment efficiencies and increased toxicities. Despite its own limitation such as relatively lower oxidation ability, the most recently developed GOP system brought EC removal to another level based on its unique, contactless system setup, overcoming many drawbacks and challenges other AOPs have been facing.^{49,51}

Overall, given the large selection of oxidants, oxidant activation approaches, and reaction mechanisms, one can easily consider different water quality parameters, target compounds, and co-existing species while developing suitable DBP control strategies based on AOPs.

8.4.4 Direct Removal of DBPs

8.4.4.1 Direct DBP Removal Approaches Using AOPs

Although most strategies for DBP control focus on precursor removal, there are still a number of studies evaluating the direct removal of DBPs using AOPs. For example, when the decomposition of DCAA and TCAA from water was examined under the conditions of O₃, UV, UV–O₃, UV–H₂O₂, O₃–H₂O₂, and UV–O₃–H₂O₂,⁹⁶ it was observed that ozonation or UV irradiation alone did not show perceptible removal of these two types of DBPs within the experimental time, while UV–O₃ showed the highest efficiency. The presence of humic acid and HCO₃[–] significantly inhibited HAA decomposition, primarily due to their radical scavenging effects. DCAA was found to be more easily oxidized than TCAA in all the processes. Similarly, a recent study reported the degradation and mineralization of DCAA using different AOPs.⁹⁷ As shown in Table 8.4, ozonation (pH = 3) and Fenton reaction alone only resulted in 2% and 19% of removal in 90 min, respectively, while their combination achieved 83% removal. As a very commonly used nanomaterial, however, TiO₂ under UV irradiation only removed 26% of DCAA in 90 min. This suggested that DCAA was very resistant toward these benchmark approaches. Overall, higher efficiencies are generally due to the excessive generation of ·OH. The details of the removal efficiencies are summarized in Table 8.6.⁹⁷ The rate constants of some of the major DBPs with ·OH are summarized in Table 8.7.^{10,98}

Table 8.6 DCAA removal efficiencies by different AOPs.^a

Number	System	Removal percentage	Experiment time (min)
1	O ₃	2%	90
2	O ₃ (pH = 11)	72%	90
3	H ₂ O ₂ –O ₃	70%	90
4	UV–TiO ₂ –O ₂	26%	90
5	UV–TiO ₂ –H ₂ O ₂ –O ₂	18%	90
6	Fenton	19%	90
7	UV–Fenton–O ₃	91%	20
8	UV–TiO ₂ –Fenton	93%	40
9	UV–TiO ₂ –O ₃	88%	90
10	UV–TiO ₂ –H ₂ O ₂ –O ₃	90%	90
11	Fenton–O ₃	83%	90

^a Note: the pH for all the systems is 3 unless otherwise specified.

Table 8.7 Second order reaction rate constants of THMs and HAAs with ·OH.

Number	DBP name	Formula	Rate constant with ·OH (M ^{–1} s ^{–1})
Trihalomethanes			
1	Trichloromethane (chloroform)	CCl ₃ H	1.1 × 10 ⁷
2	Bromodichloromethane	CCl ₂ BrH	6.4 × 10 ⁷

3	Dibromochloromethane	CClBr_2H	9.8×10^7
4	Tribromomethane	CBr_3H	1.5×10^8
Haloacetic acids			
5	Chloroacetic acid	$\text{CH}_2\text{ClCO}_2\text{H}$	2.0×10^8
6	Dichloroacetic acid	$\text{CHCl}_2\text{CO}_2\text{H}$	1.3×10^8
7	Bromoacetic acid	$\text{CH}_2\text{BrCO}_2\text{H}$	2.0×10^8
8	Dibromoacetic acid	$\text{CHBr}_2\text{CO}_2\text{H}$	1.6×10^8
9	Tribromoacetic acid	$\text{CBr}_3\text{CO}_2\text{H}$	9.2×10^7
10	Bromochloroacetic acid	$\text{CHClBrCO}_2\text{H}$	1.2×10^8
11	Bromodichloroacetic acid	$\text{CCl}_2\text{BrCO}_2\text{H}$	4.7×10^7
12	Dibromochloroacetic acid	$\text{CClBr}_2\text{CO}_2\text{H}$	8.8×10^7

Another study comprehensively examined the degradation kinetics of a large number of DBPs, including THMs, HANs, haloacetaldehydes, halonitromethanes and haloacetamides, under UV- H_2O_2 conditions and developed a model for predicting their degradation.⁹⁸ Due to the substantially different physicochemical properties of these DBPs, the direct photolysis rates varied by around three orders of magnitude, and the brominated and iodinated ones were generally more degradable. This is mainly due to the lower bonding energies of bromine and iodine with the carbon atom. With the measured rate constants of 37 species with $\cdot\text{OH}$ using gamma radiolysis, a kinetic model was then developed to predict the degradation behaviors of the DBPs in the UV- H_2O_2 system. Under the examined conditions, most of the DBPs that degraded more than 50% were brominated and iodinated species. Because these DBPs are much more toxic than the corresponding chlorinated species, their preferential removal is beneficial.

Apart from drinking water treatment, AOPs have also been reported for DBP removal from swimming pool waters as disinfection is continuously performed. Generally, the dosages of chlorine for swimming pool disinfection are much higher than those for drinking water. Although swimming pool waters are not consumed, swimmers are constantly exposed to DBPs due to dermal and respiratory (volatile DBPs) exposure. To control DBPs in swimming pool water, Glauner *et al.* reported the use of O_3 , UV- O_3 , and O_3 - H_2O_2 as three major approaches for the elimination of both DBPs and DBP precursors.⁹⁹ The latter two approaches demonstrated the highest efficiencies for eliminating TOC and organic halogen species. A contact time as short as 3 min could be efficient enough for practical applications. As a result, the study proposed O_3 - H_2O_2 as the preferred approach for high elimination rates and low cost.

8.4.4.2 Outlook on UV-HOX

The application of UV-HOX or UV- X_2 to form halogen radicals such as $\text{X}\cdot$ and $\text{X}_2\cdot^-$ also seems to be a promising approach for DBP removal. Different from the oxidation of organics by chlorine through chloride-substitution reactions,^{100,101} the oxidation by $\text{X}\cdot$ and $\text{X}_2\cdot^-$ was reported to be primarily electron transfer processes.¹⁰² These systems have been evaluated for wastewater treatment/reuse,^{103,104} but not yet for DBP control in drinking water treatment. Future studies should be conducted to evaluate whether DBPs can be effectively oxidized by $\text{X}\cdot$ and $\text{X}_2\cdot^-$. Due to the original presence of chlorine as the disinfectant, such systems would only require minimum modification by installing an UV irradiation station following disinfection. The secondary contamination of the finished water can also be largely avoided because no other chemicals are needed.

8.4.4.3 Advantages Compared to Precursor Removal

Although most strategies for DBP control focus on precursor removal, we believe direct DBP removal using AOPs still has its merits. First, finished waters generally have lower concentrations of DOM, TSS, and co-existing anions (*e.g.*, Cl^- and HCO_3^-), whose negative effects on AOP treatment can be therefore minimized.

Second, only a portion of organics can be oxidized to form DBPs during disinfection.¹⁰⁵ Focusing on the formed DBPs instead of all the organics could reduce the workload of the AOP system. Third, while brominated and iodinated DBPs are reported to have significantly higher toxicities (and also molecular weights) compared to chlorinated DBPs, AOPs generally have much higher removal efficiencies on the former, as mentioned in Section 8.4.4.1.⁹⁸ This makes it more attractive to focus on DBP removal instead of precursor removal. Finally, the AOP treatment of some DOM, especially those with high molecular weights and low halogenation potentials, prior to disinfection may lead to increased DBP formation, as mentioned in Section 8.4.1. In this case, AOP pre-treatment may not be a viable approach.

8.5 Summary

The introduction of anthropogenic DBP precursors including organic matter and halides into drinking water sources has raised increasing concerns. While different techniques, such as membrane, electrochemical, and adsorption, have been proved to be effective for the removal of certain types of precursors, the recent advances in AOPs have attracted increasing attention due to the large selection of oxidants, activation approaches, mechanisms, and system setups. Both precursor removal and direct DBP removal as the two major DBP control strategies were found to have their own advantages and drawbacks. Only after these advantages and drawbacks have been well balanced can one system be adopted for real engineering applications.

It is generally believed that the removal of precursors prior to disinfection is a better choice.¹⁴ If processed properly, the removal of organics and/or halides can lead to the reduction of overall DBP formation regardless they are regulated/identified or not. As over 600 DBPs have been identified and more than 1000 are expected given the highly and increasingly diversified precursors, precursor removal would be effective to reduce the overall DBP formation compared with the removal of specific DBP groups after they have formed. As emerging DBP precursors, ECs may be harmful to consumers by themselves without being transformed to DBPs and are usually more reactive toward AOPs compared to DBPs. Therefore, their removal by AOPs prior to disinfection could improve water safety more easily. However, there are also some drawbacks of targeting precursors instead of DBPs. For example, improper implementation of AOPs could substantially increase the formation of some DBPs (Section 8.4.1), and halides (especially bromide) can be readily oxidized by radicals during AOP treatment to form bromate, a regulated DBP. Luckily, these issues may be solved by using non-radical AOPs or GOPs.

Nevertheless, one should carefully evaluate the water quality before employing an AOP system for real water treatment applications. Even though this chapter mainly focuses on AOPs for DBP control, it does not necessarily mean AOPs are superior to other techniques from the perspectives of both applicability and cost. Other techniques could be better for certain circumstances, and only after their advantages and drawbacks being well-balanced can one formulate the most suitable strategies for specific water treatment scenarios.

Acknowledgements

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Chapter 9

Nanocatalyst-enabled Persulfate Activation for Water Decontamination and Purification

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9.1 Introduction

Advanced oxidation processes (AOPs) generally employ highly reactive oxygen species (ROS) such as hydroxyl radicals ($\cdot\text{OH}$) to eliminate organic contamination with diffusion-limited kinetics.¹ The AOPs typically utilize hydrogen peroxide (H_2O_2) as a precursor for $\cdot\text{OH}$ generation. Obstacles hindering AOPs involve the instability of H_2O_2 for storage and transportation and the short lifespan of $\cdot\text{OH}$ (half-life of $\sim 1\ \mu\text{s}$).² Recently, the application of emerging peroxide precursor compounds such as ozone and CaO_2 for $\cdot\text{OH}$ production has motivated scientists to exploit alternative precursors for AOPs with remediation demanding safety and green processes.³

Persulfate is a peroxide compound, similar to H_2O_2 . Peroxymonosulfate (PMS) and peroxydisulfate (PDS) are typical persulfates, which are formed

by replacing one and two hydrogen atoms of H_2O_2 with sulfates. As shown in Figure 9.1, the peroxide bond lengths of PMS and PDS increase from 1.453 Å (for H_2O_2) to 1.460 and 1.497 Å, respectively, thus exhibiting unique catalytic activity.⁴ Persulfate oxidizes contaminants indiscriminately *via* sulfate radicals ($\text{SO}_4^{\cdot -}$) generated from peroxide dissociation. Compared to the use of $\cdot\text{OH}$ for water purification, the advantages of using $\text{SO}_4^{\cdot -}$ produced by persulfates have been demonstrated, including 1) higher production of radicals at the same concentration of chemical precursors,^{5–8} 2) better resilience to operating conditions and solution chemistry,^{9–11} and 3) higher reactivity of $\text{SO}_4^{\cdot -}$ toward electrophilic contaminants.¹²

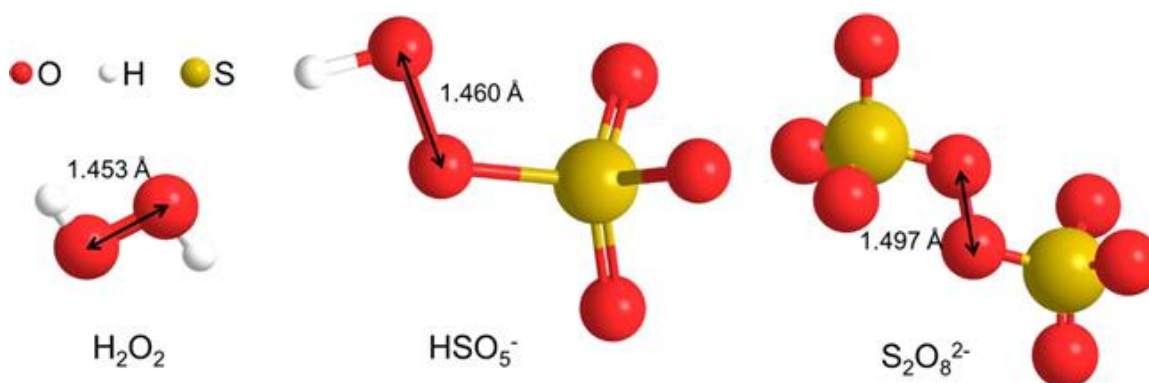
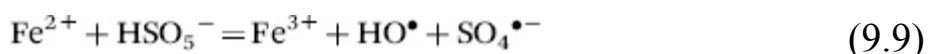
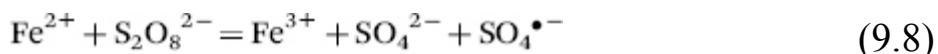
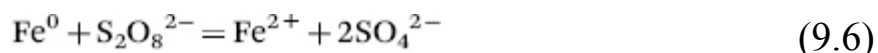
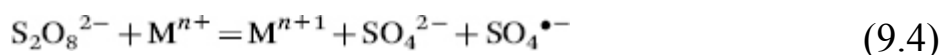
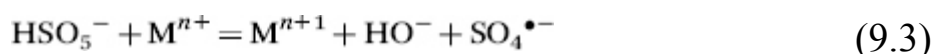
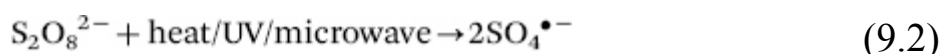
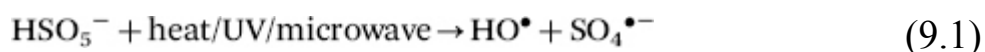


Figure 9.1 Molecular structure modes of H_2O_2 , HSO_5^- , and $\text{S}_2\text{O}_8^{2-}$.

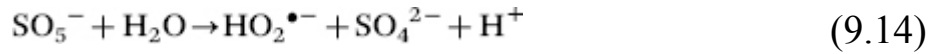
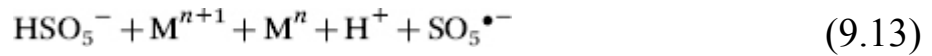
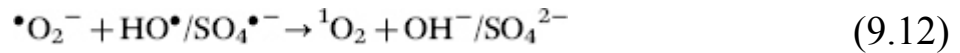
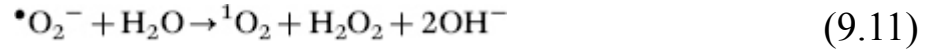
In general, the $\text{SO}_4^{\cdot -}$ radicals are formed by PMS or PDS in two approaches. One method is *via* the homolytic cleavage of peroxide bonds by absorbing solar energy, radiation energy, and thermal energy (eqn (9.1)–(9.2)).⁴ The rest are through single-electron activation processes that unleash the oxidative power of persulfates using activators, such as transitional metals ($\text{M} = \text{Fe}, \text{Cu}, \text{Co}, \text{Mn}, \text{and Mo}$), as shown in eqn (9.3)–(9.4).¹² These single-electron activators serve as electron donors, decomposing persulfates *via* homogeneous and heterogeneous catalytic reactions. Homogeneous catalytic processes generally enable ultrafast radical production by metal ions at acidic conditions.¹³ Transitional metal oxides (*e.g.*, Fe_2O_3 , CuO , Co_3O_4 , and MoO_3) are retained in near-

neutral/alkaline solutions; thereby, they are considered heterogeneous catalysts for persulfate activation. Additionally, zero-valent metals are another category of single-electron catalyst for activating persulfates.^{14,15} As shown in eqn (9.5)–(9.10), Fe(0) ions released from the zero-valent iron (ZVI) surface unleash the oxidative power of PDS and PMS to generate $\text{SO}_4^{\bullet-}$, while also regenerating ZVI *via* the reduction of Fe(III) to sustain radical production. Zero-valent Zn, Cu, and Al show identical catalytic activation processes for persulfates.¹⁶



Singlet oxygen ($^1\text{O}_2$), as a reactive oxygen derivative, exists in persulfate activation, contributing to non-radical-driven contaminant removal. Although several species have been attributed to $^1\text{O}_2$ generation, the superoxide radicals ($\text{O}_2^{\bullet-}$) are considered critical intermediates to yield $^1\text{O}_2$ *via* Haber–Weiss reactions (eqn (9.11)–(9.12))¹⁷ and PMS oxidation (eqn (9.13)–(9.15)).^{18–20} Altering the oxidative/reductive sites on the catalyst surface enables non-radical involving regimes for PMS

activation.²¹ Electron abstraction phenomena were demonstrated to be responsible for activating PDS absorbed on the surface of metal oxide catalysts.²² Compared to radical-mediated contaminant removal, the non-radical involving regimes minimize persulfate consumption. In addition to metal oxides, carbonaceous catalysts also facilitate non-radical-mediated persulfate activation.²³



Herein, we review state-of-the-art nanocatalysts for persulfate activation and their applications in water decontamination. We introduce nanocatalyst categories, fabrication methods, and the corresponding mechanisms of catalytic activation reactions. We discuss effective strategies to enhance persulfate activation by improving catalyst physicochemical properties. Exposing active sites of catalysts, downsizing catalysts, and tuning catalyst crystalline structure and morphology can accelerate persulfate activation. We also summarize photoactive nanocatalysts that activate persulfate *via* photocatalytic and photothermal reactions. Finally, we highlight that the application of nanoreactors assembled from nanocatalysts is critical for practical water treatment, with an outlook of challenges and research needs.

9.2 Nanocatalysts

Nanocatalysts can activate persulfates *via* various catalytic processes. Nanocatalysts for persulfate activation have diverse categories, exhibiting a variety of physiochemical properties. Based on the differences in elemental composition, molecular and crystalline structures, and morphology among nanocatalysts, the mechanisms of persulfate activation are distinct. In the

following sections, we introduce state-of-the-art nanocatalysts and their corresponding catalytic properties.

9.2.1 Metals and Metal Oxides

Metals and metal oxides are typical categories of catalysts that activate persulfates *via* heterogeneous catalytic reactions. Theoretically, metals with multiple valence states serve as active sites, providing electrons for persulfate activation. Therefore, the optimization of metal atoms on the catalyst surface is essential. In other words, complete oxidation of organic contaminants using persulfates will depend on the maximum exposure of metal active sites on the catalyst. Through the pyrolysis of MCl_x ·dicyandiamide in an N_2 atmosphere,^{24,25} the resultant metal nanocatalysts formed a three-dimension structure with sizes at $\sim 10\text{--}100$ nm.^{24,25} Notably, high-temperature fabrication methods are also employed to synthesize ferrite compounds with a large specific surface area, as shown in Figure 9.2A. The increase in the surface area of the catalyst enhances active site exposure, consequently resulting in ultrafast $SO_4^{\cdot-}$ generation and concomitant organic pollutant degradation. Notably, studies have demonstrated that the calcination temperature also determines the composition of $AgFeO_2$ nanocatalysts; increasing the proportion of hexagonal 2H polytypes in $AgFeO_2$ (*i.e.*, 2H- $AgFeO_2$) enhances persulfate activation.²⁶

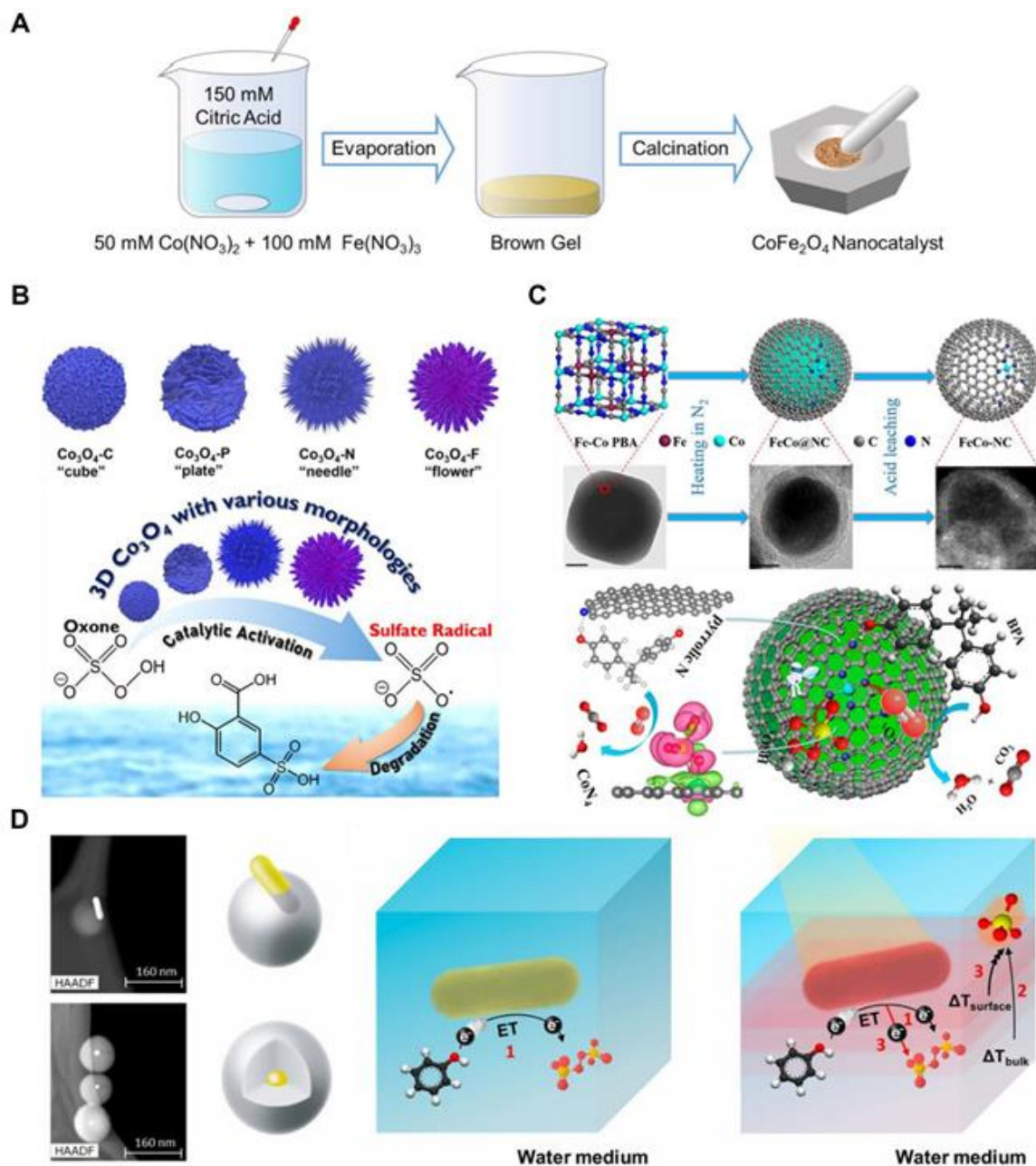


Figure 9.2 Typical metal and metal oxide nanocatalysts for persulfate activation. (A) Chemical solution precipitation fabrication procedure for CoFe_2O_4 nanocatalysts. (B) Illustrations of 3D Co_3O_4 nanocatalysts with various morphologies and corresponding catalytic degradation of 5-sulfosalicylic acid. Reproduced from ref. ²⁷ with permission from Elsevier, Copyright 2020. (C) Preparation procedure of single-atom cobalt catalysts and the catalytic mechanism for PMS activation. Reproduced from ref. ³⁵ with permission from ACS, Copyright 2018. (D) HAADF images and schematics of Au "Janus" nanorods and fully silica-coated Au nanospheres (left

panel). Schematic of the mechanisms involved in phenol degradation under dark (middle panel) and (right panel) sunlit conditions in a water medium. ET, electron transfer; ΔT_{bulk} , temperature increase in bulk solution; $\Delta T_{\text{surface}}$, temperature increase at nanorod surface. Reproduced from ref. ⁶² with permission from PNAS, Copyright 2020.

The effects of morphology and structure of metal oxide nanocatalysts on persulfate activation have also been studied. Nanoscale Co_3O_4 catalysts with a variety of morphologies were synthesized for PMS activation.²⁷ With the variation of Co_3O_4 morphologies from cubic, laminate, and needle-like to floral structures, the active sites of Co_3O_4 gradually increased (Figure 9.2B). To this end, a sol-gel combustion method was developed to fabricate metal oxide nanocatalysts with tuned specific surface area and porosity.^{28,29} In addition, structural defects such as distortion, vacancy, and tortuosity in metal oxide nanocatalysts influence catalytic persulfate activation. These phenomena apply to NiO-ZnO composite oxides, Co_3O_4 -illite composites, and $\text{Mn}_2\text{O}_3\text{-LaMnO}_3\text{-}\delta$ perovskite composites.^{18,30,31} Notably, the peroxy bond length of PMS adsorbed on nanocatalysts with an oxygen vacancy is 1.438 Å, while it is only 1.346 Å for nanocatalysts with no oxygen defects. Fundamentally, a longer peroxy bond length of PMS-catalyst adsorption intermediates indicates a lower energy barrier of PMS activation, facilitating facile ROS generation.

In addition to metal oxides, transition and precious metals are potent catalysts for persulfate activation. For instance, nanoscale zero-valent Co, Cu, Mo, W, and Ni catalysts were demonstrated to decompose PDS and PMS to yield radicals, thereby achieving organic pollutant degradation *via* oxidation.^{32,33} Overall, studies verified that various organic pollutants were removed from water in a few minutes to one hour. Studies also demonstrated that the crystal facets of metals impart a significant effect on persulfate activation. For example, noble metal catalysts such as Ru, Rh, Ir, Pt, and Au with exposed (111) facets accelerated electron transfer from organic pollutants to PMS, leading to pollutant oxidation and PMS reduction without involving $\text{SO}_4^{\cdot-}$ (*i.e.*, non-radical generation).³⁴

Single-atom metal-based catalysts were found to be usable for persulfate catalytic decomposition. Li and co-workers developed porous N-doped

graphene anchored with single-atom cobalt as highly reactive and stable PMS nanocatalysts to degrade recalcitrant organic contaminants.³⁵ The CoN₄ sites with central Co atoms act as active sites to optimize the binding energy and catalyze PMS. Meanwhile, the adjacent pyrrolic N sites are responsible for adsorbing organic molecules. This dual reaction site remarkably reduces the migration distance of singlet oxygen, maximizing the use of singlet oxygen and PMS (Figure 9.2C). In this process, the molar ratio of PMS to pollutant bisphenol A is only 3.71, much lower than the other counterparts, namely homogeneous and heterogeneous catalytic activation of PMS. In another similar study, pyridine-supported single-atom cobalt nanocatalysts were confirmed to hold a π -conjugation and metal-support interaction, allowing efficient adsorption and activation of PMS. When the as-prepared cobalt nanocatalysts were assembled with carbon supports in a thin film composite membrane, the contaminants were degraded in a single-pass filtration process with feed water containing PMS and a residency time of 36 ms.³⁶

A light-to-heat conversion enabled by Au nanorods irradiated by simulated sunlight for enhancing PDS activation was reported.³⁷ The as-prepared photothermal Au nanorods were placed on silica to enhance the colloidal stability in aqueous solutions. The isolated Au nanocatalyst islands took the role of facilitating the photocatalytic activation of PDS. In addition to behaving like an “electron shuttle”, the Au nanorods thermally decomposed PDS to generate $\text{SO}_4^{\cdot -}$. This study, for the first time, exemplifies a localized thermal effect that can catalyze PDS for pollutant oxidation (Figure 9.2D).

9.2.2 Titanium Dioxide

Titanium dioxide is a widely-studied nanocatalyst used to decompose persulfate *via* heterogeneous catalytic and photocatalytic processes. Hoffmann *et al.* developed oxygen vacancy-enriched cobalt-doped black TiO₂ nanotubes as efficient, stable, and reusable heterogeneous nanocatalysts to catalyze PMS (Figure 9.3A).³⁸ The results unveiled that increasing the oxygen vacancies in TiO₂ improved its catalytic activity. Compared to conventional TiO₂ nanotubes without defects, the defect-

abundant TiO_2 was advantageous for the adsorption of PMS on TiO_2 due to the formation of interfacial Lewis acid–base pairs.

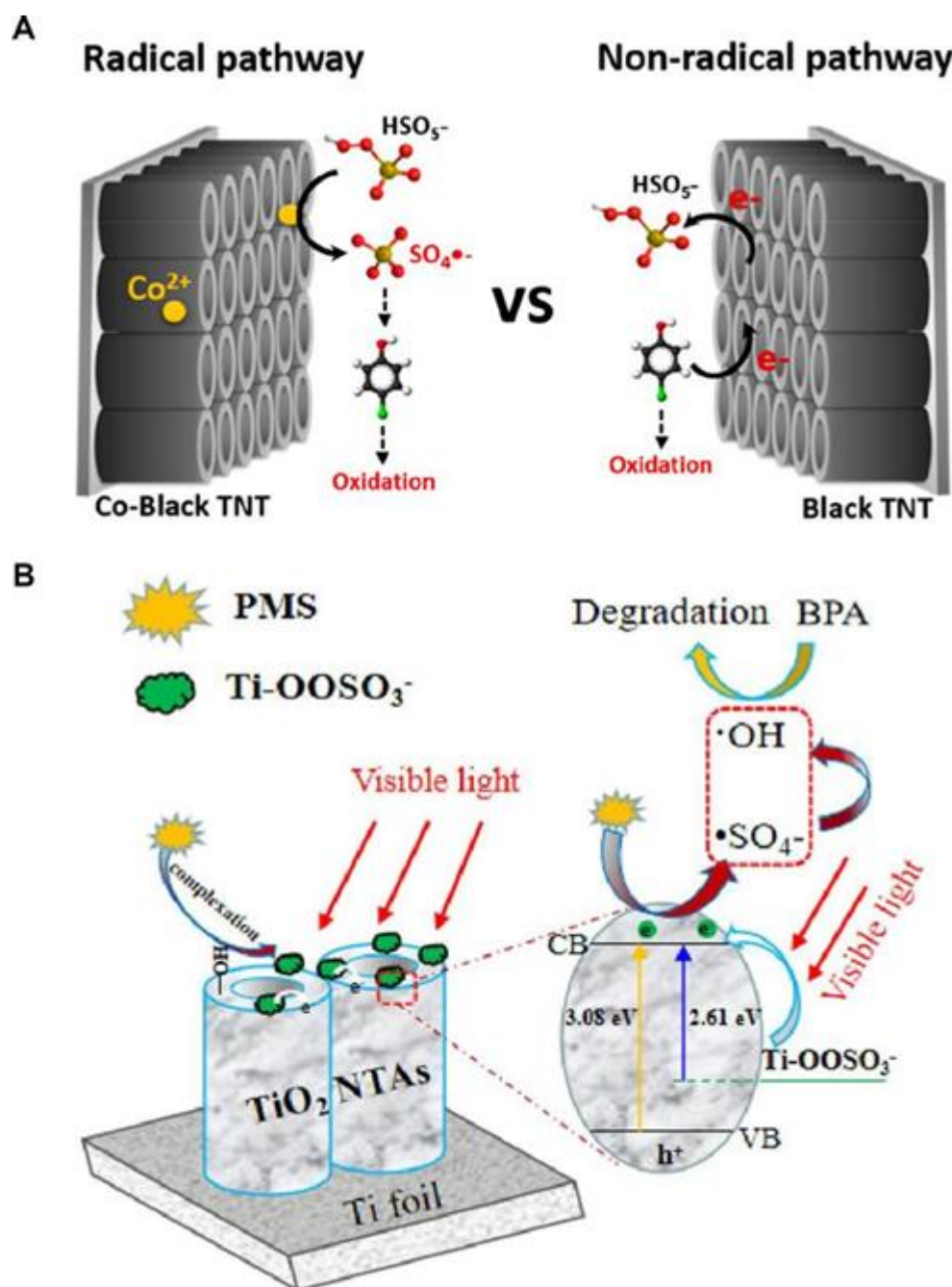


Figure 9.3 TiO_2 -based nanocatalysts for persulfate activation. (A) Schematic illustrations for the radical-involving pathway on cobalt-doped black TiO_2 nanotubes (left panel) and the non-radical-involving pathway on black TiO_2 nanotubes (right panel) for 4-

chlorophenol degradation. Reproduced from ref. ³⁸ with permission from ACS, Copyright 2019. (B) Schematic illustration of the visible light-induced activation of peroxymonosulfate using TiO₂ nanotubes arrays for enhanced degradation of

bisphenol A. Reproduced from ref. ⁴⁰ with permission from Elsevier, Copyright 2020.

Under ultraviolet light illumination the photoactive TiO₂ is excited to generate electrons to enable photocatalytic persulfate activation. The excited photoelectrons then proceed to cross over the bandgap of TiO₂ from the valance band (resulting in a hole) to the conduction band, triggering autonomous reduction and oxidation reactions on TiO₂. As an efficient electron scavenger, persulfate prevents the electron–hole recombination and facilitates hole oxidation.³⁹ A recent study demonstrated that TiO₂ nanotubes could oxidize organic contaminants under visible light irradiation in the presence of PMS.⁴⁰ Given such experimental observations, questions arise about how contaminants degrade. One hypothesis considers that contaminants are indirectly oxidized by persulfates, which accept photoelectrons to generate radicals and remove pollutants (Figure 9.3B). Another hypothesis involved hole oxidation *via* two-electron abstraction. The study further confirmed that the photoelectrons were responsible for PMS activation and pollutant degradation. Based on these observations, they modified TiO₂ by introducing coinage elements such as Co(ii), Fe(ii), Cu(i), and Ag(i) to enhance persulfate activation.^{41–44} These metals enhanced photoelectron transfer and impeded persulfate oxidation, thereby accelerating pollutant degradation.

9.2.3 Molybdenum Disulfide

Molybdenum disulfide (MoS₂) is classified as a transition metal dichalcogenide. Similar to silicon, MoS₂ is a diamagnetic, indirect bandgap semiconductor with a bandgap of 1.23 eV. MoS₂ has a layered structure, in which a plane of molybdenum atoms is sandwiched between planes of sulfide ions. These three strata form a monolayer of MoS₂. Bulk MoS₂ composes stacked monolayers, which interact *via* van der Waals forces. Crystalline MoS₂ existing in nature exhibits one of two phases, 2H-MoS₂ and 3R-MoS₂, where the “H” and the “R” indicate hexagonal and

rhombohedral symmetry, respectively. Both the 2H- and 3R-phases are semiconducting. In addition, a metastable crystalline phase known as 1T-MoS₂ was discovered by intercalating 2H-MoS₂ with alkali metals. This phase has tetragonal symmetry and is metallic.

MoS₂ has been employed as a catalyst for desulfurization, hydrogenation, and hydrogen evolution reactions in petrochemistry, organic synthesis, and energy storage, respectively. A recent study has demonstrated that a 2H/1T multiphase MoS₂ enables the complete degradation of 2,4-dichlorophenol using PMS in 60 minutes at a rate constant of $6.20 \times 10^{-2} \text{ min}^{-1}$, twice as high as that of the pure 2H-phase MoS₂.⁴⁵ This suggests that hybridizing the 2H and 1T phases of MoS₂ to optimize electron transport and generate Mo(III) is beneficial for heterogeneous PMS activation ([Figure 9.4A](#)).

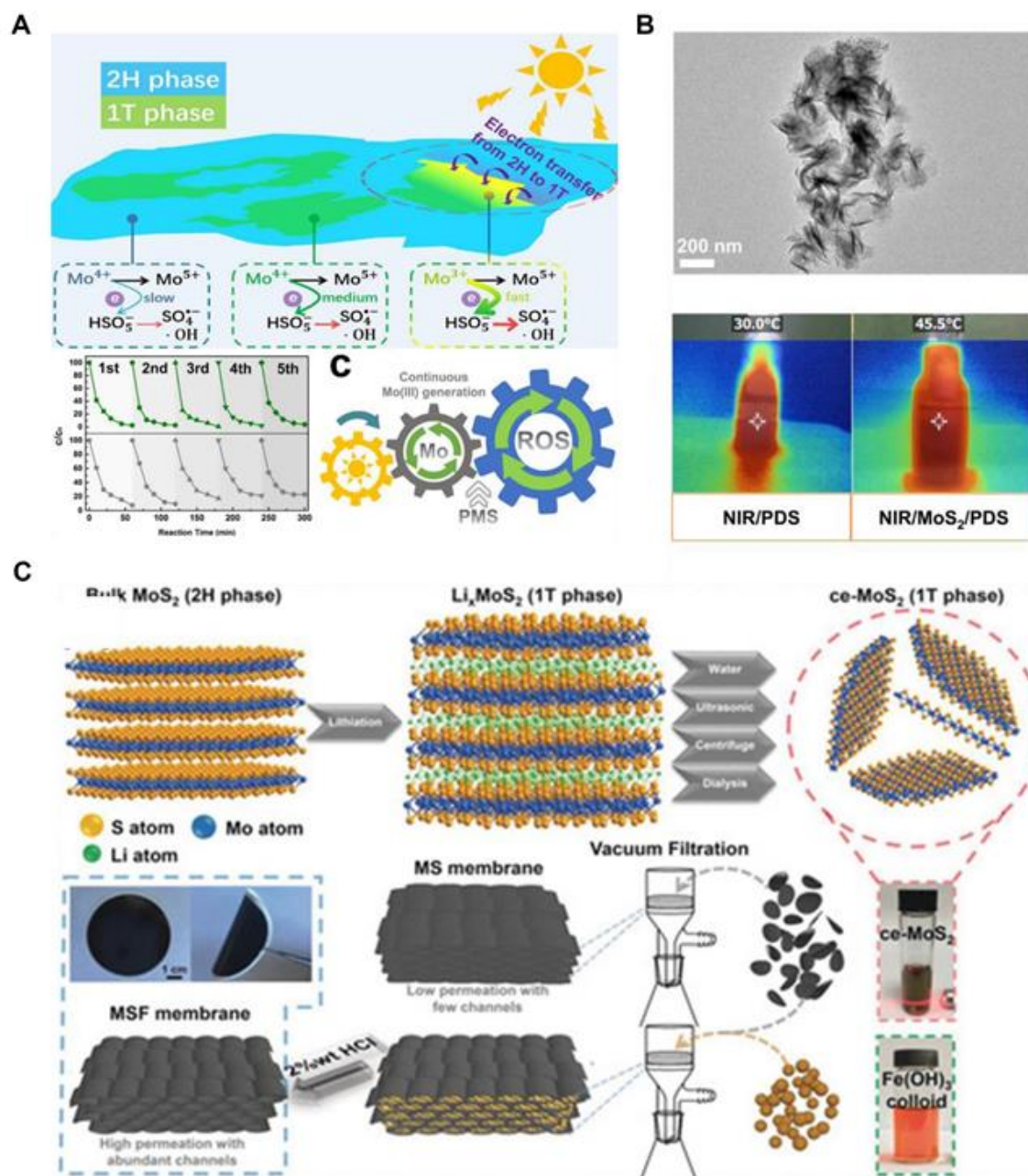


Figure 9.4 MoS₂-based nanocatalysts for persulfate activation. (A) Proposed mechanism for the photoinduced PMS activation on the surface of multiphase MoS₂. Reproduced from ref. ⁴⁵ with permission from ACS, Copyright 2019. (B) TEM and IR images of the oxidation processes enabled by MoS₂ nanosheets, indicating a significant temperature change of the NIR–MoS₂ system. Adapted from ref. ⁴⁶ with permission from Elsevier, Copyright 2021. (C) Schematic illustration of the exfoliation of MoS₂ from

bulk to monolayer and preparation procedure of a laminar MoS₂ nanoreactor. Adapted from ref. ⁴⁷ with permission from Wiley, Copyright 2019.

Notably, MoS₂ monolayers have a direct 1.8 eV electronic bandgap, which shows electrically conductive and photoactive properties. Therefore, MoS₂ has the potential to provide photoelectrons under the illumination of visible light. Irradiating using near-infrared light, a MoS₂ nanocatalyst rendered a localized high temperature at the liquid–solid interface, decreasing the energy gap of PDS activation by MoS₂, which readily facilitated radical generation and carbamazepine degradation (Figure 9.4B).⁴⁶ This phenomenon has been ascribed to the fast recombination of photoelectrons and holes of MoS₂ with a confined laminar structure.

Assembling MoS₂ nanocatalysts maximizes the use of persulfate to achieve efficient contaminant removal. In a previous study, a bulk MoS₂ was proved to oxidize bisphenol A using PMS *via* single-electron reduction, exhibiting better performance than that using an ultrathin metallic 1T phase MoS₂ (*i.e.*, ce-MoS₂) due to the dense active sites on MoS₂ with highly exposed (001) facets and (100) edges. These featured sites were found to be superior for PMS adsorption.⁴⁷ Based on these findings, the ce-MoS₂ nanosheets were then assembled into a thin, free-standing membrane with confined laminar channels (Figure 9.4C). When flowed through these nanoscale channels, PMS was effectively activated to yield free radicals and enable sustainable BPA degradation (> 90%) within 60.4 ms. The substantial mass transfer enhancement under confinement effects was verified to be attributed to the desirable performance.

9.2.4 Carbonaceous Nanomaterials

Carbonaceous nanocatalysts such as carbon nanotubes (CNTs), graphene, and graphene derivatives have been validated as organic pollutant oxidants *via* persulfate activation. Employing CNTs as PDS activation catalysts can achieve organic pollutant degradation without relying on $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $^1\text{O}_2$.⁴⁸ Remarkably, the non-radical involving oxidation efficiency was related exponentially to the electric potential of the formed CNT–PDS*

complex (Figure 9.5A).^{49,50} In addition, the oxygen functional groups on the CNTs resulted in a negative zeta potential at neutral pH, facilitating PDS adsorption on the CNTs due to increased electrostatic interactions.⁵⁰ The study confirmed that oxygen-functionalized CNTs accelerate sulfamethoxazole oxidative degradation *via* PDS activation in acidic conditions.⁵¹ These studies verified that the PMS–CNT system enabled a singlet oxygenation process for radical production.⁵² The activated carbon with carbonyl groups oxidizes organic pollutants by activating PDS in accordance with a mechanism similar to that for the CNTs.^{53–55} Similar to the roles of oxygen in CNTs, nitrogen-doping of CNTs significantly influences PDS activation, as shown in Figure 9.5B.⁵⁵ The functionalization of nitrogen on CNTs remarkably promotes PMS adsorption, essentially increasing the potential of N–CNT–PMS* complexes and boosting pollutant degradation efficiency.⁵⁵

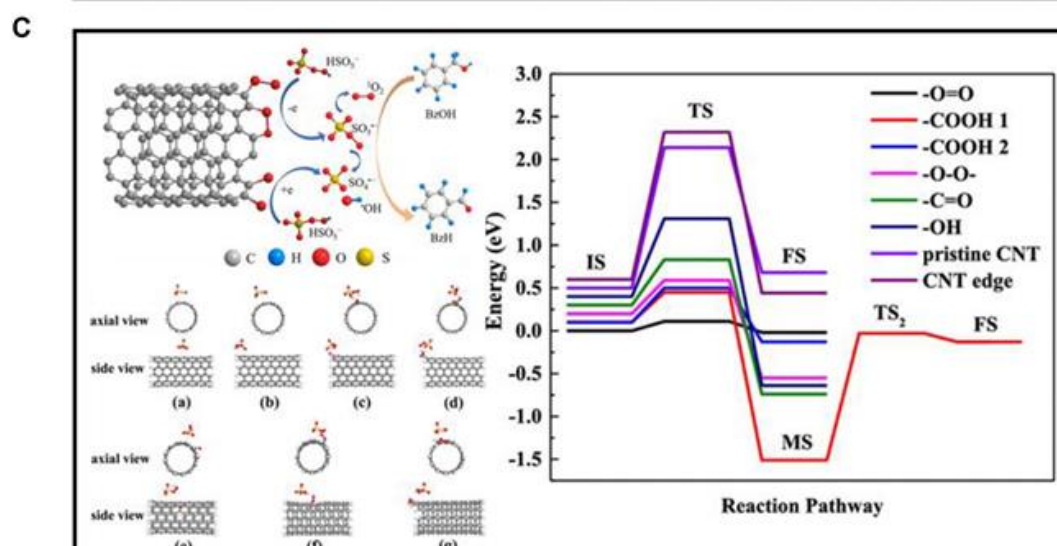
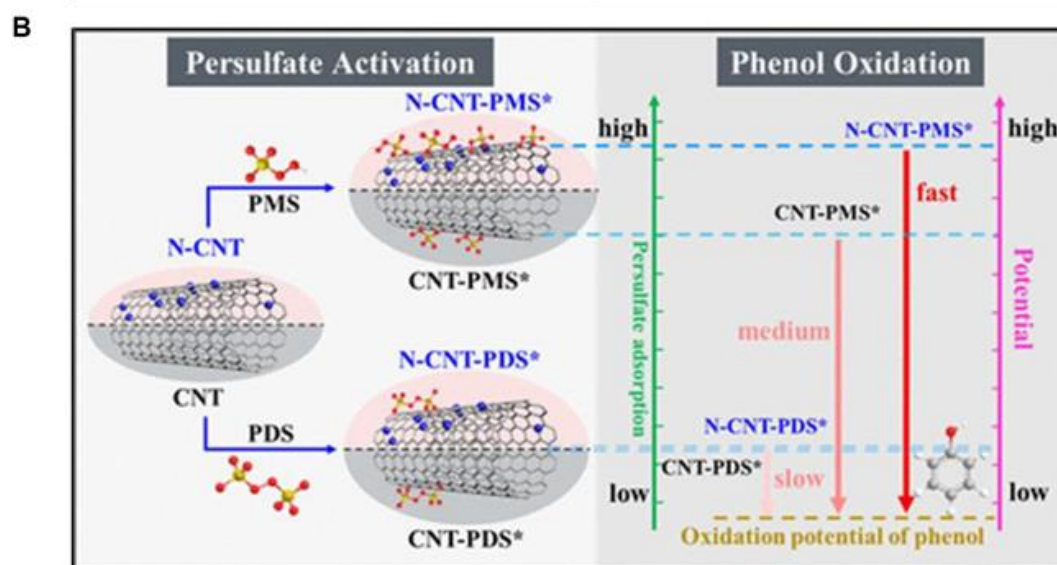
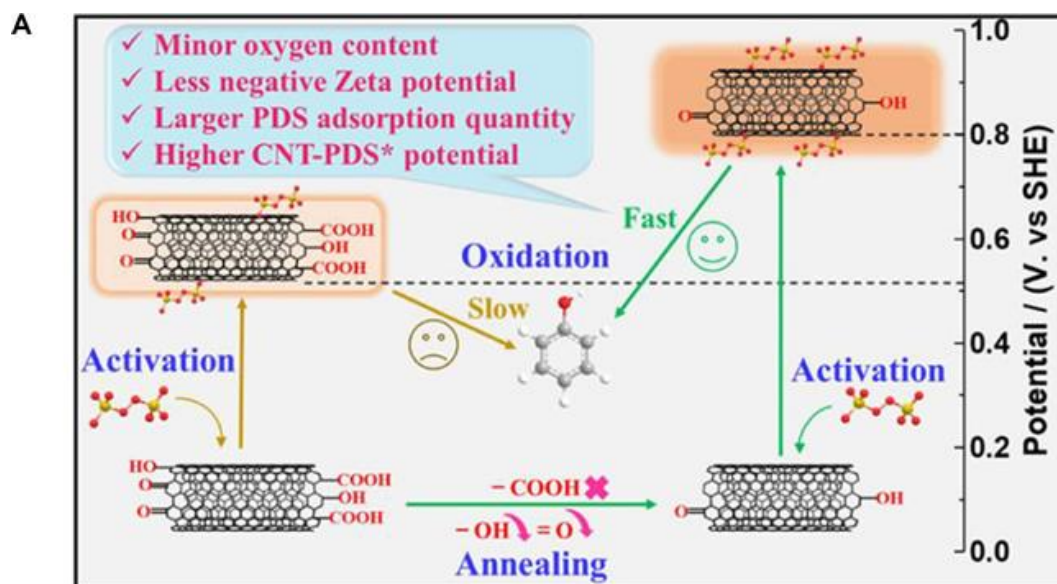
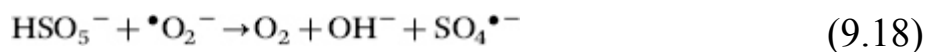
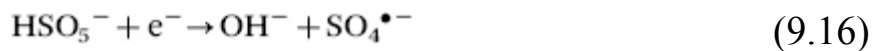


Figure 9.5 Carbonaceous nanocatalysts for persulfate activation. (A) Illustration of the non-radical oxidation of phenol with different CNTs using the PDS–CNT system and the significance of oxygen-containing groups in the PDS catalytic process. Reproduced from ref. ⁵⁰ with permission from ACS, Copyright 2020. (B) Schematic of the non-radical oxidation of phenol using the PMS–N–CNT and PDS–N–CNT systems, highlighting the influence of N-doping on the performance of PDS/PMS activation. Adapted from ref. ⁵⁵ with permission from ACS, Copyright 2020. (C) Proposed mechanism of PMS activation on OCNT-800 and the oxidation of benzyl alcohol into benzaldehyde. Schematic of the structures and reaction pathways of PMS molecules adsorbed on pristine CNTs and CNTs with different oxygen-containing functional groups. Adapted from ref. ⁵⁶ with permission from ACS, Copyright 2020.

Recent studies confirmed that nucleophilic carbonyl groups could render a redox cycle to generate $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals, whereas electrophilic oxygen-containing groups were identified as electron captors to activate PMS and form $\text{SO}_5^{\cdot-}$ (Figure 9.5C).⁵⁶ Although nanocatalysts such as biochars, activated carbon, and carbonaceous nanosheets have been investigated for PMS decomposition, the catalytic decomposition mechanisms are not well understood. The effects of material impurity on catalytic activity may be the key obstacle in future works.

Carbon nitride (*i.e.*, C_3N_4) is a type of carbonaceous material with photoactivity like that of semiconductors. Studies demonstrated a high-performance C_3N_4 catalyst–PMS system for dye degradation. The system was confirmed with a high kinetic rate constant of pollutant degradation under visible light. Quantitative PMS consumption analysis indicated that modified C_3N_4 nanocatalysts more readily activated PMS than pure C_3N_4 nanocatalysts. A high removal rate of ofloxacin was achieved using a Co_3O_4 -modified C_3N_4 nanocatalyst at a mass ratio of PMS to contaminants of 1.63.^{41,42} In sharp contrast, a comparable removal rate of dyes was enabled by conventional C_3N_4 nanocatalysts with a mass ratio of PMS to contaminants of 11.3.⁵⁷ This remarkable comparison explicitly suggested that modification of C_3N_4 nanocatalysts significantly enhanced photoelectron generation. In this photo-driven process, a mechanism for the

generation of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ from PMS with photoelectrons (*i.e.*, e^-) was proposed, as shown in eqn (9.16)–(9.18).



9.3 Prospects and Outlook

The persulfate-mediated pollutant catalytic oxidation enabled by nanocatalysts such as metals and metal oxides, TiO_2 , MoS_2 , and carbonaceous materials has become a research frontier, showing great potential for practical water treatment. Based on the gained experimental proof of ultrafast persulfate activation *via* diverse pathways, future research may focus on translating these catalytic activation processes to real-world applications, though the implementation of persulfate-based AOPs is challenging.¹² We highlight that incorporating effective nanocatalysts into mature water-treatment processes (adsorption, filtration, and coagulation) and/or materials (adsorbents and membranes) is scientifically and technically viable. For instance, integrating nanocatalysts with commercial reverse osmosis membranes (thin film composite membranes) or ultrafiltration membranes (polyelectrolyte membranes) can mitigate membrane organic fouling and biofouling,⁵⁸ as well as achieve water disinfection,⁵⁹ *in situ* remediation of groundwater,⁶⁰ and sludge reduction.⁶¹ PMS photoactive nanocatalysts have the potential to be deployed for large-scale applications, such as in the remediation of organic pollutants of rivers and streams as both C_3N_4 and PMS are environmentally benign.

Albeit an early-stage study area, explorations on nanocatalyst assembly to enhance persulfate activation are productive. Compared to traditional batch suspension catalytic processes, constructing nanocatalysts in a nanoreactor with confined structures can improve reaction kinetics, nanocatalyst stability, and mass transport of contaminants to nanocatalyst active sites, promoting persulfate oxidation efficiency and extending

persulfate-mediated AOPs to other environmental remediation scenarios. At the micro level, the fine control of crystalline structure and morphology of nanocatalysts can induce additional effects, which may minimize persulfate consumption, enhance reaction selectivity for targeted pollutants, and decrease process expense, making pollutant degradation using persulfate practicable.

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Chapter 10

Fenton-like Nanocatalysts for Water Purification

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10.1 Introduction

10.1.1 Background

Water crisis related to the release of persistent organic pollutants (POPs) to the environment is one of the most difficult conundrums.^{1–3} While being a serious threat to the aquatic system and human health, it remains a technical challenge to effectively remove POPs in trace levels by either traditional physical and chemical means or activated sludge-based biodegradation. Therefore, treatment technologies that are specifically designed for degrading POPs have become a research hotspot in the field of environmental science and technology.⁴ In recent years, the advanced oxidation process (AOP) based on the production and use of strong oxidation free radicals has advanced rapidly, during which organic molecules are gradually degraded by active radicals into small molecules, such as carbon dioxide, water, and inorganic salts, ultimately removing the toxicity and harmfulness of POPs.⁵

The Fenton reaction is an effective and easy-to-operate AOP method, in which ferrous ions (Fe^{2+}) can catalyze hydrogen peroxide (H_2O_2) by losing one electron for the generation of hydroxyl radicals ($\cdot\text{OH}$; standard electrode potential (E^0) = 2.80 V).^{6,7} However, the traditional Fenton process has suffered some drawbacks that have limited its large-scale application, such as harsh pH requirements (around pH 3), iron sludge production, and difficulties in recycling.⁸ To address these disadvantages, heterogeneous Fenton-like processes that use a solid catalyst to promote radical production have extended to a wide pH range and thus avoided the generation of iron sludge.^{9,10} Particularly, nanoscale Fenton-like catalysts have gained momentum in the research of Fenton catalysis because of their large surface area, good stability, and high activity. Indeed, the Fenton-like nanocatalysts must be recyclable in field applications. Although metal-based catalysts (*e.g.*, precious metals and metal oxides) have demonstrated excellent catalytic efficiency, the extensive use of metal materials causes high demand of resources and energy consumption; the leaching of metals in the reaction process will also cause secondary pollution.^{11–14} Therefore, as alternative Fenton-like nanocatalysts, carbonaceous materials have attracted considerable interest, due to their tunable physical and chemical properties (*e.g.*, thermal and chemical stability, adjustable pore structure, and surface chemistry). Recently, research of hybrid Fenton-like nanocatalysts, *e.g.*, metal/metal oxide@porous carbon, has also been very popular for water purification.^{15–19}

Although Fenton-like nanocatalysts utilize the redox cycle of transition metals to overcome most defects of traditional Fenton catalysis, there are still some problems deterring their further application such as low activity, poor stability, and low oxidant utilization under neutral conditions.^{11,20} Therefore, in recent years, more attempts have been devoted to creating novel Fenton-like nanocatalysts promoting electron transport pathways or specific oxidation active species that can enhance catalytic efficiency and oxidant utilization. For example, a dual reaction center Fenton-like catalytic process mimicking the mechanism of galvanic-like cells makes the oxidation and reduction reactions take place at different active sites.^{21–25} The dual-center Fenton-like catalytic

process was found to be dominated by singlet oxygen ($^1\text{O}_2$) for efficient degradation of phenolics because of the electrophilic nature of $^1\text{O}_2$.^{26–30} Likewise, the single-atom Fenton-like catalytic process draws support from a higher selectivity and greater surface free energy of a single atom to realize a catalytic process with a low dosage but extraordinary performance.^{29,31,32}

Furthermore, the combination of Fenton-like catalysis with other AOPs has been proposed to form hybrid Fenton-like processes. The typical AOP-assisted Fenton-like processes, such as photo-Fenton/Fenton-like processes, electro-Fenton-like processes, cavitation-Fenton-like processes, and microwave-Fenton-like processes, have been widely used in practical treatment because of their excellent synergistic effects and competitive costs.

10.1.2 Scope of the Chapter

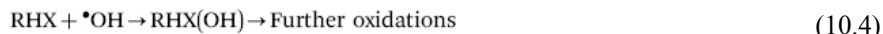
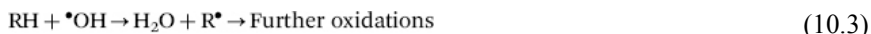
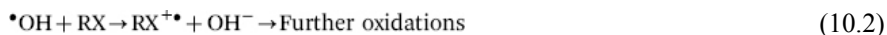
This chapter aims to give an account of the fundamental aspects of heterogeneous Fenton-like catalysis used in wastewater purification and is organized into five sections. While a general background is given in Section 10.1, Section 10.2 provides the fundamental principles of the chemistry of Fenton reactions that connects radical reactions with AOPs. Section 10.3 depicts typical heterogeneous Fenton-like nanocatalysts in detail. Next, Section 10.4 presents some novel Fenton-like catalytic processes. Lastly, Section 10.5 is devoted to the development of hybrid Fenton-like processes. Prospects and guidelines of Fenton-like research are put forward in the last section of conclusions and future research directions. We hope that this review can provide a fundamental basis for novel Fenton-like catalysis design and cast a beam of light into its future research.

10.2 Chemistry of Fenton Reactions

10.2.1 Homogeneous Fenton Catalytic Processes

Homogeneous reaction refers to the catalytic action of catalyst and reactant in the same homogeneous phase, *i.e.*, water in most cases. Homogeneous Fenton catalytic process uses Fe^{2+} as catalysts to produce $\cdot\text{OH}$ (see eqn (10.1); $k \approx 76 \text{ L mol}^{-1} \text{ s}^{-1}$) that then initiate the decomposition of organic pollutants *via* redox reactions (eqn (10.2)), dehydrogenation (hydrogen abstraction) (eqn (10.3)), and electrophilic addition to π systems (hydroxylation) (eqn (10.4)).³³ Notably, the Fe^{2+} consumed during the Fenton reaction can be regenerated by reduction of ferric ions (Fe^{3+}), as shown in eqn (10.5) ($k \approx 0.02 \text{ L mol}^{-1} \text{ s}^{-1}$) and eqn (10.6) ($k \approx 7.82 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$). In the homogeneous Fenton system, the mass transfer limitation among dissolved active reagents is negligible. Furthermore, due to the rapid electron transfer rate and high utilization rate of catalyst, soluble iron salts offer a very high process efficiency. However, although Fe^{2+} can exist even at neutral pH in a dissolved state, Fe^{3+} forms a ferric hydroxide sludge at $\text{pH} \geq 3$.³⁴ Thus, strict acidic conditions are necessary for practical applications, which not only involve the high cost of chemicals used for acidifying effluents in the pre-treatment stage but also the expense for subsequently neutralizing them to meet the need for discharge.³⁵

Moreover, the concentration of the iron ion is required to be kept in the range of 50–80 ppm for batch processes, which is far beyond the limit of the European Union (2 ppm) for direct discharge of wastewater into the environment.³⁶



10.2.2 Heterogeneous Fenton Catalytic Processes

A heterogeneous reaction is a chemical reaction where the reactants are in different phases from each other. Fenton processes can be carried out under heterogeneous conditions by stabilizing the iron within the catalyst's structure,^{35,37} such as natural and synthetic zeolites,³⁸ mesoporous materials,³⁹ pillared interlayered clays,⁴⁰ Nafion films,⁴¹ polymeric resins,⁴² activated carbons (ACs),⁴³ ashes,⁴⁴ pumice particles⁴⁵ and aluminates.⁴⁶ The heterogeneous Fenton catalytic process is a kind of interfacial reaction where H_2O_2 can be excited effectively to produce $\cdot\text{OH}$ on the surface of catalysts.⁴⁷ Owing to the limited Fe^{3+} leached from the catalysts in a heterogeneous system, the iron sludge generated from precipitation of Fe^{3+} under $\text{pH} > 3$ is hindered. Therefore, heterogeneous catalysts can not only be recycled facilely but can also circumvent the effect of a limited pH range.^{2,48} The utilization of H_2O_2 in heterogeneous Fenton systems involves two ways: (i) reaction with the leached Fe from the catalysts similar to a homogeneous Fenton reaction (see eqn (10.1)–(10.5)), and (ii) reaction with surface Fe ($\square\text{Fe(III)}$) (see eqn (10.7) and (10.8)).^{49,50}



However, in both homogeneous and heterogeneous Fenton process, the low rate constant of the reduction process of $\text{Fe}^{3+}/\text{Fe(III)}$ ($0.001\text{--}0.01 \text{ M}^{-1} \text{ s}^{-1}$) determines the overall efficiency of the whole Fenton reactions.⁵¹ Also, the reduction of $\text{Fe}^{3+}/\text{Fe(III)}$ will consume H_2O_2 to produce hydroperoxyl radicals ($\text{HO}_2\cdot$), the E^0 of which (1.50 V) is lower than that of $\cdot\text{OH}$. Therefore, this invalid decomposition of H_2O_2 greatly reduces the utilization rate of H_2O_2 in the whole catalytic process. Hence, the key issue to be dealt with in the classical heterogeneous Fenton process is how to promote the redox cycling of $\text{Fe(III)}/\text{Fe(II)}$ and enhance the utilization rate of H_2O_2 .

10.2.3 Influencing Parameters

pH: For Fe-based catalysts, it is not surprising that the optimum pH is around 3 for both Fenton and Fenton-like reactions. Working at a more alkaline pH may decrease the radical production of H_2O_2 because of the precipitation reaction between the metallic cation and hydroxide (OH^-) to form the catalyst hydroxide (see eqn (10.9)).⁵² Also, the reaction between H_2O_2 and OH^- further decreases the H_2O_2 concentration (see eqn (10.10)).⁵³



However, it is observed that depending on the experimental conditions and the Fenton-like catalyst, the radical production can be favored even at neutral or alkaline pH.

H_2O_2 dosage: The H_2O_2 concentration increases the removal efficiency of micropollutants as it enhances the $\cdot\text{OH}$ formation. Despite this, excessive concentrations of peroxide might lead to the appearance of secondary reactions challenging the efficiency of the process. Eqn (10.11) can quench the $\cdot\text{OH}$ to produce $\text{HO}_2\cdot$ radicals and water. Consequently, eqn (10.12) shows how the produced radical species hinder the degradation of the pollutant, acting as a radical scavenger for $\cdot\text{OH}$, leading to extra chemical usage and cost.



Catalyst dosage: The catalyst dosage behaves similarly to the H_2O_2 dosage. Mainly, radical production is favored when increasing the amount of catalyst. In the homogeneous Fenton systems, excessive concentrations lead to the reaction of the catalyst with the $\cdot\text{OH}$ radical inhibiting the degradation of micropollutants, according to eqn (10.13).⁵⁴



In heterogeneous Fenton-like systems, the increase in the catalyst dosage mainly increases the degradation. Despite this, some Fenton-like systems such as photo-Fenton-like systems may also be inhibited with higher amounts of catalyst. In this system, the high amounts of catalyst lead to agglomeration and a reduction in the photocatalytic efficiency.⁵⁵

10.3 Typical Heterogeneous Fenton-like Nanocatalysts

10.3.1 Metal Oxide Fenton-like Catalysts

10.3.1.1 Pure Metal Oxide Fenton-like Catalysts

Different Fenton-like Catalysts show diverse properties (see Table 10.1). Many pure metal oxides in nature, which exhibit multiple oxidation states, can be used as Fenton-like catalysts through a simple redox cycle. In this review, we classify these into two types of materials: iron-based Fenton-like catalysts and iron-free Fenton-like catalysts.

Table 10.1 Typical heterogeneous Fenton-like nanocatalysts.

	Catalyst	Synthetic method	Properties	Reference
Pure metal oxide	Fe ₃ O ₄ nanosphere	Hydrothermal method	Pure metal oxides rely on a single active site of a single metal for a redox reaction, which has the disadvantages of low reaction activity, the great influence of speed limiting steps, and low reusability	58
	Goethite	Chemical precipitation		3
	CuO nanosheet	Alkaline H ₂ O ₂ reaction		60
	CuO fibers	Electrospinning and calcination		61
	Cu ₂ O	Solvothermal method		62
	MnO ₂	Hydrothermal method		64
	Nano Mn ₃ O ₄	Hydrothermal method		65
	CeO ₂	Precipitation method	67	
Composite metal oxides	Fe ⁰ –Fe ₃ O ₄	Coprecipitation and heat-treat	The doping of heterogeneous metals can accelerate the surface electron transfer rate and slow down the rate-limiting step, but it cannot restrain the occurrence of the rate-limiting step	71
	Cu ⁰ –Fe ₃ O ₄	Solvothermal method		72
	Fe ₃ O ₄ –CeO ₂	Precipitation method		73
	Ce _x CuO _y	Hydrothermal method		74
Metal–metal oxide@porous carbon hybrids	CNTs/FeOOH	Precipitation and dipping	The addition of inorganic carbon not only improves the surface electronic conductivity but also provides a large specific surface area for adsorption and reaction sites	78
	Al ⁰ –CNTs–CNTs–Fe–Cu	Liquid phase reduction		84

FeCu@C	Solvothermal	92
Fe ₃ O ₄ @Fe-graphene aerogel	Gelation and carbonization	96
Fe- N/Pentlandite/Al ₂ O ₃ /C	Polymerization carbonization	99

Iron is a hot element in terms of the research of Fenton-like catalysis. Even though there are many kinds of elements that can be used to stimulate H₂O₂ to produce strong active oxygen species such as $\cdot\text{OH}$, iron remains dominant in practical application, which is attributed to the following advantages: (a) high abundance, (b) environmental friendliness, (c) high redox reactivity, and (d) low commercial cost.⁵⁶

Iron oxide minerals, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), ferrihydrite (FeOOH), goethite ($\alpha\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$) are considered as efficient Fenton catalysts.^{3,57,58} However, iron-based Fenton-like catalysts also show severe practical disadvantages that need to be taken into account. Due to the existence of mass transfer resistance, the reduction rate of Fe^{3+} on the surface of catalysts is at least three orders of magnitude slower than that in the homogeneous Fenton reaction. Furthermore, uncontrolled leaching of iron ions from the catalyst surface will also lead to rapid sludge generation without pH adjustment.⁵⁶ Therefore, research efforts have been put into finding new practically-acceptable and economically-viable Fenton-like nanocatalysts like copper oxide, manganese oxide, and cerium oxide.

Compared with iron, copper, which has the same redox characteristics, has a wider pH response range (3–9). In addition, the reduction rate of Cu^{2+} in the H₂O₂ system is about $460\text{ M}^{-1}\text{ s}^{-1}$ which is faster than that of iron ($76\text{ M}^{-1}\text{ s}^{-1}$).⁵⁹ Notably, copper species are more likely to form complex compounds with phenolic organic ligands in solution, which is beneficial for the degradation of phenolics.^{11,14,20} Therefore, promising progress concerning Cu-based Fenton-like catalysts, *i.e.*, Cu₂O and CuO,^{60–62} has been made in the past decade.

Manganese, on the other hand, can exist in extra oxidation states ranging from Mn(0) to Mn(+7), which is conducive to electron transfer in a Fenton-like reaction. Besides, its abundant presence in soil and low toxicity promote its wide application in Fenton-like catalysis.⁵⁶ MnO_x (MnO, Mn₂O₃, MnO₂, and Mn₃O₄) has been deemed to be a promising candidate to activate H₂O₂ as the variation of the oxidation state involving a single electron transfer enables them to act as active sites for catalytic reactions.^{30,63–65}

Cerium oxide, a key component of the rare earth metal oxides, has been widely used in heterogeneous Fenton reactions due to its excellent $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle ability.⁶⁶ Different from the radical-attacking mechanism in most Fenton-like systems, the process of organic degradation is located on the surface, where the complexation of H₂O₂ on the CeO₂ surface will generate brown peroxide-like species that are relatively chemically stable and can realize the degradation of surface adsorbed organics *via* an intermolecular rearrangement.^{67–70}

Due to the limitation of a single active site and gradual deactivation caused by frequent valence changes of the metal, the application of pure metal oxide Fenton-like catalysts is uncommon. However, there are still numerous research studies exploring how to improve their performance *via* manufacturing defects such as oxygen vacancies and metal vacancies to create more active sites, controlling crystal growth to induce the exposure of crystal surfaces with high energy, regulating morphology to construct a high specific surface area, and so on. These studies not only further tap their potential in the field of Fenton-like process but also give us more basis to enrich their applications.

10.3.1.2 Composite Metal Oxide Fenton-like Catalysts

Pure metal oxide Fenton-like catalysts, based on a single redox-active site, are inevitably characterized by low activity and poor reusability leading to limited utilization of oxidants on the catalyst surface. Therefore, the breakthrough of electron transfer is highly desirable between different redox couples to realize the efficient activation of oxidants.

It was confirmed that zero-valent metals could serve as an electron transfer agent to enhance the redox recycling of transition metals like Fe.^{72,81–85} For example, Costa *et al.* prepared a Fenton-like catalyst Fe⁰/Fe₃O₄ using H₂ temperature-programmed reduction, which exhibited an excellent activity to degrade methylene blue

(MB).⁷¹ It was reported that the thermodynamically favorable electron transfer that occurred at the interface of $\text{Fe}^0\text{--Fe}^{3+}$ significantly enhanced the decomposition of H_2O_2 to $\cdot\text{OH}$ and was conducive to the rapid reduction of Fe^{3+} to Fe^{2+} (see Figure 10.1A). Ding *et al.* also observed that zero-valent copper (Cu^0) can act as a reducing agent to regenerate $\text{Fe}(\text{ii})$ species via an electron transfer from Cu^0 to Fe_3O_4 and thus generate $\text{Cu}(\text{i})$ species *in situ* (see Figure 10.1B).⁷² The E^0 of Cu^+/Cu (0.522 V) and $\text{Cu}^{2+}/\text{Cu}^+$ (0.17 V) are lower compared with $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.771 V).

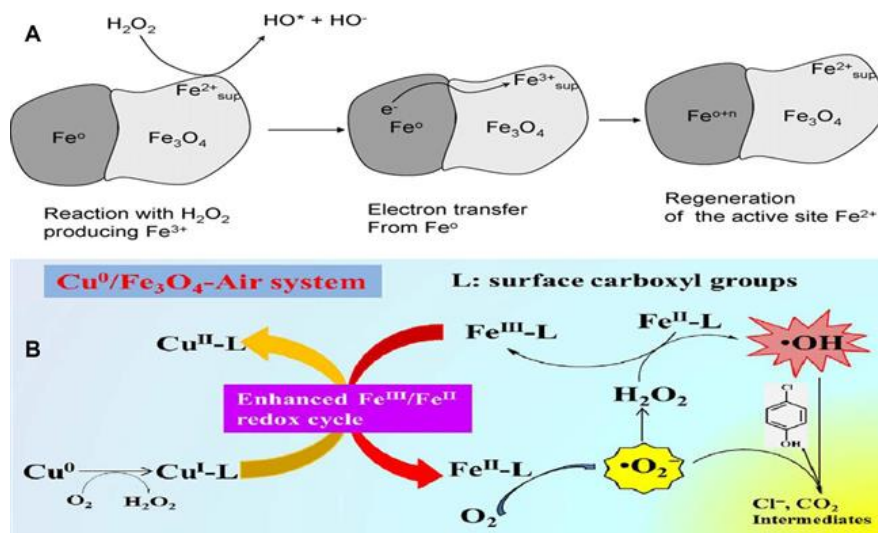


Figure 10.1 (A) Schematic representation of the electron transfer from Fe^0 to Fe^{3+} magnetite to regenerate $\text{Fe}^{2+}_{\text{surf}}$. (B) A possible mechanism for the activation of O_2 on $\text{Cu}^0\text{--Fe}_3\text{O}_4$ composites. Reproduced from ref. ⁷¹ and ⁷² with permission from Elsevier, Copyright 2008 and 2017.

In addition, the combination of various metal oxides and lattice doping can also realize the rapid transfer of interface electrons and promote the formation of active radicals. Xu *et al.* prepared magnetic nanoscale $\text{Fe}_3\text{O}_4\text{--CeO}_2$ composites using impregnation method to promote the Fenton oxidation of 4-chlorophenol (CP) by H_2O_2 .⁷³ In this system, $\cdot\text{OH}$ was generated in two ways. One is the adsorption of $\cdot\text{OH}$ on the surface of catalyst ($\cdot\text{OH}_{\text{ads}}$), which is activated from H_2O_2 by both interface electron circulation between $\square\text{Fe}^{3+}$ and $\square\text{Fe}^{2+}$ (0.77 V for $\text{Fe}^{3+}/\text{Fe}^{2+}$) and between $\square\text{Ce}^{4+}$ and $\square\text{Ce}^{3+}$ (1.44 V for $\text{Ce}^{4+}/\text{Ce}^{3+}$). The other is the free $\cdot\text{OH}$ in the bulk solution ($\cdot\text{OH}_{\text{free}}$), where CeO_2 can accelerate the release of Fe^{3+} and Fe^{2+} from Fe_3O_4 leading to activation of H_2O_2 to form $\cdot\text{OH}_{\text{free}}$ (see Figure 10.2A). Zhang *et al.* utilized Ce to modify Cu-based catalysts through a one-pot synthesis.⁷⁴ The various characterization techniques applied showed that Ce doped into the Cu-based catalysts plays an important role in the properties change in catalysis including morphology Cu(i) ratio, specific surface area, interface electron transfer rate, and unpaired electron content. Notably, due to the increase of Cu(i) ratio and unpaired electron content, more electron-rich centers and active sites can be induced to generate on the surface of the composite, facilitating oxidant conversion to radicals (see Figure 10.2B).

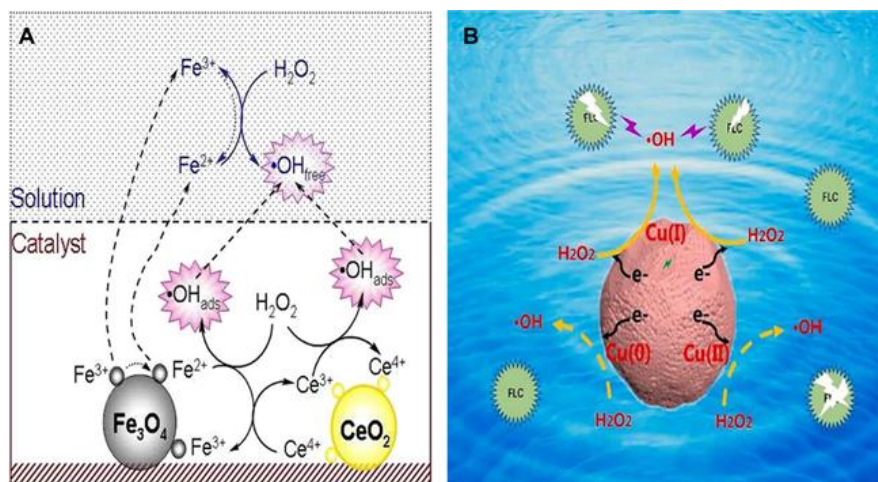


Figure 10.2 (A) Schematic diagram of the reaction mechanism of H_2O_2 activation by the Fe_3O_4 - CeO_2 catalyst under acidic conditions. (B) Schematic presentation of the fluconazole degradation mechanism involved in the Cu_xCuO_y - H_2O_2 system. (A) Reproduced from ref. ⁷³ with permission from American Chemical Society, Copyright 2012. (B) Reproduced from ref. ⁷⁴ with permission from Elsevier, Copyright 2020.

Even though composite metal oxide Fenton-like catalysts have made great progress in terms of catalytic efficiency and application, some shortcomings also need to be considered. For example, lattice doping may lead to lattice distortion that breaks the balance between atoms, so the metal atoms with decreased stability can break away from the catalyst and then be released into the water body. Metal leaching will not only damage the performance of the catalyst but also may cause heavy metal pollution in the water environment. Besides, for the composites of different metal oxides, it is crucial to construct a close interaction among the components. Weak force may cause each component to act independently, but cannot show a good synergistic effect.

10.3.2 Metal–Metal Oxide@Porous Carbon Hybrid Fenton-like Catalysts

10.3.2.1 Fenton-like Catalysts with Carbon Coatings

With an interconnecting mesoporous and/or microporous structure, many nanocarbons such as graphene, carbon nanosheets, and carbon nanotubes (CNTs) can be used directly to act as supports for Fenton-like catalysts, which can not only offer unimpeded transfer channels for the pollutants and oxidants, but also provide considerable active sites due to their high exploitable surface area.^{75–77} Zhu *et al.* used oxidized multi-walled CNTs to encapsulate FeOOH to synthesize a highly efficient Fenton-like catalyst (CNTs-FeOOH) via a facile stirring method.⁷⁸ In this reaction system, the calculated apparent rate constants (k_{app}) of 3% CNTs-FeOOH (labeled via the calculated weight ratio of CNTs to FeOOH), determined from the regression curves of $-\ln(C/C_0)$ versus reaction time, was 0.0811 min^{-1} , nearly 7.1 times that of pure FeOOH (0.0114 min^{-1}). In addition, the density functional theory (DFT) calculations and the cyclic voltammetry curves both indicated the CNTs played a key role in accelerating $\text{Fe(III)}/\text{Fe(II)}$ redox cycling during the reaction. Such a process enhances the generation rate of $\cdot\text{OH}$ to promote the catalytic activity, with a bisphenol A (BPA) degradation rate of 96% within 30 min, but also facilitated the decomposition of H_2O_2 up to 87.5% using the 3% CNTs-FeOOH within 60 min (see Figure 10.3A). Notably, due to the stable graphitic structure of the CNTs, the CNTs-FeOOH could maintain high Fenton activity after being reused for four cycles, showing excellent catalytic stability.

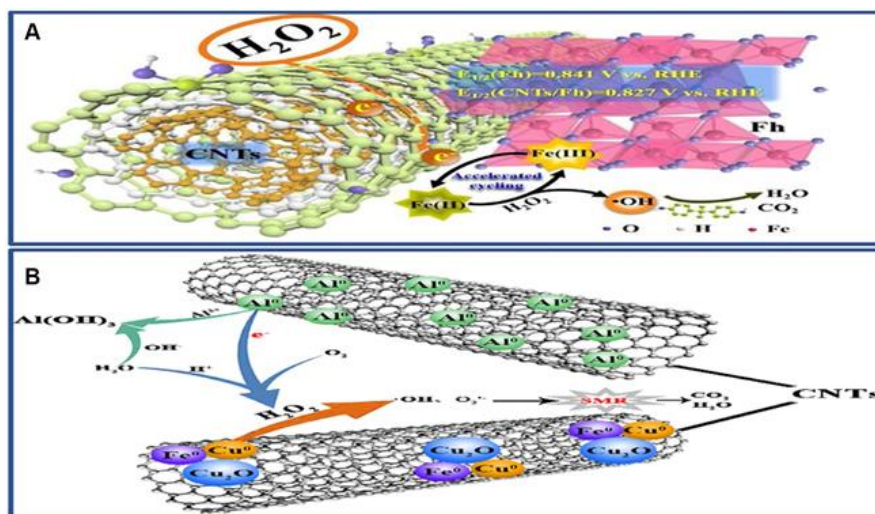


Figure 10.3 (A) Possible heterogeneous Fenton catalytic mechanism in the CNTs-FeOOH system. (B) The reaction mechanism of the Al⁰-CNTs-CNTs-Fe-Cu-O₂ system. Reproduced from ref. ⁷⁸ and ⁸⁴ with permission from Elsevier, Copyright 2020.

In recent years, CNTs have been proved to have great potential for activating O₂ for the highly efficient generation of H₂O₂ *in situ* when working as a carrier of metal/metal oxide catalysts.^{79,80} The *in situ* production of H₂O₂ by activating O₂ is very attractive in Fenton-like catalysis due to its simple operation, mild conditions, and no requirement of external energy.^{81,82} However, the limited activity of single metals or metal oxides and the low solubility of O₂ in water has hindered the utilization of oxygen, resulting in ineffective degradation of contaminants.⁸³ Chen *et al.* constructed a new catalyst (CNTs-Fe-Cu) working together with Al⁰-CNTs to realize the in-situ generation of H₂O₂ for the degradation of sulfamerazine (SMA).⁸⁴ In the Al⁰-CNTs-CNTs-Fe-Cu-O₂ system, Al⁰-CNTs was responsible for activating O₂ to form H₂O₂ and producing H⁺ via aluminum hydrolysis to reduce O₂ (see Figure 10.3B). Meanwhile, CNTs-Fe-Cu was mainly used to catalyze the decomposition of *in situ* generated H₂O₂ into reactive oxygen species (ROS). With the cooperation of these two catalysts, the synergistic effect was verified by 85% degradation of SMA (50 mg L⁻¹) and 60% removal of total organic carbon (TOC), respectively, within 60 min when the catalyst dosage was 1 g L⁻¹. More importantly, the material can realize *in situ* production of H₂O₂ in mild conditions, and work stably even at the initial pH of 5.8.

10.3.2.2 Fenton-like Catalysts with Carbonized MOF Structures

As metal-organic frameworks (MOFs) combine the respective advantages of inorganic and organic components,⁸⁵⁻⁸⁷ MOF-derived carbon hybrid Fenton-like catalysts show lots of distinct merits, such as hierarchical porous structures, tunable chemical composition, and abundant active sites, which are advantageous to promote the activation of oxidants.⁸⁸⁻⁹¹ Tang and Wang synthesized a novel MOF-derived three-dimensional (3D) flower-like Fenton-like catalyst *via* simple pyrolysis of a [Fe, Cu]-BDC precursor, in which iron-copper bimetallic nanoparticles are coated with a mesoporous carbon shell (FeCu@C).⁹² When applied to degrade sulfamethazine (SMT) in the presence of H₂O₂, the catalyst showed 100% organics removal within 90 min and a 72.3% TOC conversion within 240 min (initial conditions: 20 mg L⁻¹ SMT, 0.25 g L⁻¹ catalyst, 1.5 mM H₂O₂, pH 3.0). There is a possible synergistic effect between iron and copper species existing in the inner bimetallic nanoparticles that can facilitate the generation of a large amount of •OH to enhance SMT degradation; likewise, the mesoporous carbon shell also plays an important role in promoting reactant diffusion to react with the inner active sites and providing specific adsorption sites for SMT molecules through π - π interactions. It was noted that, according to the atomic absorption spectrometry analysis, the concentrations of leached iron and copper

ions from FeCu@C were much lower than that of bare CuFe₂O₄ and Cu-doped iron oxide catalysts. This result proved the robustness of the mesoporous carbon matrix (see Figure 10.4).

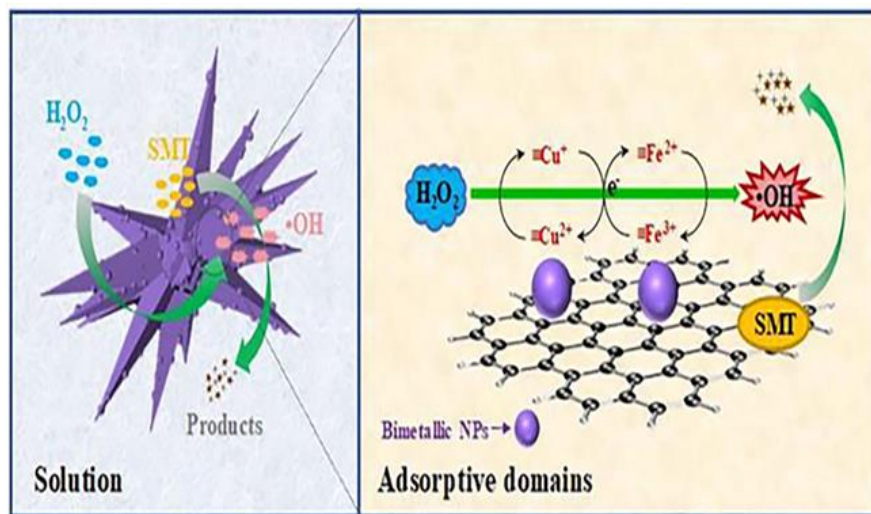


Figure 10.4 Possible reaction mechanism of SMT degradation in the FeCu@C-H₂O₂ system. Reproduced from ref. ⁹² with permission from Elsevier, Copyright 2019.

10.3.2.3 Fenton-like Catalysts with Carbonized Polymer Coating Structures

Carbon precursors have an important effect on the final physical and chemical properties of the resulting catalytic materials.^{93,94} In addition to MOFs, the fabrication of carbon shells through self-polymerization has also attracted considerable attention. For instance, polymer monomer contains a large number of functional groups that can chelate with most transition metals (Fe, Cu, Mn) to form a complex and then arrange into ordered, hierarchical urchin-like structures with abundant active sites.⁹⁵ Besides, the thickness of such a conformal coating can be precisely controlled by adjusting the polymerization time and monomer addition. Notably, this synthesis method is usually less energy-consuming and easy to operate.

In order to promote electron transmission in the Fenton-like reaction *via* strong interactions between metal species and nanocarbon materials, Zhuang *et al.* proposed a polymer templated method for Fe-graphene-based Fenton-like catalyst synthesis.⁹⁶ In this work, a novel catalyst Fe₃O₄@Fe-graphene aerogel (MGA) was prepared *via* Fe²⁺-mediated polymerization of polyvinyl alcohol as a precursor combined with an *in situ* carbonization process, thus allowing the entire encapsulation of active Fe₃O₄ and α -Fe nanoparticles in the interior of a graphene aerogel (see Figure 10.5A). The MGA achieved 15% tetracycline removal (~) and 20% TOC (~) removal. The degradation mechanism using the MGA is proposed as follows: the tetracycline with benzene ring structure strongly interacts with graphene *via* strong π - π interactions and hydrogen bonding. The adsorbed tetracycline molecule acts as an electron donor to Fe through Fe-O-C linkage and Fe-C bonds (π -Fe interactions) active sites. The π -Fe interactions speed up the generation of Fe(II) from Fe(III) *via* electron transport from $\pi \rightarrow$ Fe(III) to avoid speed limiting steps. In addition, O₂ adsorbed on the defect sites of graphene were also converted into ROS by the low-electron-density region. The abundant contact sites and rapid electron transfer led to the high tetracycline removal efficiency and effective regeneration of MGA (see Figure 10.5B).

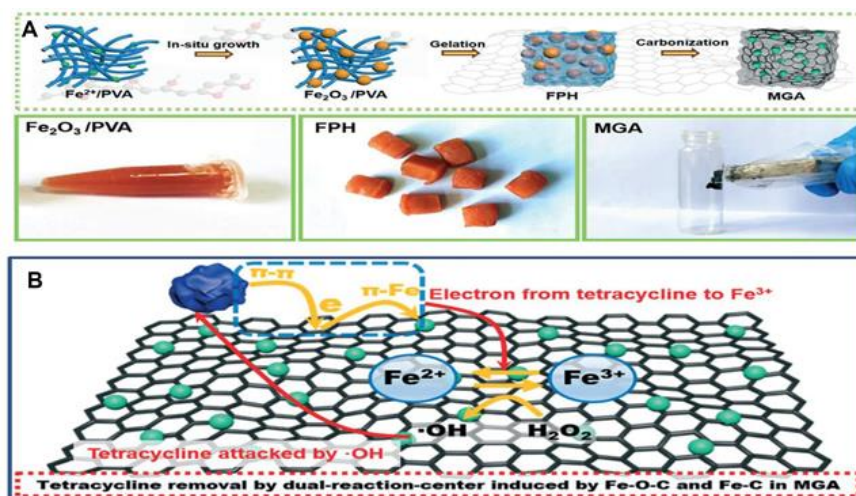


Figure 10.5 (A) The preparation process and photographs of the samples. (B) Mechanism of antibiotic removal through a Fenton-like reaction by MGA. Reproduced from ref. ⁹⁶ with permission from the Royal Society of Chemistry.

While M(metal)–O–C and M–C can be used as electron transfer bridges, the current state-of-the-art research proved that M–N–aromatic rings, M–O–aromatic rings, and M–N_x–C can also serve as electron-transfer mediators in heterogeneous Fenton catalysis to facilitate the electron transfer for enhanced Fenton reactions.^{96–99} For example, Ma *et al.* used an aniline polymer to prepare a novel nano-Fenton-like catalyst Fe–N–graphene-wrapped Al_2O_3 –pentlandite with a unique, layered N-doped graphene and Fe–N complex structure.⁹⁹ Interestingly, sphere-shaped algae with a uniform size of 2 μm in diameter were collected and used to serve as a natural template for fabricating this catalyst with a hollow porous carbon matrix. Fe, Ni, and Al in this catalyst can also be fixed on the surface of the algae due to its high metal binding activity. Then, the polyaniline–metal complex was carbonized to form a graphene shell. The synthesized catalyst degraded up to 95% of tested organic pollutants (*i.e.*, phenol and Acid Red 73 (AR 73)) after 30 min, achieving 76.0% and 69.9% removal of TOC for phenol and AR 73, respectively, under neutral pH. Moreover, the accumulated turnover numbers reached 1955.7 (for phenol) and 449.8 (for AR 73). Notably, the H_2O_2 utilization efficiency was as high as 66.3% in the degradation of AR 73. Characterization results disclose a unique mechanism: first, $\cdot\text{OH}$ generated *via* the reaction between Fe^{2+} and H_2O_2 can rapidly attack organics to form the product of reactive organic radicals ($\text{R}^\cdot$), which then immediately linked to the graphene region, where N atoms were adjacent and worked as an electron donor to enhance electron transfer from $\text{R}^\cdot$ to Fe^{3+} for its quick reduction. It has been proved that the doping of Ni into the α -FeOOH structure could promote the reduction of Fe^{3+} while Al_2O_3 can also facilitate the electron transfer by acting as a Lewis acid to attract electron density from the iron and destabilize the Fe^{3+} state (see Figure 10.6). With the benefits of these effects, the Fe–N–pentlandite– Al_2O_3 –C catalyst showed noble activity, reusability, and stability.

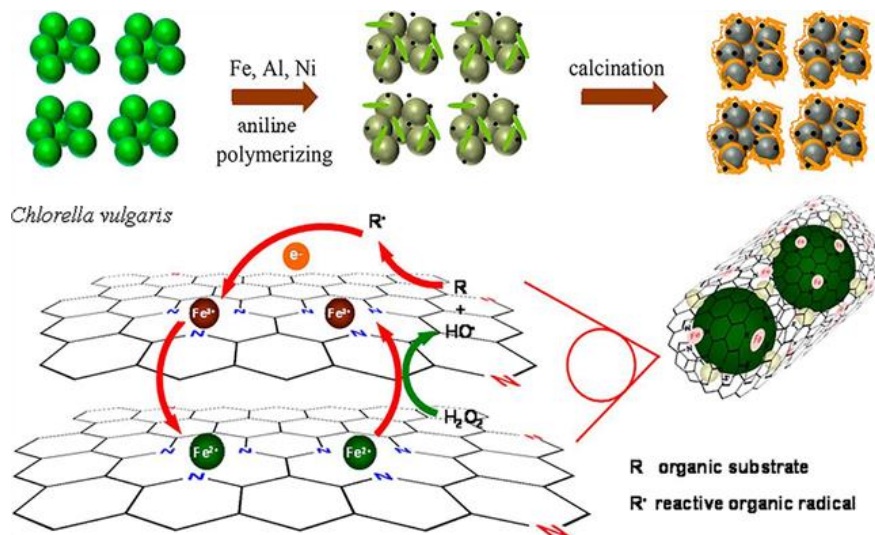


Figure 10.6 Scheme of the possible mechanism for the Fe-N-pentlandite- Al_2O_3 -C catalyst in the Fenton reaction. Reproduced from ref. ⁹⁹ with permission from American Chemical Society, Copyright 2018.

In a Fenton-like catalytic system, porous carbon materials provide a large number of active sites for the whole reaction process, including both adsorption sites for pollutants and oxidants and a large number of reaction sites. Also, the upright conductivity of carbon materials can improve the surface electron transfer rate of the catalyst, thus improving the activity of the catalyst. Furthermore, the inorganic carbon shell on the surface of metal oxides can prevent the leaching of metal elements from corrosion or passivation by acids/alkalines. Therefore, these studies confirmed the carbon materials-metal oxides composites can serve as promising Fenton-like catalyst when applied in wastewater treatment.

It should be noted that most studies of Fenton-like catalysis have been conducted with simulated wastewater, which has no distractors except for specific pollutants. Likewise, the actual wastewater may contain a large number of inorganic salt ions (Cl^- , CO_3^{2-} , F^-) which may complex with the transition metals on the surface of the metal-based materials and hinder the electron migration.¹⁰⁰ In addition, after leaching the transition metal components will quickly form precipitates in the salt-containing system and adhere to the surface of the metal-based materials, which will also inhibit the catalytic reaction. On the other hand, the life of $\cdot\text{OH}$ is short ($\tau(\cdot\text{OH}) = 1 \mu\text{s}$),²⁹ especially in salt-containing systems, because the redox potential of halogen ions (such as Cl^- , Br^-) is lower than that of $\cdot\text{OH}$ and they are easily oxidized into $\text{Cl}\cdot$ and $\text{Br}\cdot$ (e.g., $\text{Cl}\cdot/\text{Cl}^- = 2.41 \text{ V}$, $\cdot\text{OH} = 2.8 \text{ V}$).¹⁰¹ As a result, most $\cdot\text{OH}$ are consumed before they react with organic pollutants. Besides, the $\text{Cl}\cdot/\text{Br}\cdot$ generated by the side reaction can react with organic pollutants to form more toxic halogenated hydrocarbon disinfection by-products.¹⁰² Therefore, metal/metal oxide@nanocarbon materials may have more potential than metal-based catalysts in actual wastewater treatment: 1) the carbon shell can effectively prevent the leaching of the inner metal and hinder the complexation between inorganic salt ions and transition metals. 2) The surface of the carbon shell can provide many active sites for binding radicals generated in the system to prolong the life of the radicals and avoid their reaction with halogen ions, thus increasing the utilization efficiency of the oxidants.

10.3.3 Metal-free Fenton-like Catalysts

While inorganic carbon materials can work as carriers for metal or metal oxide Fenton-like nanocatalysts to enhance their catalytic activity, metal-free materials have attracted increasing attention as a sustainable alternative to the metal-based Fenton-like catalysts.^{103–105} The metal-free catalysts, usually at low cost, can not only avoid deactivation of metal catalysts but also prevent production of secondary contamination, which is especially important in water remediation.^{106,107} Zhuang and co-workers used biomass waste to invent a new 3D macroscopic modified graphene-based metal-free Fenton-like catalyst to degrade perfluorooctanoic acid (PFOA)¹⁰⁸. The experimental data and theoretical calculations indicate that electron density migration that took

place on the surface of the catalyst can weaken the C–F bonds in PFOA, resulting in an obvious increase in the HOMO (Highest Occupied Molecular Orbital) of F from 0.95% to 15.46% due to electron loss from the unstable PFOA. Besides, the structure of 3D graphene has been proved to construct confinement effects, which could be beneficial for stretching of C–O bond lengths and activation of C atoms to promote H_2O_2 decomposition. A dual reaction center, which will be discussed in detail in the next section of this review, has been constructed where O in this catalyst can give electrons to H_2O_2 for its effective reduction to $\cdot\text{OH}$, whereas C worked as an electron-poor center that can capture electrons from PFOA (electron donor). It is also worth mentioning that the energy barrier of H_2O_2 dissociation in the catalyst (1.10 eV) was much smaller compared with the two-dimensional (2D) graphene state (1.60 eV), which also contributed to its excellent performance (see Figure 10.7). The results showed 93.4% PFOA was degraded within 150 min and the defluorination rate reached 38.3%. This study provides us with a new path to convert waste into practical catalysts.

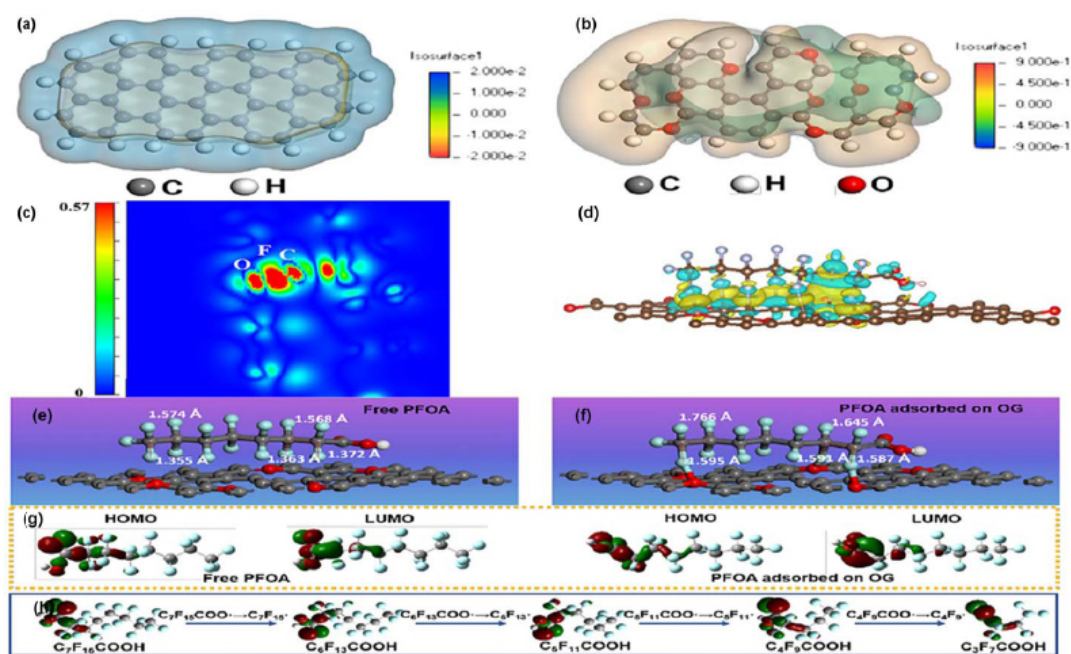


Figure 10.7 (a) Electrostatic potential distributions (ESPs) of porous graphene, (b) ESPs of the catalyst, (c) electron density map of PFOA adsorbed on the catalyst, (d) charge density difference of PFOA adsorbed on the catalyst, and electron density of PFOA adsorbed the catalyst, (e) optimized structure and Ce–F bond length of free PFOA, (f) optimized structure and Ce–F bond length of PFOA adsorbed on the catalyst, (g) HOMO and Lowest Unoccupied Molecular Orbital (LUMO) energies of free PFOA and PFOA adsorbed on the catalyst, (h) HOMO and LUMO energies of PFOA intermediates during degradation. Reproduced from ref. ¹⁰⁸ with permission from Elsevier, Copyright 2020.

Many reports have shown that diverse defects or chemical functionalities on the graphene layers play a key role in the catalytic reactions, including oxygenated functional groups (such as carbonyl groups, hydroxyl groups, and carboxyl groups), carbon vacancies and holes, edge effects, and the presence of dopant elements.^{109–111} Besides discrete active sites, metal-free catalysts can also activate the substrates adsorbed on the surface by charge transfer, which can also promote the degradation process.¹¹¹ Therefore, in future work, we can enhance the application and performance of metal-free Fenton-like catalysts by following the below methods: 1) fabricate more defects *via* adjustment of the synthesis conditions and methods or doping heterogeneous nonmetallic elements; 2) anchor special functional groups that can not only promote the electron transfer as active sites but also provide adsorption sites for pollutant activation. In general, the design of these carbocatalysts with specific functional groups and/or architectures is costly and complicated, so green and sustainable methods need to be deeply researched.

10.4 Design of Novel Fenton-like Nanocatalysts

10.4.1 Dual Reaction Center Fenton-like Catalytic Processes

In a Fenton-like catalyst, bonded atoms are actually active components rather than free metal elements. Notably, the outer electrons of these atoms are not only bonded by the intrinsic elements but also constrained and influenced by other neighboring atoms, making them favorable to polarization. Such distribution often induces the formation of electron intensive areas and electronic scarce areas. If the polarization distribution is enhanced to reach a certain degree, obvious electron-rich centers and electron-poor centers (*i.e.*, dual reaction centers) will be constructed, mirroring the galvanic cell with cathode and anode poles. On the surface of the catalyst, numerous micro galvanic cells are thus distributed. When this catalyst was exposed to a Fenton-like reaction, the electron-rich center underwent a reductive reaction with the oxidants, while the electron-poor center underwent an oxidation reaction with the pollutants. In particular, pollutants and their organic free radical intermediates occupy the electron-poor centers, which prevents H_2O_2 from contacting with these active sites to form superoxide radicals ($\cdot\text{O}_2^-$) and O_2 . On the other hand, H_2O_2 can be easily adsorbed in the electron-rich sites *via* its electrophilic region and reduced to $\cdot\text{OH}$. The whole process avoids the oxidation of H_2O_2 , effectively promoting the conversion efficiency of H_2O_2 to $\cdot\text{OH}$. Therefore, in the Fenton-like catalytic reaction system, the dual reaction center can directly capture the electrons of organic compounds (or degradation intermediates) and transfer them to oxidants to generate active radicals, thus overcoming the defect of low effective utilization of oxidants due to the “oxidation–reduction” cycle of transition metals.

In recent years, the construction of dual reaction centers has attracted many researchers' attention. Metal, nonmetal, and even oxygen vacancies can be combined to form a dual-reaction center catalyst (DRCC) using appropriate synthesis methods according to their electronegativity difference or bonding force.^{24,25,112–118} In this section, we will mainly introduce three types of Fenton-like materials with dual reaction centers in detail: metal–metal DRCC, metal–nonmetal DRCC, and nonmetal–nonmetal DRCC.

10.4.1.1 Metal–Metal Dual Reaction Center Fenton-like Catalysts

In terms of metal–metal DRCC, Hu and co-workers prepared a dandelion-like Fenton-like catalyst *via* a hydrothermal process to dope Cu, Ti, and Al into the lattice of silica nanosphere containing silica (d-TiCuAl– SiO_2 NSs).¹¹⁵ The result showed that the lattice substitution can cause the formation of charge inhomogeneous regions on the catalyst surface due to the different electronegativity of these metals, which is mainly manifested by a higher electron density of the lattice O^{2-} formed around the lattice Cu and a lower one formed near the lattice Ti and Al. The electron-rich Cu centers and the electron-poor Ti and Al regions can be compared to the cathodes and anodes of galvanic cells, respectively, which enhanced the selective adsorption of H_2O_2 on d-TiCuAl– SiO_2 NSs. During the process of Fenton-like reaction, H_2O_2 was reduced to $\cdot\text{OH}$ by the electrons from the “cathode”, while the oxidation of BPA was induced on the “anode” where the electrons of $\text{R}^\cdot$ can be captured due to the characteristic of electron deficiency. From the path of electron transfer, it can be concluded that almost all H_2O_2 can be selectively converted into $\cdot\text{OH}$ with a strong oxidation ability to rapidly degrade organic compounds, avoiding the ineffective decomposition of H_2O_2 to a greater extent. The independent partition reaction process in different parts of the catalyst surface not only ensures the high utilization rate of oxidants but also avoids the loss of activity of a single metal element due to frequent valence state transition (see [Figure 10.8A](#)). Therefore, d-TiCuAl– SiO_2 NSs with dual reaction centers showed a very highly effective catalytic ability and excellent degradation stability at neutral pH values, in which BPA could be completely degraded within 60 min and approximately 70.5% of TOC removal can be achieved within 180 min. As shown in [Figure 10.8B](#), it is also observed that the utilization efficiency of H_2O_2 remained at a relatively high level (above 60%) during the degradation of BPA.

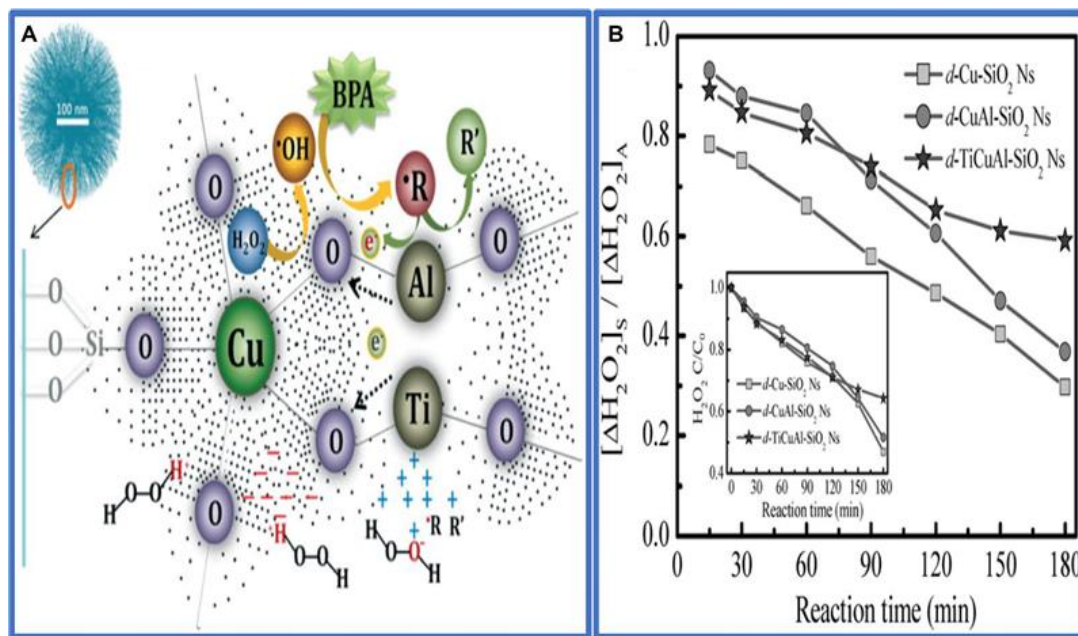


Figure 10.8 (A) The Fenton-like reaction mechanism on the surface galvanic-like cells of d-TiCuAl-SiO₂ NSs. (B) The utilization efficiency of H₂O₂ in the d-Cu-SiO₂ NSs, d-CuAl-SiO₂ NSs, and d-TiCuAl-SiO₂ NS suspensions. The inset shows the corresponding decomposition of H₂O₂. Reaction conditions: 0.1 mmol L⁻¹ (23 mg L⁻¹) BPA, 12 mmol L⁻¹ H₂O₂, 0.8 g L⁻¹ catalyst, initial pH 7, room temperature. Reproduced from ref. ¹¹⁵ with permission from the Royal Society of Chemistry.

10.4.1.2 Metal–Nonmetal Dual Reaction Center Fenton-like Nanocatalysts

Compared with metal–metal DRCC, metal–nonmetal DRCC seems to attract more attention due to the unique characters of carbonaceous materials. We all know that graphene-based materials can bind with metal elements to form cation– π interactions, which is one of the most important intermolecular binding forces.¹¹⁹ Therefore, cation– π interactions have been considered to modify the charge distribution on the catalyst surface to induce the formation of a dual reaction center.¹²⁰ In addition, doping of a variety of nonmetallic elements (N or S) into inorganic carbon nanomaterials will influence the spin density and charge distribution of carbon atoms, which induces the “activation region” on the catalyst to enhance the polarization difference.^{99,121} In recent work, Lyu proposed a new catalyst with a dual reaction center that used water as an electron donor, in which a surface complex of Cu combines with carbon-doped graphitic carbon nitride (g-C₃N₄) by binding with a hydroxyl group on its aromatic ring (OH–CCN/CuCo–Al₂O₃).¹¹⁷ OH–CCN and CuCo–Al₂O₃ were linked by a C–O–Cu bond bridge and confirmed using extended X-ray absorption fine structure (EXAFS) curve fitting. Due to the Cu(ii)– π interactions of the Cu–O–C bond on the catalyst surface, the electron density around Cu increased to form an electron-rich center. According to DFT calculations of the electron density, the formation of electron-deficient nitrogen centers was also proved. Around the electron-rich Cu center, a large number of electrons were transferred to H₂O₂ that mainly undergo a reduction reaction and convert to ·OH. Meanwhile, the electrons of H₂O were deprived by the electron-deficient nitrogen center of OH–CCN, leading to a selective conversion of H₂O to ·OH. During the reaction, the system achieved a balance *via* electron transfer between the electron-rich copper center and electron-deficient nitrogen center through Cu–O–C bond (see Figure 10.9). Therefore, the OH–CCN/CuCo–Al₂O₃ Fenton-like system exhibits excellent catalytic activity, stability, and utilization rate of H₂O₂ for the degradation of a variety of organic pollutants (BPA, 2-CP, 4-isopropylphenol and diphenhydramine).

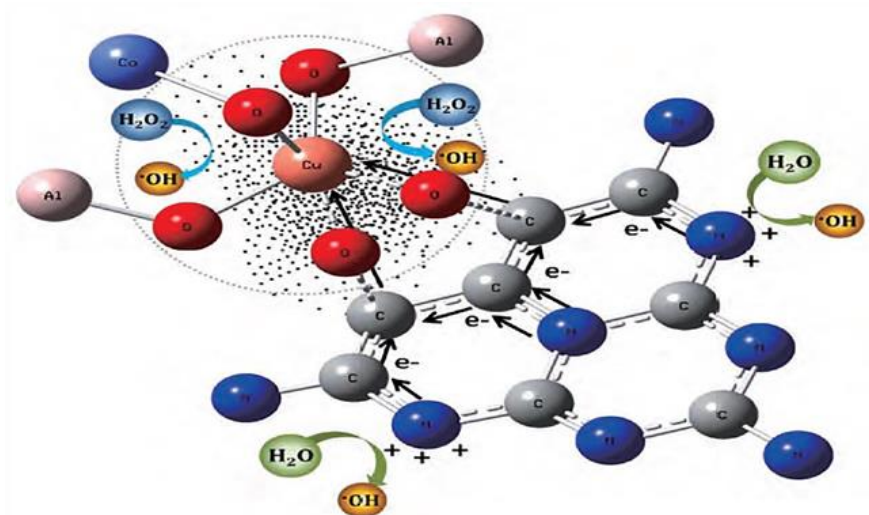


Figure 10.9 The reaction mechanism on OH-CCN-CuCo-Al₂O₃ with H₂O₂ and H₂O. Reproduced from ref. ¹¹⁷ with permission from the Royal Society of Chemistry.

In addition, Han *et al.* combined reduced graphene oxide (rGO) nanosheets with CoMoS₂ nanospheres (CMS NSs) to prepare a novel and special nanocatalyst CMS-rGO NSs.¹¹⁶ The highlight of the catalyst is the simultaneous generation of H₂O₂ *in situ* and activation of H₂O₂ in different activity centers. Mo-S-C bonding in CMS-rGO NSs work as a bridge to fix CoMoS₂ nanospheres on the surface of rGO nanosheets where π electrons can transfer to the metal centers *via* cation- π interactions to induce the electron-rich center. Besides, due to the electronegativity difference of Mo and Co, different electron density distribution regions are produced on the surface of CoMoS₂ nanospheres *via* the formed Mo-O-Co bonds. Thus, a combined dual reaction center mechanism has been proposed: first, O₂ dissolved in the water accumulated on the Mo center and then reduced to HO₂[•] and [•]O₂⁻ that were further reduced to H₂O₂ around the Co center. Then, the formed H₂O₂ acted as electron acceptors in the mechanism of the dual reaction center, promoting the electron transfer cycle (see Figure 10.10). According to the experiment data, the degradation of rhodamine B (Rh B) is around 21 times higher compared with the Fe₃O₄ Fenton-like system.

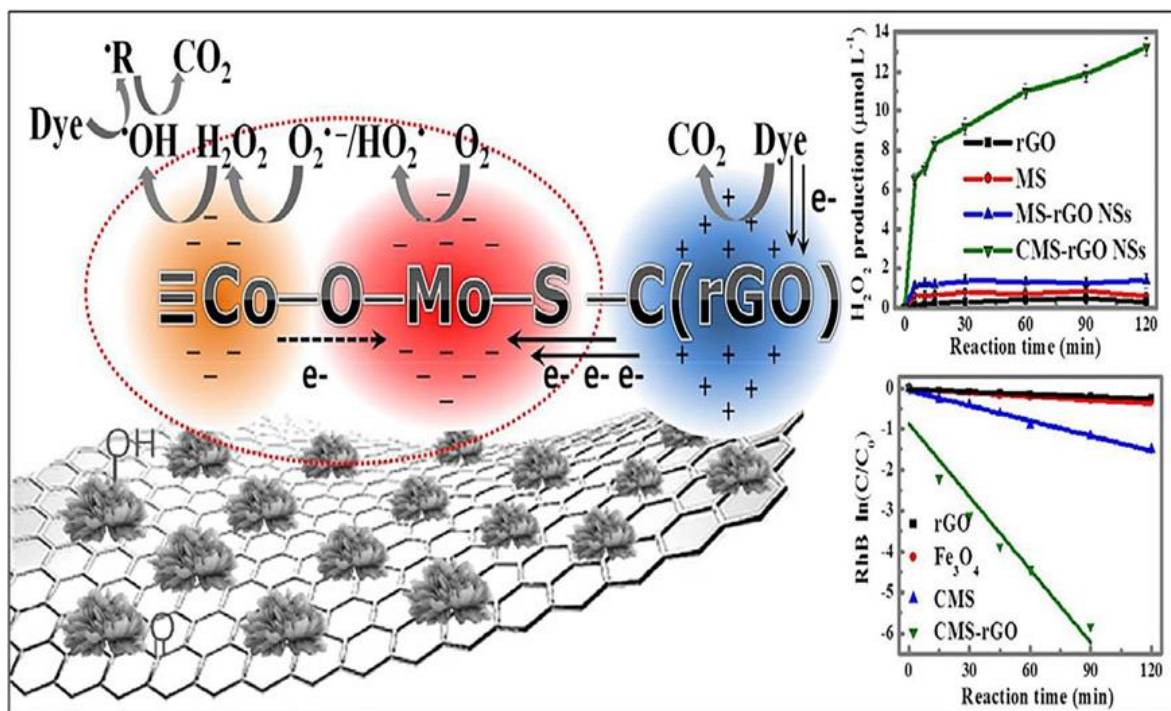


Figure 10.10 Schematic for the novel Fenton-like reaction process in the CMS-rGO NSs system. Reproduced from ref. ¹¹⁶ with permission from Elsevier, Copyright 2019.

10.4.1.3 Nonmetal–Nonmetal Dual Reaction Center Fenton-like Nanocatalysts

As the mechanism of dual reaction centers does not depend on the valence transition of transition metals, there is a possibility of using metal-free materials to construct dual reaction centers by polarizing the distribution of electrons. This will overcome many common problems in the metal-based Fenton-like catalytic system, such as the pollution caused by metal leaching, metal passivation, and the need for an acidic environment. Lyu *et al.* reported for the first time a highly effective and stable metal-free Fenton-like catalyst with dual reaction centers (4-phenoxyphenol-rGO NSs) that was prepared *via* surface complexation and copolymerization between functionalized 4-phenoxyphenol and rGO nanosheets.²⁵ The 4-phenoxyphenol molecule was linked with rGO *via* both C–O–C bridges and π – π interactions, thereby affecting the electron distribution of the surface of rGO and drawing a large number of single electrons around the introduced O. Such changes in the electronic properties of the catalyst resulted in dual reaction centers on the C–O–C bridge of 4-phenoxyphenol-rGO NSs. In this system, H₂O₂ was reduced to ·OH on the electron-rich center around the oxygen atom, while pollutants adsorbed on the electron-poor center around the carbon atom were oxidized, *i.e.*, lose electrons that were transferred to the O center (see Figure 10.11A). DFT calculations also proved the different electric charges of the O and C atoms. For the catalytic degradation, 88.7% 2-CP and 75.7% BPA removal rates were reached within 120 min. These dual reaction centers enable separation of the reaction sites for the selective reduction of H₂O₂ and the oxidative degradation of pollutants, achieving a high H₂O₂ utilization efficiency. Besides, the degradation and mineralization of pollutants were extended to a wider pH range, requiring no additional energy input.

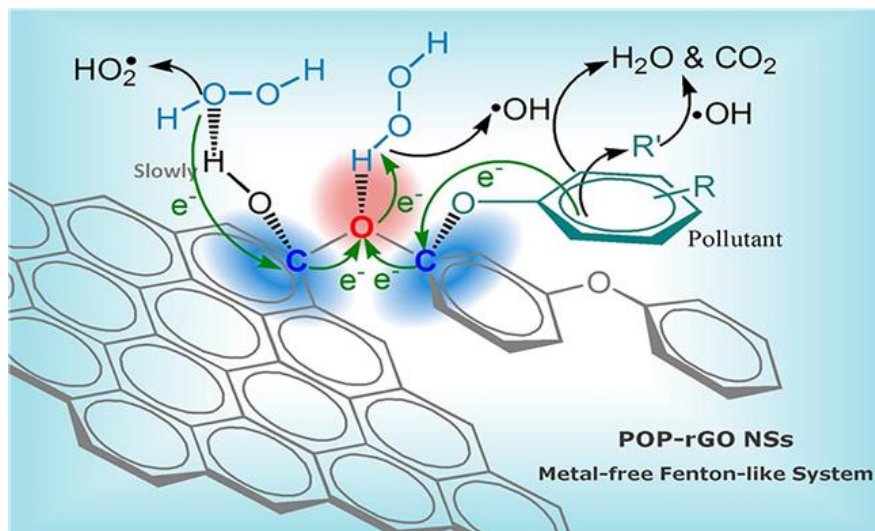


Figure 10.11 The mechanism of the novel Fenton-like catalyst 4-phenoxyphenol-rGO NSs. Reproduced from ref. ²⁵ with permission from American Chemical Society, Copyright 2018.

The dual-reaction center Fenton-like process involves three stages of electron transfer including the pollutant giving electrons to the electron-poor center, the electron-poor center transferring electrons to the electron-rich center, and the oxidant capturing electrons from the electron-rich center. Every stage can greatly affect the whole catalytic process. Even though dual-reaction center Fenton-like catalysts have excellent reusability and good oxidant utilization, some drawbacks also need to be improved by deep research such as the weak oxidation of macromolecular organic pollutants. According to the dual-reaction center mechanism, some modifications and designs can be carried out to accelerate electron transfer. For example, graphene-based DRCC can enhance the electron-donating effect of pollutants with a benzene ring structure *via* π - π conjugation effects.¹¹¹ In addition, some pollutants with special function groups like phenolic hydroxyl groups can form complexes with some metals to accelerate electron transfer.¹²² On the other hand, the surface of a catalyst modified with special functional groups ($-\text{OH}$ or $-\text{COOH}$) can adsorb the oxidant through hydrogen bonds to accelerate the electron capture rate of H_2O_2 .¹²³

10.4.2 Fenton-like Catalytic Processes Dominated by Singlet Oxygen

In general, there are four major ROS in the Fenton-like system, *i.e.*, $\cdot\text{O}_2^-$, H_2O_2 , $^1\text{O}_2$, and $\cdot\text{OH}$.¹²⁴ The use of salt-resistant $^1\text{O}_2$ instead of radicals typically manifested a mild redox capacity (2.2 V) but with high selectivity to attack from electron-rich functional groups and some unsaturated compounds over a wide range of pH values because of its electrophilic nature and key role in chain initiation and propagation with aromatic organic compounds such as Rh B, phenol, *etc.*.^{125–128} In addition, $^1\text{O}_2$ resides at 94 kJ mol^{-1} (ΔGH_{298}^0), which is above ground state triplet oxygen.¹²⁹ Hence, Fenton-like catalytic process dominated by $^1\text{O}_2$ is an effective path to remove aromatic organic pollutants from wastewater. In this section, we will introduce two types of $^1\text{O}_2$ -dominated Fenton-like catalytic processes: radical conversion Fenton-like catalytic processes and nonradical Fenton-like catalytic processes.

Typically, $^1\text{O}_2$ can be produced by a series of complex radical chain steps. Yang *et al.* prepared a kind of Fenton-like catalyst anchoring Fe_2O_3 nanoparticles inside the CNT ($\text{Fe}_2\text{O}_3@\text{FCNT-H}$) to realize $^1\text{O}_2$ -mediated Fenton-like catalysis with H_2O_2 *via* nanoconfinement.²⁸ During the reaction, the $\text{Fe}(\text{III})$ species on the surface of the Fe_2O_3 nanoparticles inside CNT are reduced by H_2O_2 to produce $\text{HO}_2\cdot$ and $\cdot\text{O}_2^-$, which can be facilitated by strong electron migration between CNT and Fe_2O_3 nanoparticles due to the nanoconfinement. The confined space along with the unique electronic structure of CNTs promoted the radical–radical reactions including $\text{HO}_2\cdot$

and $\cdot\text{O}_2^-$ recombination and the reaction between $\text{HO}_2\cdot$ and $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ to generate $^1\text{O}_2$ (see Figure 10.12). When Fe_2O_3 nanoparticles were located on the outer surface of the CNT ($\text{Fe}_2\text{O}_3\text{-FCNT-L}$), they showed a completely different catalytic pathway. The $^1\text{O}_2$ radical was observed as the main reactive intermediate generated in the $\text{Fe}_2\text{O}_3\text{-FCNT-H-H}_2\text{O}_2$ system instead of $\cdot\text{OH}$ and achieved $22.5 \times$ faster MB degradation kinetics than $\text{Fe}_2\text{O}_3\text{-FCNT-L-H}_2\text{O}_2$.

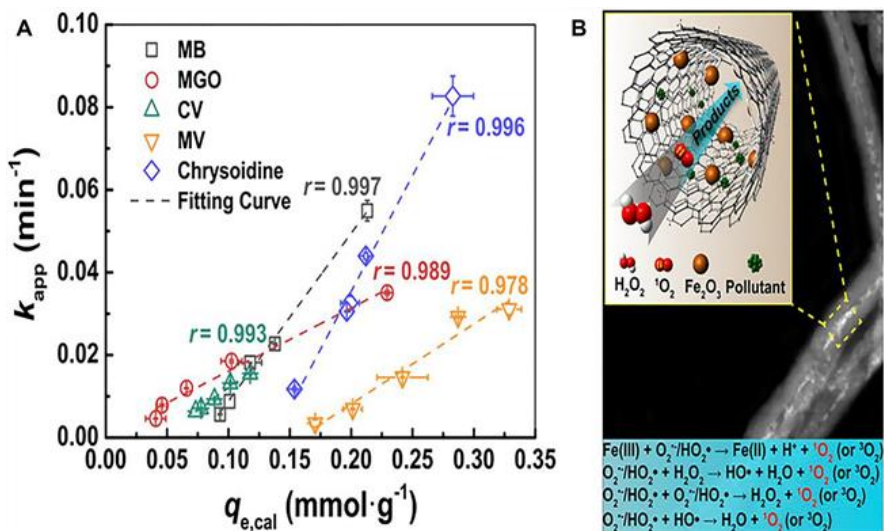


Figure 10.12 Illustration of the possible mechanism of pollutant degradation in the $\text{Fe}_2\text{O}_3\text{@FCNT-H-H}_2\text{O}_2$ system. Reproduced from ref. ²⁸ with permission from National Academy of Sciences.

The lifetime of $^1\text{O}_2$ produced by a radical chain reaction in local space is very short, unlike $\cdot\text{OH}$ that can extend its lifetime by surface bonding. However, $^1\text{O}_2$ as a non-radical cannot form bonds with the catalyst surface. Therefore, we need to find an appropriate way to reduce the migration distance of $^1\text{O}_2$ in order to ensure the effective utilization of $^1\text{O}_2$. Likewise, in the $^1\text{O}_2$ degradation system, the adsorption of pollutants on the catalyst surface is particularly important. Although many reports have proposed various pathways for $^1\text{O}_2$ generation, the mechanism of $^1\text{O}_2$ formation is still controversial and needs more in-depth investigation.

10.4.3 Single-atom Fenton-like Catalytic Processes

Recently, single-atom catalysts have become a promising approach to break through many performance bottlenecks in the field of catalysis.^{130,131} Typically, metal atoms can provide abundant and uniform catalytic sites and the strong interaction to enhance the stability of catalysts in the application. Specifically, using N to anchor dispersed metal atoms in metal–nitrogen–carbon (M–N–C) framework can provide a high density of active transition metal–nitrogen coordination sites that have been considered as an effective approach to improve Fenton-like catalysis.^{132,133} Wu *et al.* dispersed single-atom Cu on N-doped graphene oxide (Cu-SA-NGO) by pyrolysis of a melamine–Cu complex with cyanuric acid and graphene oxide (GO) after freeze drying¹³⁴ (see Figure 10.13). The loading of Cu reached 5.8 wt%, which is the highest value yet reported for the dispersion of single metal atoms on graphene. The high-angle annular dark-field technique of scanning transmission electron microscopy (HAADF-STEM), X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), and DFT calculations were used to prove the formation of atomically dispersed CuN_4 moieties. The sufficient number of CuN_4 sites with a single Cu atom acting as building units were proposed to be the main active sites for H_2O_2 activation to produce $\cdot\text{OH}$. In addition, DFT calculations also confirmed that CuN_4 active sites have low energy barriers for $\cdot\text{OH}$ generation *via* the proton-mediated H_2O_2 -homolytic pathway. The

prepared Cu-SA–NGO indeed showed remarkable activity and stability in the degradation of various organic contaminants at neutral pH. For example, the paracetamol degradation efficiencies using Cu-SA–NGO-800, which was calcined under an Ar atmosphere at 800 °C for 2 h, reached 97.3% in 60 min and its activity was almost unchanged after six runs.

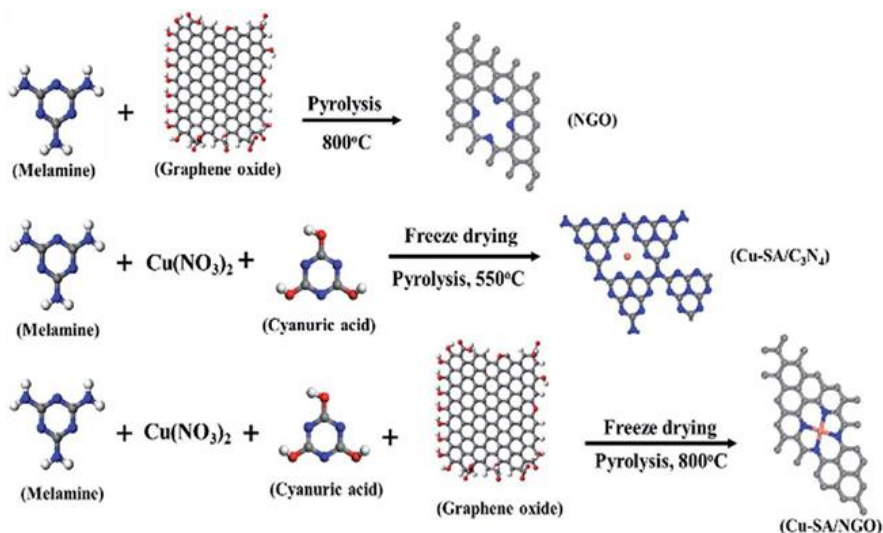


Figure 10.13 Schematic diagram of the synthesis method of NGO, Cu-SA–C₃N₄, Cu-SA–NGO-800. Reproduced from ref. ¹³⁴ with permission from the Royal Society of Chemistry.

Although single-atom catalysis has become a hot spot due to its attractive performance, there are still many challenges waiting to be addressed, including 1) how to guarantee a loading content high enough for practical applications but also maintaining the reaction centers as isolated sites under catalytic conditions; 2) how to provide enough bonding sites to coordinate with an isolated atom with strong interaction; 3) how to resolve the problem of the non-uniform distribution of metal sites resulting from the intrinsic heterogeneity of support surfaces.

10.5 Hybrid Fenton Processes

The hybrid Fenton processes are a set of processes assisted by an external field or phenomenon to improve its performance. The most commonly employed external fields are electrochemical-, photochemical-, microwave-, and cavitation- assisted fields. A summary of the current state-of-the-art research focused on Fenton-like processes is made in this section, and some recent developments in nano-applications are also summarized.

10.5.1 Electro-Fenton Processes

10.5.1.1 Electro-Fenton Principles

The electro-Fenton processes combine anodic oxidation, cathodic H₂O₂ generation, and the Fenton reaction including catalyst regeneration (see Figure 10.14). The cathodic generation of H₂O₂ (see eqn (10.14)) can occur due to the reaction of dissolved or purged oxygen, which is one of the main advantages of electro-Fenton processes because it avoids chemical addition and the related operating costs. The process is an effective way to degrade micropollutants leading to an eco-friendly technology with reduced chemical usage. The main electrochemical reactions are described in eqn (10.14) and (10.15).



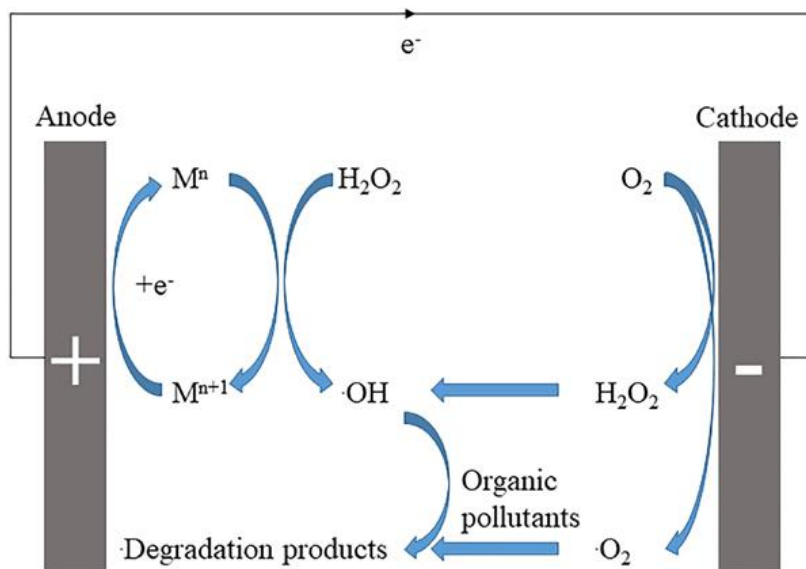


Figure 10.14 Schematic representation of an electro-Fenton-like process.

The mechanism¹³⁵ underlying electro-Fenton degradation can occur by direct electron transfer, or indirect oxidation *via* the chemisorbed oxygen formed from water discharge (see eqn (10.16)). Secondary reactions involving water to form $\cdot\text{OH}$ can also occur at the anode, as shown in eqn (10.17). The reduction of oxygen is also an important secondary reaction that leads to the formation of $\cdot\text{O}_2^-$ (see eqn (10.18)) that can either form H_2O_2 (see eqn (10.19)) or oxidize organic species. In both cases, the electrode materials, along with the current required, might limit the reaction kinetics.



The current density is one of the most important parameters to enhance degradation. It is reported that a higher current leads to increased production of $\cdot\text{OH}$ radicals from the Fenton reaction and the oxidation of water molecules, along with enhanced Fe^{2+} regeneration.^{135–138} Carbon-based nanomaterials and composites are the main family of materials employed as cathodes. Graphite,^{135,138} AC,¹³⁹ and recently graphene¹⁴⁰ have been used due to their relatively low cost, high surface area, chemical stability, and their surface and structural functionalization potential, which can enhance oxygen trapping. Regarding the anode, platinum is widely used at lab scale^{138,140–142} due to its excellent electrical conductivity and stability, but its cost hinders its practical application. Besides, titanium-based anodes have also become popular in the electro-Fenton process because of their ability to generate $\cdot\text{OH}$ radicals on their surface.^{53,137}

Different reactor configurations can also enhance the mass transfer between different phases favoring the oxygen present in the cathode. For example, Yu *et al.* observed that the concentration of H_2O_2 obtained in a vertical flow reactor (1418 mg L^{-1}) was higher than that in the horizontal flow reactor (870 mg L^{-1}).⁵⁴ Therefore, optimizing the production of H_2O_2 without compromising energy consumption is one of the most promising research pathways to enhance the performance of the electro-Fenton processes.

Gümüş *et al.* reported a decrease in the cost (0.334 \$ kg⁻¹ phenol) and an increase of 34% in the degradation efficiency of phenol comparing Fenton and electro-Fenton processes.¹⁴³ Despite its good performance, some limitations hinder the practical application of this process. Among them, sludge production and difficulty to reuse and recover the catalyst, the current efficiency, and the slow production rate of H₂O₂ emerge as major concerns.^{54,143,144}

10.5.1.2 Electro-Fenton-like Nanocatalysts

A lot of research has been recently published that focuses on optimization of the cathode and the catalyst at the nanoscale. Some of the most relevant recent solutions are summarized in Table 10.2. For example, plasma nanoscale surface modifications¹³⁸ exhibited good results leading to an increase in the roughness of a graphite cathode (from 2094 to 3873 nm) and also to the improvement of the surface area of α -Fe₂O₃ from 0.91 to 1.8 m² g⁻¹. Liu *et al.* designed a novel cathode made of CNTs and gold nanoclusters, which had the ability of gold to catalyze H₂O₂ decomposition⁵³ while CNT exhibits high hydrophobicity. This synergy allows higher H₂O₂ generation than other carbon materials.¹⁴⁵ Similarly, a novel carbonized skimmed cotton–CeO₂ hollow sphere (< 500 nm) cathode material was found to enhance the H₂O₂ production due to the high oxygen ion conductivity. The Ce³⁺/Ce⁴⁺ Fenton-like catalyst used in this work achieved a phenol degradation of 97.6% under optimized conditions.¹³⁷

Table 10.2 Summary of electro-Fenton-like catalysts and electrode materials.

Cathode/anode	Fenton catalyst	Pollutant/dose (mg L ⁻¹)	Degradation (%)	Time (min)	Degradation (%)/cycle number	Reference
Graphite/platinum sheet	Nanostructured Fe ₂ O ₃	Paraquat/20	85.8	150	~ 85/10	138
Graphite felt functionalized/platinum sheet	Nanoglobular Fe ₃ O ₄	Amoxicillin/1	98.2	60	~ 88/8	136
3D carbon felt electrode/platinum gauze	GO–Fe ₃ O ₄	Chloramphenico and Metronidazole/80	73/86	300	~ 68 and 81/4	142
Meso-NiMn ₂ O ₄ nanoparticles–carbon felt/Pt plate	(Mn ⁴⁺ /Mn ³⁺ and Ni ³⁺ /Ni ²⁺)	Ciprofloxacin/10	100	90	> 97/5	141
Au (nanoclusters)– CNT/Ti sheet	Au ⁰ –Au ⁺	Tetracycline/17.78	83.3	120	75/5	53
Carbonized skimmed cotton–CeO ₂ /Ti–IrO ₂ – RuO ₂	Ce ³⁺ and Ce ⁴⁺	Phenol/100	97.6	120	93.2/20	137

Interestingly, two catalyst redox couples (Mn⁴⁺/Mn³⁺ and Ni³⁺/Ni²⁺) have also been produced¹⁴¹ observing a synergistic effect when combining both. The material developed was a modified graphite cathode with meso-NiMn₂O₄ nanoparticles. Also, some researchers have developed novel strategies to overcome the drawbacks regarding the catalyst regeneration and sludge production using magnetic Fe₃O₄ nanoparticles as Fenton catalyst,^{136,142} which can enhance the Fenton-like reaction and the catalyst recovery. The development of catalyst recovery strategies is a necessary approach not only in Fenton processes but also in photocatalysis and other AOPs involving catalyst recovery.

10.5.2 Photo-Fenton Processes

10.5.2.1 Photo-Fenton Principles

The photo-Fenton processes rely on the excitation of an electron from the valence band to the conduction band of a catalyst using the external application of Ultraviolet–visible (UV–vis) radiation. The excited electron can favor the regeneration of the oxidized cations of the catalyst and enhance radical production. The photo-Fenton mechanism of the formation of these radical species is summarized in Figure 10.15.

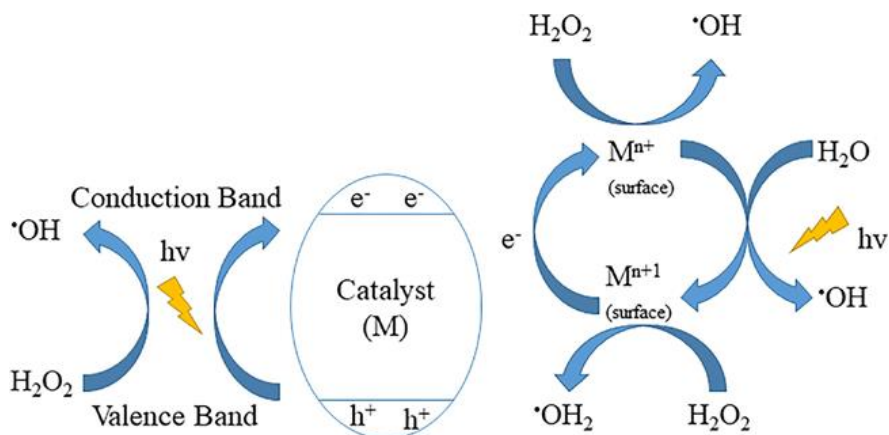


Figure 10.15 Schematic representation of a photo-Fenton-like process.

The metal and metal oxide-based materials for photo-Fenton-like processes share a common role, which is the decomposition of H_2O_2 for $\cdot\text{OH}$ production. The photo-Fenton-like reactions based on iron catalysts are described elsewhere^{146,147} and are summarized in eqn (10.20)–(10.27). Eqn (10.20) and (10.21) describe the catalyst electron production and transference to the Fenton catalyst. Eqn (10.22) and (10.23) promote catalyst reduction and regeneration using irradiated light. Eqn (10.24) and (10.25) favor the formation of ROS according to the conventional Fenton mechanism. Eqn (10.26) and (10.27) describe the effect of irradiation on the formation of $\cdot\text{OH}$ due to H_2O_2 and H_2O bond breakage.



The quantum yield and radical generation in photo-Fenton processes are dependent on the irradiation wavelength. The $\cdot\text{OH}$ generation increases with the decrease of wavelength due to the higher energy applied to excite the electrons.¹⁴⁸ The excitement of electrons favors the ejection of $\cdot\text{OH}$ from the solvent cages, therefore the availability of the radicals in the system increases. The characteristic absorption spectrum of the photocatalysts often requires the irradiation of short-wavelengths that are energy-consuming. The development

of novel composite photocatalysts able to absorb a broad spectrum range would overcome one of the main drawbacks in photo-Fenton processes. This research track is even more important in the development of visible light catalysts able to run under sunny outdoor conditions.

In summary, the main advantages of photo-Fenton against Fenton processes are 1) an increase in the mineralization of the micropollutants; 2) less pollutant adsorption required because of the higher radical yield, and 3) the possibility to use a renewable energy source like the sunlight.¹⁴⁹ It is, however, important to have a transparent solution, otherwise excess suspended particles might prevent the light penetration affecting the system performance.¹⁵⁰ This phenomenon is a problem, especially when dealing with large water bodies. Therefore, developing concentrate-and-destroy strategies to deal with reduced or concentrated volumes might be a suitable alternative to overcome this issue while decreasing energy consumption.

10.5.2.2 Photo-Fenton-like Nanocatalysts

The development of photo-Fenton-like nanocatalysts is summarized in Table 10.3. The two mainly explored catalysts are Cu- and Fe-based, despite other catalysts having been studied. The development of UV-vis Cu catalysts resulted in the production of several different catalysts, *e.g.*, a $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ catalyst with a crystallite size below 100 nm. This catalyst has a large number of surface hydroxyl groups and high surface area increasing the interfacial electron transfer and favoring the degradation of azure-B compared to CuO and V_2O_5 catalysts alone.¹⁵¹ The combination of Cu-based catalysts with carbon species, *i.e.*, the $\text{CuO-g-C}_3\text{N}_4\text{-H}_2\text{O}_2$ nanosystem, was successfully evaluated for the degradation of 2,4-dimethyl phenol (99%) under visible light irradiation,⁵⁵ in which the role of $\text{g-C}_3\text{N}_4$ is highlighted due to its 2D nanostructure capable of transferring excited electrons to the catalyst enhancing the radical production.

Table 10.3 Summary of photo-Fenton-like nanocatalysts.

Wavelength (nm)	Fenton catalyst	Pollutant/dose (mg L^{-1})	Degraded (%)	Time (min)	Degradation (%) / Cycle number	Reference
$\lambda > 420$	$\text{Ag}_3\text{PO}_4@\text{nanoNiFe}_2\text{O}_4$	BPA and methyl orange/10	> 95	30	> 75/4	¹⁴⁶
520	Nano $\text{Cu}_3\text{V}_2(\text{OH})_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	Neutral red/1118.9 and azure-B/305.8	75–60	120	~ 70 and ~55/5	¹⁵¹
Visible	$\text{nanoCuO-g-C}_3\text{N}_4$	2,4-dimethyl phenol/12.22	99	120	94/5	⁵⁵
365	$\beta\text{-FeOOH}@GO$	MB/40	~ 100	60	~ 100/5	¹⁵²
Visible	$\text{MoS}_2\text{-MnFe}_2\text{O}_4$ nanocomposite	Acid Blue 113/25	> 99	42	—	¹⁵³
> 420	$\alpha\text{-(Fe,Cu)OOH}$ nanorods	Diclofenac/40	~ 100	90	90/5	¹⁵⁴
365–450	CuFe_2O_4 nanoparticles	MB/50	92.1	80	—	¹⁵⁵
420	$\text{Cu-Fe}_3\text{O}_4@\text{carboxylate-rich carbon}$ nanocomposite	MB/40	97.5	40	~ 92.5/5	¹⁵⁶
> 420	WO_3 nanowire-rGO	BPA/20	~ 90	180	~ 5% decrease in TOC/5	¹⁵⁷
< 420	$\text{WO}_3\text{-g-C}_3\text{N}_4$	Ciprofloxacin/50	~ 100	120	94/5	¹⁵⁸

Likewise, the Fe-based catalysts are also commonly employed as photo-Fenton-like catalysts because of their higher stability, lower price, and less potential toxicity. $\beta\text{-FeOOH}$ nanorods (100 nm length $\times$ 20 nm width) and GO nanocomposite material were prepared for effective adsorption and degradation of MB under 365 nm irradiation.¹⁵² The combination of Ag_3PO_4 with Fe-based catalysts such as NiFe_2O_4 enhanced the degradation of methyl orange and BPA under visible light irradiation ($\lambda > 420$ nm) compared to pristine Ag_3PO_4 .¹⁴⁶ Similarly, a

MoS₂-MnFe₂O₄ nanocomposite was also studied for the degradation of Acid Blue 113 under visible light achieving 99% removal of this model pollutant.¹⁵³ This composite exhibited a suitable bandgap for visible light absorption and a large surface area due to the presence of MoS₂ nanosheets.

The combination of both Cu and Fe for the development of novel Fenton photocatalysts is also a strong current research line. An α -(Fe, Cu)OOH nanorod catalyst working under visible light irradiation (420 nm cut-off filter) was developed by doping Cu in the lattice sites of α -FeOOH.¹⁵⁴ It exhibited a complete degradation of diclofenac under optimum conditions. Recently, CuFe₂O₄ has been reported¹⁵⁵ as an effective visible light photocatalyst to enhance MB degradation up to 92.1% when employing tartaric acid and H₂O₂ to enhance the $\cdot$ OH generation. The combination of Fe and Cu catalysts with carbon material has also attracted the attention of researchers. The Fe : Cu ratio was evaluated in a Cu-Fe₃O₄@carboxylate-rich carbon nanocomposite for the degradation of MB reaching a 97.5% degradation under visible light.¹⁵⁶

Other interesting nanocatalysts have also been reported. For example, Xiao *et al.* developed a WO₃ - x nanowire-rGO composite for the photodegradation of BPA, achieving a maximum removal rate of ~90% under the visible region.¹⁵⁷ Similarly, Bai *et al.* removed the 2D structure, the wide absorption spectrum, and the capability to act as a Fenton catalyst of g-C₃N₄ to produce WO₃ nanocomposites for the effective degradation of ciprofloxacin, reaching ~100% removal within two hours.¹⁵⁸

The development in photo-Fenton-like processes has currently focused on the development of novel composite materials. Research with hardly degradable pollutants such as Per- and polyfluoroalkyl substances or different natured micropollutants (hydrophobicity and hydrophilicity) is suggested in the photo-Fenton-like systems. Additionally, the development of novel strategies to reduce treatment volumes (*e.g.*, concentrate-and-degrade) might be a research pathway that allows reduced energy consumption.

10.5.3 Microwave-Fenton Processes

10.5.3.1 Microwave-Fenton Principles

A microwave (MW) is a form of electromagnetic radiation ranging approximately from 1 GHz to 200 GHz using a wavelength of 30 to 0.15 cm⁻¹,¹⁵⁹ which can homogeneously dissipate energy in the reaction system. The thermal mechanism mainly depends on the frequency and the material that can promote the molecular motion and favor degradation reactions. There are two pathways to transform microwave energy into heat:¹⁶⁰ dipolar polarization and ionic conduction. In the dipolar polarization mechanism, heating is created due to friction resistance and collisions by a polarized molecule rotating in phase with an alternating field. In the ion conduction mechanism, the alternating field moves the charged particles that creates an electric current. The collision of ions does not allow the movement of the electrical current created, therefore it is dissipated as heat. The heat in both cases enhances the mass transfer and degradation and regeneration reactions in the system.

On the other hand, the MW catalysts present non-thermal effects that can also selectively adsorb the radiation-producing “hotspots” that promote the generation of $\cdot$ OH from H₂O₂.¹⁶¹ The increase in the vibration and rotational energy levels of polar H₂O₂ molecules increases the molecular motion and contact between the H₂O₂ and the hotspots. These hotspots can promote the breakage of the peroxy bond promoting the generation of free radicals during the catalytic process.¹⁶² Therefore, the oxidation efficiency of the overall process and degradation are increased (see Figure 10.16). Several different Fenton-like catalysts such as Fe(0),¹⁶³ CuFeO₂,¹⁶⁴ Fe₂O₃ (from iron ore tailing)¹⁶⁵ were demonstrated to perform better degradation than the classical Fenton reaction under MW-enhanced H₂O₂ activation.

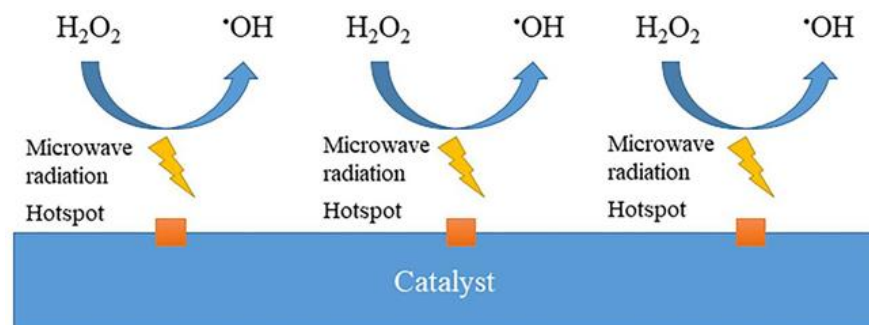


Figure 10.16 Schematic representation of a microwave-Fenton-like process.

Several studies were carried out to determine the parameters directly related to microwave degradation.^{164–168} Among them, microwave power is a key parameter as it increases the temperature and energy of the system using radiation which leads to an increase in the molecular motion and H_2O_2 decomposition, causing higher $\cdot\text{OH}$ production and pollutant removal rates according to eqn (10.28).



However, high energy consumption is still the main drawback to be overcome for the practical application of this technology. This issue could be overcome by finding low-cost and efficient concentration strategies to deal with smaller volumes of micropollutants.

In summary, microwave-Fenton-like^{169,170} processes are more effective than the thermal Fenton-like processes, Fenton-like processes, microwave- H_2O_2 , and microwave processes alone. Microwave-assisted Fenton processes can provide many advantages: 1) it is a clean way to enhance degradation; 2) a short application time is required; 3) high efficiency is usually achieved.

10.5.3.2 Microwave-Fenton-like Nanocatalysts

The heterogeneous catalysts that emerged for the microwave-assisted Fenton-like processes can be categorized into two main groups: Fe-based materials and non-Fe-based materials, as demonstrated in Table 10.4. Among the most interesting developments on Fe-based catalysts, BiFeO_3 nanoparticles have been highlighted due to their stability, enhanced catalytic properties, and reusability in microwave-enhanced Fenton-like processes.^{171,172} Nanocomposite materials of Ni-BiFeO_3 ⁴⁴ nanoparticles and $\text{Pb-BiFeO}_3\text{-rGO}$ ¹⁶¹ were also developed to increase the surface area and enhance the removal of BPA and PFOA, respectively. Besides, Fe/carbon-based catalysts had a considerable impact mainly due to their high surface area and regeneration capacity. For example, AC-based photocatalysts such as Fe-AC and FeOOH-AC composites were developed to use the surface properties of AC for pollutant adsorption.^{173,174} The reuse of nanoporous coal fly ash in microwave Fenton-like technologies has also been described^{175,176} mainly due to its capacity to substitute Fe^{2+} to form Fenton-like processes. Mixtures of Fe and other metals/metallic composites have also been reported, especially Cu-Fe bimetallic catalysts. A rGO composite loaded with copper ferrite nanocubes has achieved a degradation efficiency of 95.7% for Rh B in one minute, the role of rGO is to prevent electron-hole recombination, while the metals can act as MW catalysts producing hotspots.¹⁷⁷

Table 10.4 Summary of microwave-Fenton-like nanocatalysts.

Catalyst	Power (W)	Pollutant	Degradation (%)	Time (min)	Degradation/%/Cycle number	Reference
BiFeO_3 nanoparticles	300	Rh B	94.8	6	—	171
BiFeO_3 nanoparticles	200	BPA	94	6	87.5/6	172
	200	BPA	98.4	5	89.2/6	167

Ni foam–BiFeO ₃ nanoparticles						
Pb–BiFeO ₃ –rGO nanocomposite	300	PFOA	~ 90	5	~ 85/6	161
FeOOH nanoparticles inside porous AC	700	Methyl Orange	99.1	4	97.8/10	174
Nanoporous coal fly ash	700	Polyacrylamide	75 (TOC)	10	—	175
Nanoporous raw coal fly ash	100	Rh B	91.6	20	~ 70/7	176
rGO@Cu–Fe ₂ O ₃ nanocubes	500	Rh B	95.7	1	87.4/5	177
Pine needle-like CuCo ₂ O ₄ nanocatalyst	400	Metacycline	95.1	4	86.4%/5	179
Fe nanolayer–SiC	540	Norfloxacin	100	20	99/5	168

The research on non-Fe-based materials is not that extensive, especially at the nanoscale level. Despite this, many different materials have been developed. It is reported that a MW–Mn Fenton-like system obtained complete degradation of BPA under optimal conditions,¹⁶⁹ while CuO–Al₂O₃¹⁷⁰ was developed to effectively widen the applicable initial pH range of the degradation reaction of *p*-nitrophenol. A CuO_x–AC composite¹⁷⁸ was also prepared to target phenol degradation achieving 99.96% removal. More recently, the development of novel inorganic nanocomposites emerged, *i.e.*, CuCo₂O₄ nanoneedles¹⁷⁹ achieved a removal rate of 97.4% for metacycline within minutes. To achieve a faster and more efficient degradation of norfloxacin, a Fe(0) nanolayer was electrodeposited to form a Fe–SiC rod and applied in Fenton-like reactions.¹⁶⁸ The results revealed an increment of 61% in the removal rate when MW was applied to the system.

10.5.4 Cavitation-Fenton Process

10.5.4.1 Cavitation-Fenton Principles

Cavitation is a set of processes based on the formation and violent implosion of cavitation bubbles with a short lifetime. The mechanism underlying this procedure is the decomposition of the water molecules upon the collapse of the cavitation bubbles resulting in high pressure (100–5000 atm) and temperature (500–15 000 K) conditions.¹⁸⁰ The decomposition of the water molecules produces ROS (*i.e.*, [•]OH, [•]O₂H, and H₂O₂).



Acoustic (see Figure 10.14A) and hydrodynamic (see Figure 10.17B) are the most typical mechanism to generate cavitation.¹⁸¹ The first occurs because the violent vibration of the soundwave creates the gas cavities, whereas, in the latter, gas cavities are created due to the pressure difference driven by the difference in diameter of the piping. In this context, the formation, growth, and collapse of cavities in a liquid medium lead to violent cavitation. The most important reactions^{182,183} are summarized in eqn (10.29)–(10.31), which also occur in the hydrodynamic cavitation as the radical production mechanism is the same despite the different formation mechanisms of the cavitation bubbles.

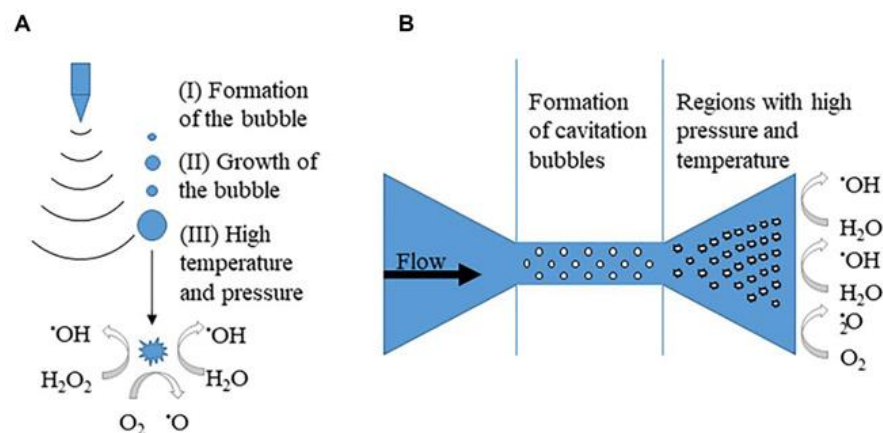


Figure 10.17 Schematic representation of acoustic (A) and hydrodynamic (B) cavitation-Fenton-like processes.

When combining cavitation with Fenton-like processes, a synergistic effect is observed. Gagol *et al.* extensively summarized the advantages and limitations of the cavitation phenomenon combined with AOPs.¹⁸⁴ Some of the main advantages include: 1) low operational costs compared to other AOPs; 2) limited byproduct formation compared with ozonation (producing bromate); 3) reduction of mass transfer resistance due to microcirculation and turbulence areas; 4) synergism of cavitation processes and Fenton processes; 5) enhancement on the degradation; 6) reduction of the H_2O_2 dosage required; 7) relatively easy scaling up for hydrodynamic cavitation.

During the cavitation-Fenton-like processes, power and hydrodynamic pressure are the most important factors for acoustic and hydrodynamic cavitation, respectively. On one hand, during acoustic cavitation, the increase of the sonication power promotes the formation of cavitation bubbles and radical species, although excessive cavitation power almost does not increase the cavitation efficiency.¹⁸⁵ On the other hand, during the hydrodynamic cavitation, the increase in the inlet pressure leads to an increase in the flow rate of the cavitation and ROS yield. However, it is reported that further increase in pressure beyond optimum value leads to the formation of cavity clouds that in turn reduces cavitation intensity resulting in a decrease in the extent of degradation.^{186,187}

Concerning the drawbacks of both technologies, sonication suffers from noise that may lead to the need for acoustic insulation, the energy costs due to the low conversion efficiency to collapse bubbles (compared to hydrodynamic cavitation), the volume limitations due to the almost exclusive formation of the cavitation bubbles close to the sonicator walls, and the costs of the equipment when scaling up the system.¹⁸³ These drawbacks strongly challenge the scaling up of acoustic cavitation potential unless dealing with micropollutant concentrates, albeit acoustic cavitation was proven to be almost ten times more expensive than hydrodynamic cavitation.¹⁸⁴ On the other hand, fewer hydrodynamic-Fenton works have been published,^{188,189} and even fewer on hydrodynamic-Fenton-like processes. Interestingly, Yi *et al.*, reported a synergetic effect when combining both cavitation processes for the degradation of small volumes of Rh B.¹⁸¹ Despite the fact that hydrodynamic cavitation is less common at the lab scale, it is a promising scalable process and does not present most of the acoustic cavitation drawbacks. The density of the fluid, the election of the pump, and the costs related to erosion due to the extreme local conditions are the main drawbacks. Therefore, research on this technology is encouraged to test its large-scale applicability due to its promising properties.

10.5.4.2 Cavitation-Fenton-like Nanocatalysts

Both acoustic- and hydrodynamic-Fenton-like processes can be divided into two groups: Fe-based catalysts and non-Fe-based catalysts. Table 10.5 summarizes the nanocatalysts employed for this process. Regarding the sonication Fe-based catalysts, Elshafei *et al.* investigated the sonication effect in a Fenton-like catalyst system using $\alpha\text{-Fe}_2\text{O}_3$ for nitrobenzene degradation, confirming the synergistic effect of the catalyst and sonication.

Without sonication, only 40% of degradation was achieved after one hour for α -Fe₂O₃, while almost complete degradation was achieved when combining sonication in just 30 minutes.¹⁹⁰ Natural Fe-based minerals like martite¹⁹¹ and argon plasma modified pyrite¹⁹² (FeS₂) have also been tested as catalysts to enhance degradation in the sono-Fenton system. Li *et al.* bio-synthesized schwertmannite for its use in Fenton-like processes,¹⁹³ where they defined two steps in the degradation of BPA: first, an induction period with low degradation rate, and later rapid catalysis periods. Enhanced reusability of this material was also observed due to the surface cleaning ability of the sonication process. Likewise, Hassani *et al.* developed a novel selective CoFe₂O₄-rGO catalyst combined with sonication which exhibited a maximum of 90.5% removal for Acid Orange 7 (AO7) dye under optimum conditions.¹⁸⁵ Interestingly, Li *et al.* tested a sonication-iron foam Fenton system that enhanced degradation of Rh B from <80% to 94.43% when using sonication, proving the importance of the external field applied in this a system.¹⁹⁴ For non-Fe-based catalysts, the research volume is much smaller. As an example, CuO nanocatalysts have been tested for the sonication assisted-Fenton-like degradation of nitrobenzene,¹⁹⁰ despite this catalyst exhibiting less efficiency than nano α -Fe₂O₃ (35 versus 40%).

Table 10.5 Summary of cavitation-Fenton-like nanocatalysts.

Cavitation	Power or Pressure	Frequency (kHz)	Catalyst	Pollutant	Degradation (%)	Time (min)	Reference
Sonication	100 W	20	Nano CuO	Nitrobenzene	~ 50	10	¹⁹⁰
Sonication	100 W	20	Nano α -Fe ₂ O ₃	Nitrobenzene	~ 95	10	¹⁹⁰
Sonication	300 W	40	FeS ₂ nanostructure	Reactive red 84	93.7	120	¹⁹¹
Sonication	150 W	36	Nano Fe ₂ O ₃	AB92 dye	~ 100	20	¹⁹²
Sonication	—	20	Nanovilli schwertmannite	BPA	98.0	60	¹⁹³
Sonication	350 W	40	CoFe ₂ O ₄ nanoparticles assembled in rGO	AO7 dye	90.5	120	¹⁸⁵
Sonication	300 W	20	Iron foam	Rh B	94.4	2	¹⁹⁴
Hydrodynamic	400 kPa		Fe(0) nanoparticles	Orange II sodium salt	99	60	¹⁹⁶
Hydrodynamic	200–500 kPa		Cu(0) nanoparticles	Methyl orange	83	20	¹⁹⁵

Concerning the hydrodynamic cavitation, fewer Fenton-like nanocatalysts have been developed. Cu(0) nanoparticles were studied for methyl orange degradation achieving 83% degradation after 20 minutes.¹⁹⁵ Recently, Badmus *et al.* developed a nano Fe(0) catalyst to degrade Orange II sodium salt¹⁹⁶ using a hydrodynamic pressure of 400 kPa and observed 99% decolorization and an enhancement of 56.8% of TOC removal compared with the usage of the advanced Fenton processes without cavitation.

10.5.5 Combination of Hybrid Fenton Processes

10.5.5.1 Combination of Electro- and Photo-Fenton Processes

The combination of photo- and electro-Fenton processes have also attracted the attention of researchers. Ganyiu *et al.* reviewed the recent developments in heterogeneous catalysts for photo-electro-Fenton systems.¹⁹⁷ For instance, a photo-electro-Fenton system employing nano Fe(0) has been tested for phenol degradation. Under the addition of UV light irradiation (254 nm), the electro-Fenton increased the degradation efficiency from 87.38% in 60 minutes to complete degradation in 30 minutes.¹⁹⁸ Composite materials employing TiO₂ nanotubes and nano α -Fe₂O₃ have been synthesized as anode materials to be tested as photo-electro-Fenton systems for phenol degradation.¹⁹⁹ At 420 nm irradiation, the α -Fe₂O₃ nanoparticles and TiO₂ nanotubes formed heterojunctions to

avoid the electron-hole recombination for enhanced performance of the system. The design of mixed catalysts may also help to improve the performance of both external fields, such as Fe_2O_3 @carbon felt²⁰⁰ and Fe_3O_4 @graphite.²⁰¹

Mercury discharge lamps are also used in photo-electro-Fenton processes as they can emit at a wide range of wavelengths. Some authors^{202,203} used a microwave discharge electrodeless lamp (MDEL) as a UV irradiation source under different electro-Fenton systems, ordering the degradation efficiency of ciprofloxacin as $\text{MDEL} < \text{anionic oxidation (AO)} < \text{AO-H}_2\text{O}_2 < \text{MDEL-AO-H}_2\text{O}_2 < \text{EF} < \text{MDEL photo-electro-Fenton process}$. This behavior was justified due to the extra $\cdot\text{OH}$ formed from H_2O_2 and Fe(OH)^{2+} photolysis and the photodegradation of intermediates when irradiated under MDEL.

The work published related to the combination of photo-electro-Fenton processes confirms the enhancement in micropollutant degradation for several catalysts. Despite this, materials design is critical to take a maximum rid of the two processes. Additionally, energy considerations must be taken into account to evaluate the economic viability of the procedure due to the high energy consumption of the system.

10.5.5.2 Combination of Microwave-Fenton Processes

The microwave-Fenton-like processes have also been studied in combination with other external fields to enhance the degradation performance. UV-vis and electro external fields are the most widely employed. Among the UV-vis external fields, the use of both metallic discharge lamps and electron discharge lamps has been extended. Particularly, microwave electron discharge lamp technology presents clear advantages²⁰⁴ compared to classical Hg lamps because it: 1) is not damaged by the microwaves, 2) has good photochemical efficiency, 3) presents a longer life, 4) has lower costs, 5) uses simpler photocatalytic equipment and 6) has adjustable intensity to modify the power of the microwaves and wavelength. It is important to notice that, to achieve a synergistic effect the catalyst must have microwave catalytic and photocatalytic activities.

Using a Cd discharge lamp²⁰⁵ along with microwave irradiation showed an increment in the reaction rate by at least a factor of 50 and also an improvement in the extent of degradation of a commercial phosphate pesticide, demonstrating a synergistic effect of microwave and photo-Fenton processes. Similarly, the microwave-assisted electron discharge lamp in combination with a microwave- ZnFe_2O_4 nanoparticle system²⁰⁶ increased tetracycline hydrochloride degradation to 91.6% in 4 min compared to microwave (~ 40%) and photo (~20%) irradiation combined with the ZnFe_2O_4 without microwave irradiation.

These hybrid reactions are still challenged by the insufficient microwave or visible light absorption of catalysts. Therefore, the main concern is to find out an appropriate catalyst for the system that can remove both external fields.

Regarding the microwave-assisted electro-Fenton reactions, less research has been carried out. Despite this, Wang *et al.* demonstrated²⁰⁷ that the external application of microwaves on an electro-Fenton-like process enhanced the mineralization of methyl orange by the activation of the electrode surface and accelerated $\text{Fe(III)}/\text{Fe(II)}$ redox cycles, leading to relatively steady Fe(II) recovery and increased formation of $\cdot\text{OH}$. Yet, more studies need to be done to discuss the efficiency of this technology.

10.5.5.3 Combination of Cavitation-Fenton Processes

The combination of cavitation-Fenton-like processes with other external fields has also been tested. Moradi recently summarized the current state-of-the-art photo-sono-Fenton-like processes and extensively discussed the influence of operational parameters, providing some insights to the future research lines in the field.²⁰⁸ Dükkancı developed a LaFeO_3 photo-sono-Fenton catalyst and observed a 21.8% degradation of BPA in three hours, which is the highest among the tested procedures.²⁰⁹ Similarly, Artal *et al.* also obtained an enhancement of 25% for the MB degradation in UV-sono-Fenton processes compared with UV-Fenton processes when employing raw cyanobacterial ash as a catalyst.²¹⁰ Despite this, a group reported higher rate constant values for photo-electro-Fenton processes than sono-electro-Fenton processes.¹⁹⁸

Hydrodynamic-electro-Fenton-like processes are less explored, although its combination also increases the degradation performance of the pollutants in the water bodies. A group observed that under optimum conditions,

the percentage of removal by electro-Fenton and sonication was 81.7% and 9%, respectively, but the hybrid process exhibited a removal percentage of 97.5%.²¹¹ The combination of sonication with microwave-assisted Fenton processes also has the potential to improve the Fenton-like processes. Wu *et al.* tested different reaction conditions observing an increase in the degradation rate of phenol from 7% (microwave) and 28% (sonication) to 65% when combined.²¹²

Regarding the combined-cavitation-Fenton processes, deeper research should be performed on hydrodynamic cavitation as it is easily scalable and a more promising approach. This process has barely been tested in combination with other processes. Sonication has proven to be hardly scalable and some studies¹⁹⁸ suggest it can be less effective than other external fields. Therefore, despite its easy operation and effectiveness at the lab scale, new methods or alternatives need to be developed to overcome its current drawbacks.

10.6 Conclusions and Future Research Directions

As a mainstream technology in AOPs, the Fenton reaction has been widely used. However, the development of Fenton catalytic technology is greatly limited by its various defects. Even though Fenton-like catalytic technology greatly improves the deficiency of Fenton technology and the application of nonmetallic materials also enriches the function of Fenton-like catalyst, there are still many problems because it does not get rid of the limitations of the traditional Fenton reaction principle. In this chapter, the principles of traditional Fenton and Fenton-like technology are reviewed. The use of metal, nonmetal, and hybrid Fenton-like catalysts is introduced. The Fenton-like materials based on the traditional Fenton principle and various new Fenton-like catalytic processes are cited. At the same time, the hybrid process between Fenton technology and other technologies is also introduced. In summary, the following conclusions are drawn.

1. Although the Fenton-like materials based on the traditional Fenton principle can accelerate the electron transfer rate through a surface modification to achieve the efficient conversion of ROS, the accumulation of high valence metals and the ineffective decomposition of oxidants still lead to rapidly decreased activity of such catalysts and low utilization rate of oxidants.
2. The dual reaction center based on the principle of a galvanic-like cell separates the oxidation reaction from the reduction reaction, which completely avoids the occurrence of the speed limiting step of Fenton reaction and improves the utilization efficiency of oxidant.
3. The Fenton-like catalytic process dominated by $^1\text{O}_2$ derived from free radical conversion or direct conversion is prone to attack electron-rich functional groups and degrade unsaturated pollutants due to the selective degradation of $^1\text{O}_2$.
4. Nonmetallic materials play an increasingly important role in the preparation of Fenton-like materials. Inorganic carbonaceous materials provide a variety of possibilities for the preparation of materials, whether as carriers to provide adsorption sites or as electron transfer media to accelerate the reaction process.
5. The combination of single atom and nonmetal provides more efficient active sites and atom conversion for Fenton catalysis.
6. Using different mechanisms, the application of external fields is an effective way to enhance the performance of the Fenton process, by promoting the $\cdot\text{OH}$ production and subsequently micropollutant degradation.
7. While systematic profiling research on the Fenton-like catalytic system has surfaced, researchers are still suggested to put forward relatively new improvement methods. In order to move further steps for the heterogeneous Fenton catalytic technology to practical application and promotion, the following aspects shall be improved:
 - a. Explore the potential of nonmetallic materials in the Fenton field, such as free radical fixation, nanoconfinement, or pollutant capture.
 - b. Integrate the dual reaction center and other mechanisms to solve the lack of mineralization ability for refractory substances and the limitation of electron transfer. For example, interfacial reaction or chemical bonding can improve the electron migration of pollutants on the catalyst surface.
 - c. Understand how to use the new Fenton-like catalytic system to solve the practical wastewater treatment problems, such as whether the treatment of high salt wastewater can use the fixing radicals on the surface to avoid the quenching of free radicals by inorganic salts.
 - d. Combine and optimize hybrid Fenton technologies as well as the development of suitable catalysts to explore their commercial applications.

e. Develop feasible engineering strategies to realize the *in situ* implementation of Fenton catalytic systems for water purification and reuse.

Abbreviations

2D	Two-dimensional
3D	Three-dimensional
AC	Activated Carbon
AO7	Acid Orange 7
AOP	Advanced Oxidation Processes
AR	Acid Red
Cu ⁰	Zero-valent Copper
CNTs	Carbon Nanotubes
CP	Chlorophenol
DFT	Density Functional Theory
DRCC	Dual-reaction Center Catalyst
E^0	Standard Electrode Potential
EXAFS	Extended X-ray Absorption Fine Structure
Fe ²⁺	Ferrous ion
FeS ₂	Pyrite
Fe ₃ O ₄	Magnetite
α -Fe ₂ O ₃	Hematite
α -FeOOH	Goethite
γ -Fe ₂ O ₃	Maghemite
γ -FeOOH	Lepidocrocite
FeOOH	Ferrihydrite
g-C ₃ N ₄	Graphitic Carbon Nitride
GO	Graphene Oxide
H ₂ O ₂	Hydrogen Peroxide
HAADF-STEM	High-angle Annular Dark-field Technique of Scanning Transmission Electron Microscopy
HO ₂ [·]	Hydroperoxyl Radical
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
MB	Methylene Blue
MDEL	Microwave Discharge Electrodeless Lamp
MOFs	Metal–Organic Frameworks
¹ O ₂	Singlet Oxygen
OH [−]	Hydroxide
O ₂ ^{·−}	Superoxide Radical
·OH	Hydroxyl Radical
·OH _{free}	Free ·OH
·OH _{ads}	·OH Adsorbed
PFOA	Perfluorooctanoic Acid
POP	Persistent Organic Pollutants
rGO	Reduced Graphene Oxide
Rh B	Rhodamine B
ROS	Reactive Oxygen Species
R [·]	Organic Radicals
SMA	Sulfamerazine
SMT	Sulfamethazine

TOC	Total Organic Carbon
UV-vis	Ultraviolet-visible
UVA	Ultraviolet Radiation A
UVB	Ultraviolet Radiation B
XAFS	X-ray Absorption Fine Structure
XPS	X-ray Photoelectron Spectroscopy

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Chapter 11

Functional Carbon Nanomaterials for Advanced Oxidation Processes

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11.1 Introduction

The rapid growth in the industrialization and urbanization of human society comes at the great cost of environment deterioration. A diversity of organic microcontaminants, such as endocrine disrupting chemicals, pharmaceuticals, antibiotics and pesticides have emerged, which have posed serious ecological impacts and are resistant to natural degradation.^{1,2} In order to remediate the contaminated water, physical separation and chemical oxidation have been adopted as effective strategies to remove the associated aqueous micropollutants. However, physical approaches including membrane separation, evaporation, filtration, and adsorption require an intensive energy input or long-term operation. After physical processing, these pollutants transfer and accumulate into another phase and still require further treatment. Thus, an effective technology to directly degrade recalcitrant organics into harmless compounds is required for water purification. To this end, advanced oxidation processes (AOPs) are an alternative chemical decomposition strategy, which have been widely

studied for degrading recalcitrant organics and purifying wastewater. The history of AOPs can be traced back to 1886 when ozone was first used to sterilize contaminated water. In 1894, Fenton discovered that ferrous ions can activate hydrogen peroxide (H_2O_2) to produce hydroxyl radicals ($\text{HO}^\cdot$) with a high oxidation capacity. These ozonation and Fenton processes are categorized as hydroxyl radical-based advanced oxidation processes (HR-AOPs) and have been developed for decades for practical applications. However, HR-AOPs have limitations of reagent instability, difficulty in storage/transport of H_2O_2 /ozone (O_3), pH dependence of $\text{HO}^\cdot$, and generation of massive iron sludge especially in Fenton reactions.³ Sulfate radicals ($\text{SO}_4^{\cdot-}$) can be generated *via* activating the parent persulfate salts of peroxymonosulfate (PMS) or peroxydisulfate (PDS) and have a few merits over $\text{HO}^\cdot$. For instance, $\text{SO}_4^{\cdot-}$ not only possesses a higher oxidation potential and a longer life span than $\text{HO}^\cdot$, but also demonstrates great effectiveness in a wider pH range. Moreover, persulfate salts are solids and are more chemically stable than H_2O_2 , resulting in a lower cost for transportation and storage of the reagents. Sulfate radical-based or persulfate-based AOPs (SR-AOPs or PS-AOPs) have proven effective in the decomposition of various recalcitrant organic contaminants such as pharmaceuticals and endocrine disruptors; also, the SR-AOPs techniques have been applied in dewatering/decomposition of activated sludge⁴ and disinfection of urban wastewater.⁵

Sulfate radicals can be generated by PMS and PDS activation *via* multiple methods, such as heat, UV, chemicals, transition metal ions and ultrasound. However, the requirement for external energy intensively increases the operational cost; the application of transition metal ions (Ag^+ , Fe^{2+} and Cu^{2+}) is limited to a narrow working pH range to prevent precipitation and requires a post treatment of the dissolved metals.⁶ Heterogeneous systems based on metals/oxides, such as Fe^0 , Co_3O_4 ,⁷ Fe_3O_4 ,⁸ MnO_2 ⁹ and CuO ,¹⁰ have been extensively investigated in recent years.¹¹ Nonetheless, the drawbacks of metal catalysts such as scarcity, high cost, and potential biotoxicity of the leached metal ions prohibit the

practical application, calling for the development of next-generation low-cost and stable catalysts for water treatment.

Carbonaceous materials such as graphene, carbon nanotubes (CNTs), and biochar demonstrate excellent biocompatibility, great stability in a wide pH range, and tunable physicochemical features,¹² and are capable of overcoming the inherent shortcomings of metal-based catalysts without compromising the efficiency. In order to further enhance the catalytic performances of graphitic carbons, chemical and/or structural engineering has been applied such as heteroatom doping and encapsulation of metal elements. This chapter will present a general introduction of carbocatalysts, the properties of PMS/PDS and corresponding reactive oxygen species (ROS). On this basis, we will then summarize the application of carbocatalysts in SR-AOPs and the corresponding mechanisms.

11.2 Carbocatalysts

Carbocatalysts are typically carbon-based materials with a conjugated graphitic network, unique molecular symmetries, and functionality. As a result, carbocatalysts show intriguing mechanical, electronic, electrocatalytic, magnetic, and photonic properties.¹³ Carbonaceous materials are appealing in environmental catalysis¹⁴ because they avoid toxic metal lixiviating and can effectively activate PMS and PDS at neutral pH without external energy and chemicals.¹³ In addition to their superior catalytic performances, the strong adsorption capacity of carbon materials toward organic pollutants also contributes to catalytic oxidation.¹³ So far, different dimensions of carbon allotropes have been exploited to activate persulfates. For example, zero-dimensional (0D, D for dimensional) nanodiamonds (NDs) and fullerene, 1D CNTs, 2D graphene, and 3D cubically-ordered mesoporous carbon (CMK-8) have been investigated in SR-AOPs.¹⁵ Additionally, bulk carbonaceous materials including activated carbon (AC), carbon fiber and biochar are characterized by the complex structure and non-stoichiometry, which demonstrate mediocre performances with unclear active sites.¹⁶ Herein, low dimensional nanocarbons with simplified configurations are model candidates for investigating the origins

of carbocatalysis in AOPs, which help reveal the principle for the precise design of on-demand carbocatalysts with a high efficiency and low cost.¹⁷

11.2.1 Graphene

Graphene is a 2D planar nanosheet packed with hexagonally arranged carbon atoms, which can be obtained by the exfoliation of natural graphite.^{18,19} Graphene is the thinnest and the most resilient material and possesses outstanding thermal conductivity, a large specific area, superior electrical conductivity, and a higher fracture strength than steel. It is also the building block of other dimensional carbocatalysts as it can be bent or stacked into 0–3D carbon allotropes (see [Figure 11.1](#)). There are two main developed approaches that have been adopted to prepare graphene, which are bottom-up and top-down methods.²⁰ The bottom-up strategies include chemical vapor deposition (CVD) and chemical synthesis, which are suitable for manufacturing high-quality graphene but at a high cost and under complicated conditions. The top-down methods are less-expensive and simpler, and have been applied in graphene synthesis by exfoliating graphite into acid-oxidized graphite oxide (GO), followed by chemical reduction of GO. The obtained product is also termed reduced graphene oxide (rGO, see [Figure 11.2](#)).²¹

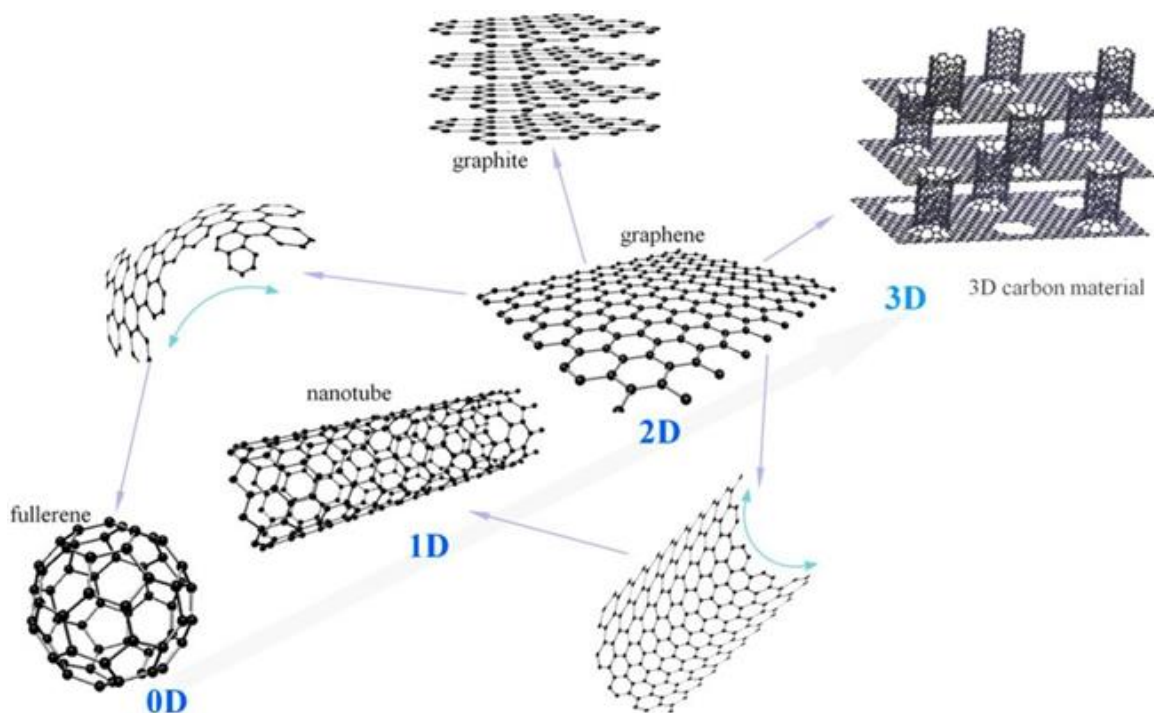


Figure 11.1 Structure of carbon allotropes in different dimensions, demonstrating 2D graphene can be the building block of other structures. Reproduced from ref. ²⁰ with permission from American Chemical Society, Copyright 2015.

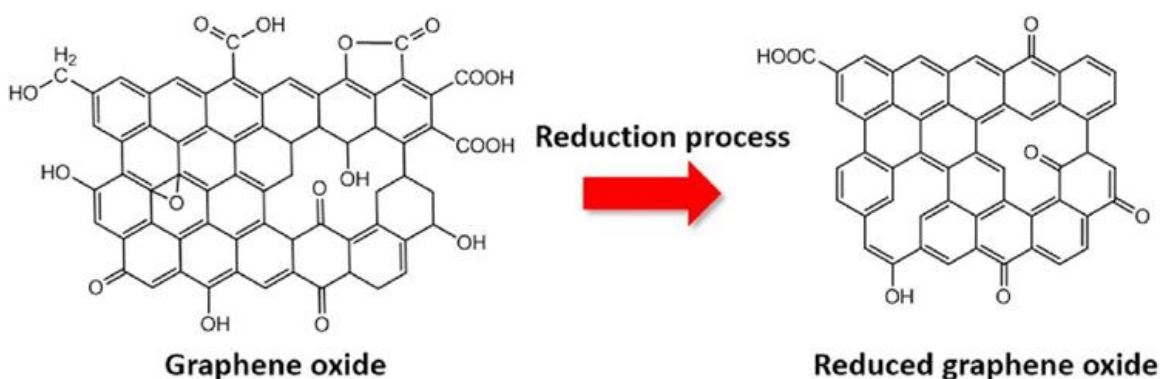


Figure 11.2 Reduction process of GO to rGO. Reproduced from ref. ²¹ with permission from Elsevier, Copyright 2016.

Despite the excellent physical properties, graphene is catalytically inert due to the intact sp^2 hybridized honeycomb network and near-zero bandgap. Thus, pristine graphene and CNTs normally show a poor activity in

catalysis.¹⁸ Equipping defects and functional groups on graphene will introduce new catalytic centers and effectively enhance the activity of graphene in redox reactions.¹⁷ In addition, the defects and edges of the carbon network possess high-density unpaired electrons that can provide anchoring sites for heteroatoms.

Another pathway to break the inertness of graphene is to incorporate heteroatoms into graphene with different electronegativities. The foreign atoms can alter the structural and chemical properties of graphene, as well as disorientate the homogeneously conjugated electron network by tailoring the charge/spin density of the doped region.^{14,22} Pre-oxidation of graphitic carbons is conducive to chemical doping because of the intimate interactions between the induced defects/oxygen groups and the precursors of heteroatoms.^{17,23}

11.2.2 Carbon Nanotubes

CNTs possess a curved, 1D sp^2 hybridized framework that is highly graphitic with limited functionality and defects.²⁴ CNTs have the virtues of low mass transfer limitations, high mechanical resistance, excellent electrical properties (high-level electron mobility and electrical conductivity), and high thermal stability.²⁵ CNTs are also excellent adsorbents for organic molecules, and multiple mechanisms (*e.g.* hydrophobic interactions, hydrogen bonds, π - π interactions and electrostatic interactions) may contribute to the adsorption processes.²⁶ CNTs can be single-walled (SWCNTs) or multi-walled (MWCNTs). SWCNTs are characterized by the small diameter (in the nm range), tunable electrical properties (from semiconducting to metallic relying on chirality), and superior thermal and mechanical properties.^{27,28} MWCNTs are composed of a series of co-axial SWCNTs with a larger diameter. MWCNTs exhibit unique electronic properties determined by the chirality of the SWCNTs.²⁹

Low-temperature CVD techniques are more attractive than high temperature techniques (*e.g.*, arc discharge and laser ablation) in CNT synthesis, because the properties such as nanotube length, density, alignment, purity and diameters can be controlled precisely. Also, other

approaches such as liquid pyrolysis and bottom-up organic methods have been developed to produce high-quality CNTs.²⁹

Typically, PMS/PDS activations include the cleavage of O–O bonds and electrons transport between the peroxides and catalysts. Thus, the defective level and electronic structures of CNTs are critical for persulfate reactions. Similar to intact graphene, pristine CNTs lack defects and functional groups, giving rise to limited catalytic activity. Introducing metal-free heteroatoms (such as O, N, S and B) is a feasible strategy to enhance the catalytic activity. Substitutional doping can regulate the properties such as specific surface area (SSA) and hydrophilicity, interrupt carbon configuration, alter electron states, and create more active sites.^{22,30} Together with graphene, the doping methods for CNTs can be classified into two categories, which are direct synthesis and post treatment. The direct synthesis is based on the molecular carbon and dopant precursors, while the post treatment starts from pristine graphene (or GO) and CNTs. It has been reported that the catalytic performances of graphene and CNTs in PMS-based AOPs follow the sequence: pristine graphene < rGO-700 < SWCNT < N-SWCNT < N-graphene-350 < N-graphene-700.³¹

11.2.3 Nanodiamonds

NDs are nano-scaled sp^3 hybridized carbons packed with tetrahedral bonding units (see Figure 11.3). NDs demonstrate outstanding chemical stability, great biocompatibility and extremely low toxicity, which enable its popularity for applications in biotechnology such as drug delivery,³² bioimaging,³³ and biosensing.³⁴ Also, NDs have been adopted as a candidate for metal-free catalysis in recent years due to their promising catalytic potential.

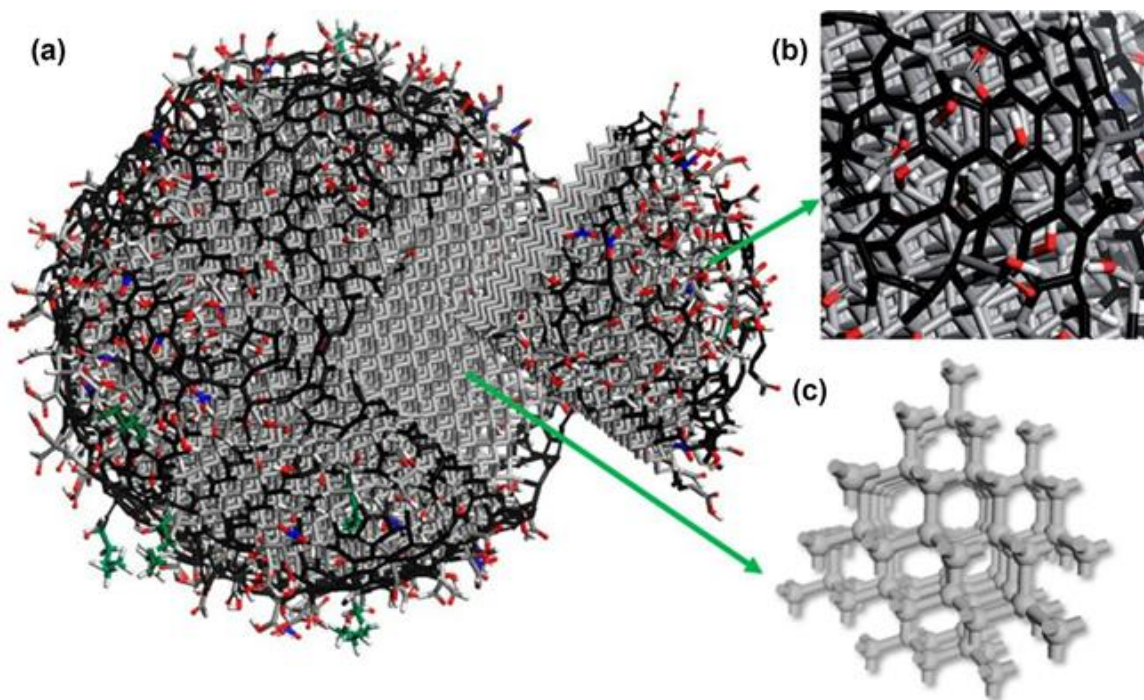


Figure 11.3 (a) Illustration of the structure of detonation ND, (b) closer view of the ND surface covered with functional groups and sp^2 carbon, (c) sp^3 carbon framework in the core. Reproduced from ref. ³⁵ with permission from Springer Nature, Copyright 2012.

NDs can be manufactured by three approaches as illustrated in Figure 11.4.³⁵ To be specific, NDs can be obtained by 1) physical ball-milling microscale synthetic or natural diamond crystals with ceramic beads,³⁶ 2) CVD with carbon-rich molecules and hydrogen carrier gas on a metallic or silicon substrate,³⁷ and 3) converting carbon-rich explosives (*e.g.* trinitrotoluene (TNT), octogen (HMX) and hecogen (RDX)) into diamond nanocrystals with a closely packed cubic phase in sp^3 hybridization.³⁸ Detonation is the most commercially used method, and the derived products are covered with nondiamond carbons due to the incomplete transition of the precursors and spontaneous graphitization on the surface.³⁹ Thus post treatments using liquid oxidizers⁴⁰ and ozonation⁴¹ are required for purification.

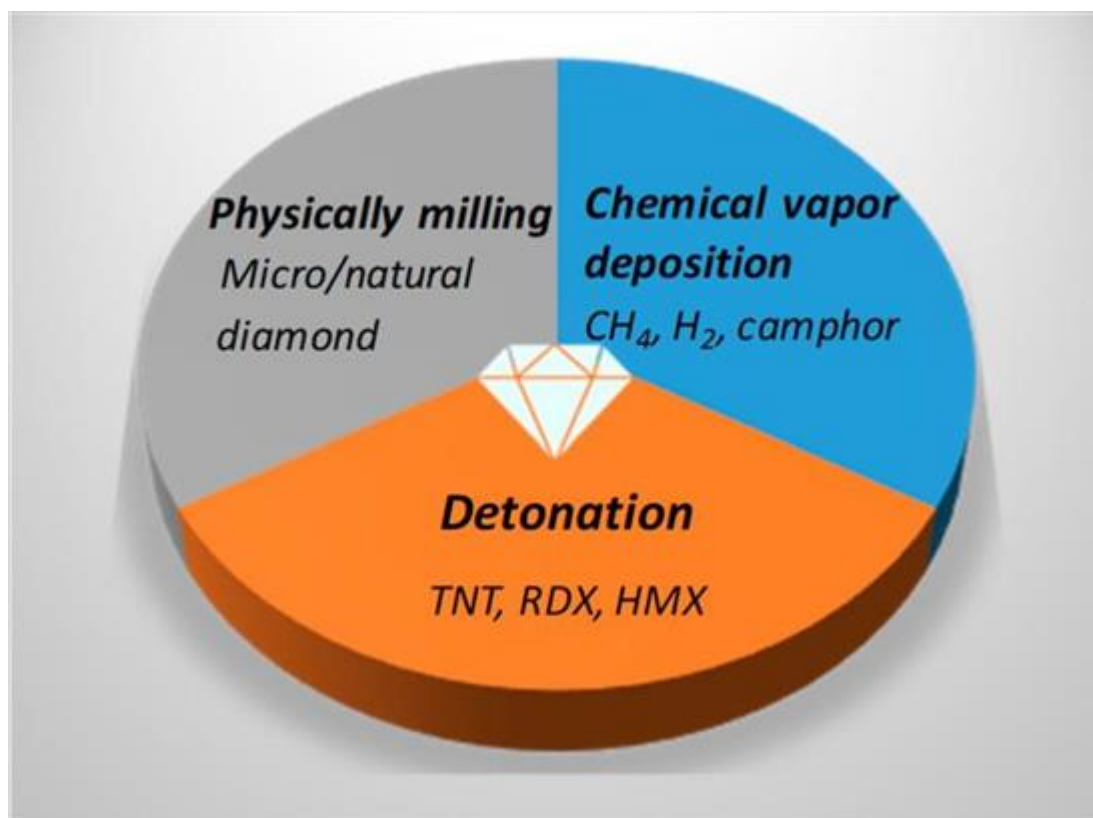


Figure 11.4 Synthesis methods of nanodiamonds. Reproduced from ref. ⁴² with permission from American Chemical Society, Copyright 2019.

Different from bulk carbons, NDs present as spherical nanoparticles (NPs) with a high surface-to-volume ratio, exposing a large percentage of carbon atoms at the surface and subsurface, which is available for chemical reactions. This ND surface has high chemical activity to form a variety of surface moieties such as oxygen functional groups and hydrogen bonds to stabilize the surface.⁴² Treatments with liquid/gaseous oxidizers can help to achieve this aim and increase surface acidity. These oxygen functional groups can in turn serve to functionalize the surface, determining various properties in graphitization, aggregation and solubility/stability.^{43–45} On the contrary, annealing under reductive or inert gas will reduce the oxygen content and modulate the basicity.⁴²

The unsaturated surface carbons (such as the defects or dangling bonds depicted in Figure 11.3) of NDs tend to detach and re-fabricate into an sp^2 hybridized sphere (a fullerene shell).⁴⁶ Thermal annealing can significantly

facilitate this process to construct a uniform core(sp^3)–shell(sp^2) nanocomposite, named bulky nanodiamonds (BNDs). BNDs possess the properties of both the graphitic shells and the diamond core, and may exhibit new features due to the hybrid structure with high stability. As the annealing temperature increases, the proportion of sp^2 hybridization increases, eventually forming sp^2 hybridized onion-like carbons (OLCs) when annealing temperature is over $1700\text{ }^\circ\text{C}$ ⁴⁷ (see Figure 11.5). The graphitization degree and rate can be influenced by various factors including surface index, metal impurities/catalysts, annealing conditions, and the particle size of the NDs.^{46,48}

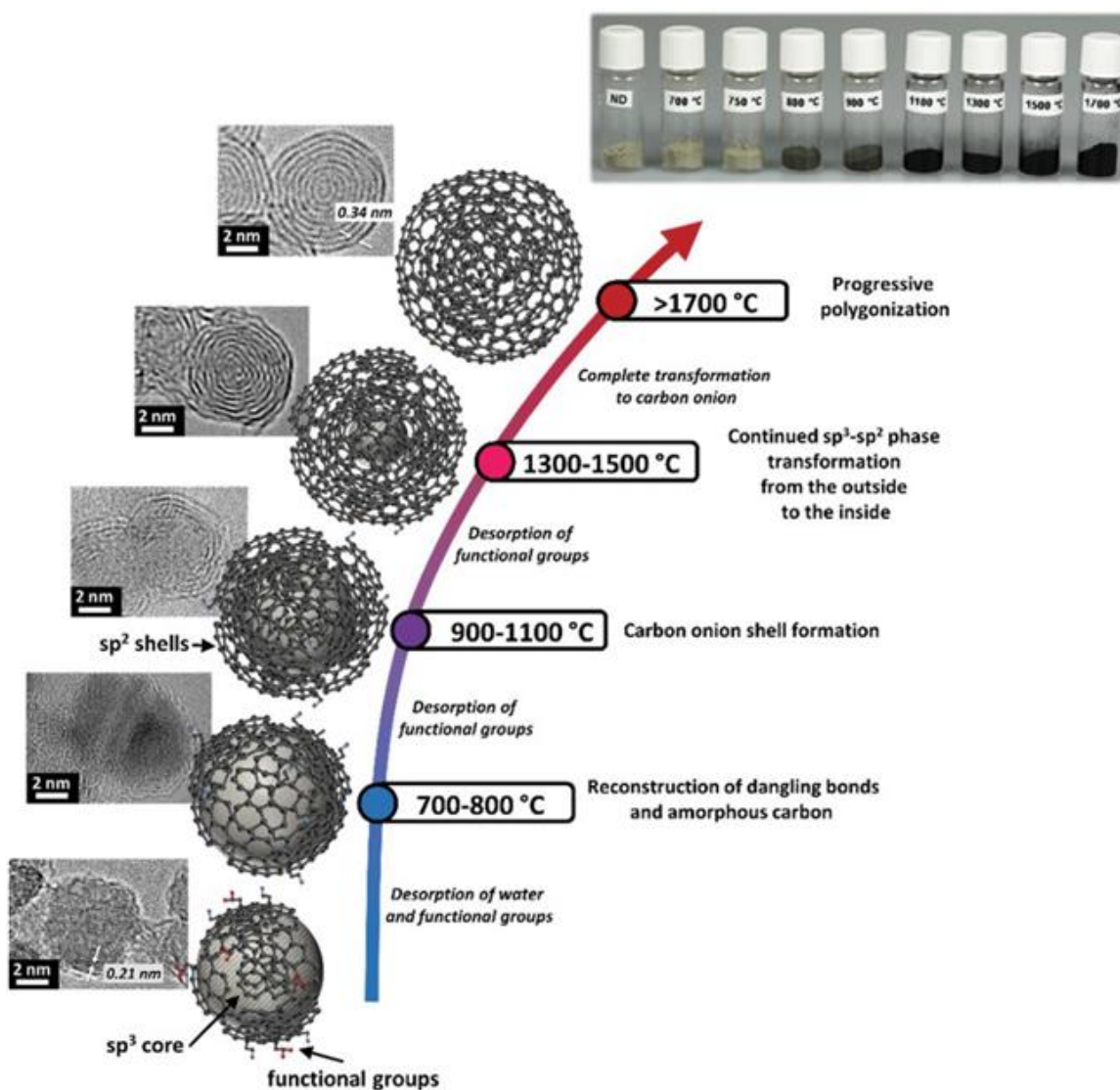


Figure 11.5 Structural transformation ($sp^3 \rightarrow sp^2/sp^3 \rightarrow sp^2$) of ND at increasing annealing temperatures. Reproduced from ref. ⁴⁸ with permission from the Royal Society of Chemistry.

11.2.4 Metal–Carbon hybrids

Though transition metal ions and heterogeneous metal-based materials are highly effective in PMS/PDS activation, the use of metal catalysts may suffer from poor stability and toxic metal leaching. On the contrary, carbonaceous materials show the merits of non-toxicity and high stability. Thus, construction of composites *via* the encapsulation of metal NPs beneath carbon layers will provide a highly efficient and robust catalyst for SR-AOPs.

For metal–carbon composites, graphene is a superior carrier compared to AC because of its high chemical stability, superior conductivity, and high adsorption capacity.¹³ The oxygen functionalities on the GO surface will provide active regions for the nucleation and growth of metal NPs without aggregation. Also, CNTs are ideal substrates for the encapsulation of zero-valent iron, cobalt and nickel-based NPs. Intriguingly, these NPs prefer to sit at the defect sites of CNTs and will generate new defects as well as active sites.⁴⁹ For NDs, some researchers incorporated transition and noble metals (*e.g.* Fe, Co, Ni, Pt) along with nitrogen into the carbon lattice; as a result, novel characteristics and catalytic behaviors emerged for the new composites.^{50,51} In return, transition metal NPs (*e.g.* Fe and Ni) can serve as catalysts to fabricate carbon precursors into a well-defined graphitic matrix during thermal synthesis; meanwhile, the metal NPs will be enclosed beneath the carbon layer.⁵²

11.3 Advanced Oxidation Processes

11.3.1 Water Treatment Methods

Pump–heat treatment and microbial degradation are two approaches for groundwater remediation.^{11,53} However, the former is expensive and time-consuming, and the latter needs harsh conditions such as anaerobic environments in some scenarios. Also, the microorganisms are applicable to

a limited type of pollutants, which narrows its applications. Biodegradation is the most adopted technology in wastewater treatment, but some recalcitrant contaminants are resistant to removal using this strategy.⁵⁴ AOPs possess the merits of high capability and adaptability for pollutant oxidation and have become a more powerful technology to degrade persistent organic contaminants in water.

11.3.2 Different Advanced Oxidation Processes

AOPs were first used to treat potable water in the 1980s, mainly relying on the formation of $\text{HO}^\cdot$ to purify organic pollutants. Subsequently, sulfate radical-based oxidation was developed,⁵⁵ and now receives increasing attention. In AOPs, various superoxides have been exploited such as O_3 , H_2O_2 , PDS, and PMS.

Hydroxyl radicals are the primary reactive oxygen species in AOPs. Because of the high oxidation potential ($E^\circ (\text{HO}^\cdot/\text{HO}^-) = 1.9\text{--}2.7 \text{ V}_{\text{NHE}}$) and fast high reaction rate constants of $\text{HO}^\cdot$ with most of organics, a myriad of research has endeavored to increase the applicability of HR-AOPs. Numerous methods have been applied to produce $\text{HO}^\cdot$ *in situ*, including ozone-, UV- and Fenton-related AOPs.⁵⁵ For Fenton systems, modifications have been applied to promote the activity, including Fenton-like, photo-Fenton, electro-Fenton based systems and their combinations. Even so, there are some drawbacks of homogeneous Fenton reactions, such as high consumption of H_2O_2 , production of ferric hydroxide sludge, and a narrow working pH window. Ozone is a common oxidant for $\text{HO}^\cdot$ generation and is different from other oxidants, because it is in the gas phase and needs to be transferred to the aqueous phase. The low mass transfer efficiency and the instability of O_3 restrain the ozonation processes.¹⁷ In addition, the high cost of O_3 generating hinders real applications.⁵⁶

Compared with H_2O_2 and O_3 , persulfates (including PMS and PDS) have the advantages of high yield of ROS, various activation methods, and a stable and solid form for storage and transport.¹⁷ SR-AOPs have several features. 1) $\text{SO}_4^{\cdot -}$ shows high effectiveness and selectivity towards pollutants *via* electron transfer with the unsaturated bonds or aromatic π

electrons of target organics. 2) The oxidation potential of $\text{SO}_4^{\bullet-}$ (2.5–3.1 V_{NHE}) is higher than that of $\text{HO}^\bullet$. 3) Sulfate radicals have a longer half-life (30 μs –40 μs) than $\text{HO}^\bullet$ (< 1 μs), signifying mass transfer and contact with pollutants. 4) Sulfate radicals are reactive in a wide pH range from 2 to 8.^{13,57}

The common PMS used in laboratories is in the form of oxone ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$), and the normal PDS salts include sodium peroxydisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$). The molecular structures of PMS and PDS are shown in Figure 11.6. The principle of PMS/PDS activation is the activation of O–O bonds to trigger electron transfer between catalysts and the oxidants. Then, the activated peroxide O–O bond will be decomposed and persulfate will evolve into reactive radicals (eqn (11.1) and (11.2)). This process is determined by the O–O bond energy and the ability of the catalyst to coordinate a redox process with a specific peroxide.¹⁷ In addition, persulfate activation can also be achieved *via* energy transfer in the presence of UV or heat (see Figure 11.7).

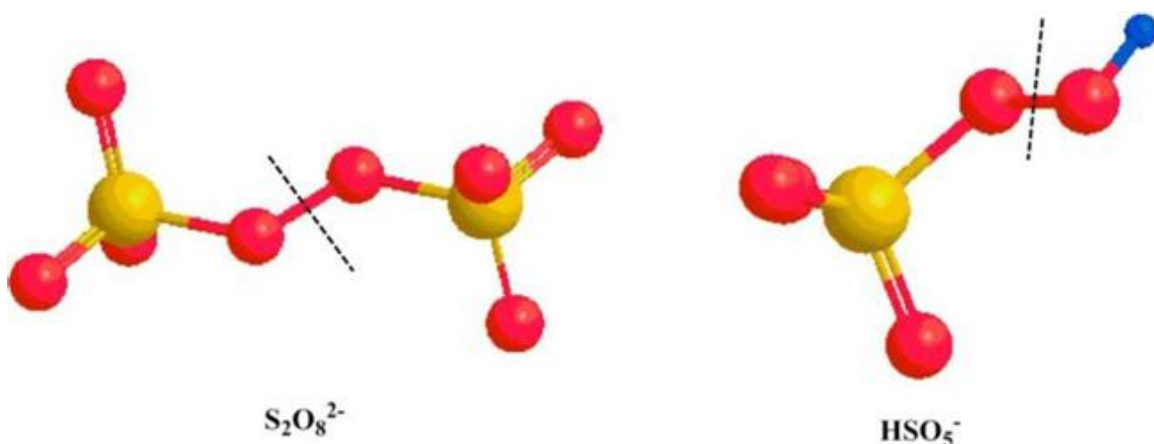
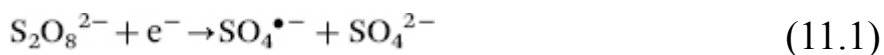


Figure 11.6 Molecular structures of PDS (left) and PMS (right). Dashed line is the fission position of the O–O band for the generation of $\text{SO}_4^{\bullet-}$. Reproduced from ref. ¹¹ with

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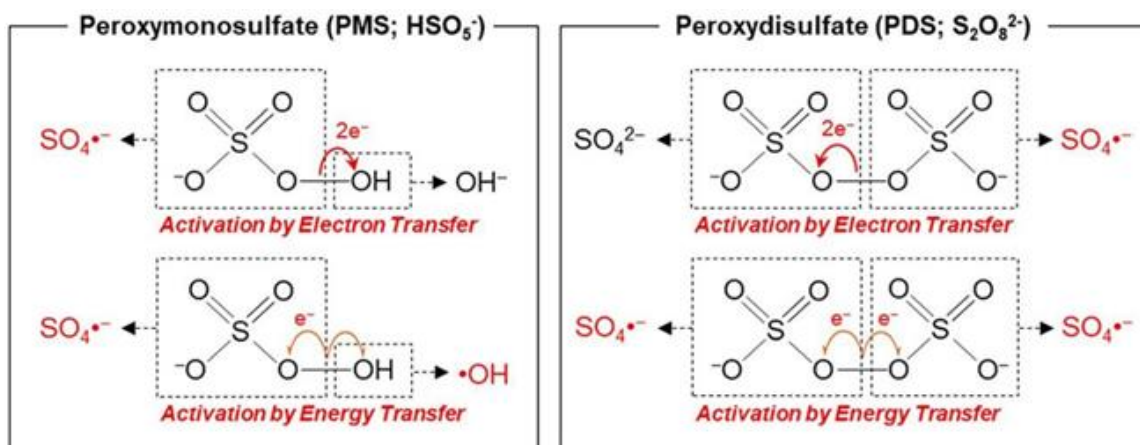


Figure 11.7 Activation of PMS and PDS *via* energy- and electron-transfer processes. Reproduced from ref. ⁵⁸, <https://doi.org/10.1021/acs.est.9b07082>, with permission from American Chemical Society, Copyright 2020. Further permissions requests relating to the material excerpted should be directed to the ACS.

Different from PDS, PMS has an asymmetric structure (see Figure 11.6), a relatively low redox potential and adsorption ability, rendering it more vulnerable to activation by polarized species.²⁴ The structural differences between PMS and PDS also result in distinct activation behaviors. For example, due to its asymmetric structure, PMS is more active in generating $\text{SO}_4^{\bullet-}$ when exposed to transition metals. In contrast, due to the lower bond dissociation energy of PDS (see Table 11.1), energy transfer processes are more effective at breaking the O–O bonds of PDS than PMS.⁵⁸ In carbocatalytic processes, there are intrinsic differences between PMS and PDS activation. In general, PMS–carbon systems are free radical-dominated, while PDS–carbon reactions proceed *via* singlet oxygen- or nonradical-based pathways.¹⁶

Table 11.1 Physical and chemical properties and price comparisons between PMS, PDS and H_2O_2 . Reproduced from ref. ¹⁷ with permission from Elsevier, Copyright 2018.

PMS	PDS	H_2O_2

Length of O–O bond (Å)	1.460	1.497	1.460
Bond energy (kJ mol ⁻¹)	377	92	213
Molecular symmetry	Asymmetric oxidant, HO–O–SO ₃	Symmetric oxidant, SO ₃ –O–O–SO ₃	Symmetric oxidant
Average estimated lifetime in groundwater	Hours to days	> 5 months	Hours to days
Solubility in water at 25 °C (g L ⁻¹)	298	730	Soluble
Redox potential	E° (HSO ₅ ⁻ /HSO ₄ ⁻) = 1.82 V _{NHE}	E° (S ₂ O ₈ ²⁻ /HSO ₄ ⁻) = 2.1 V _{NHE}	E° (H ₂ O ₂ , H ⁺ /2H ₂ O/pH = 0) = 1.776 V
Price	\$2.2 per kg (oxone)	\$0.74 per kg (K ₂ S ₂ O ₈)	\$1.5 per kg

11.3.3 Reactive Oxygen Species

Wang *et al.*⁵⁹ reported that the typical ROS in diverse AOPs systems can be HO·, hydrogen radicals (H·), hydrated electrons (e_{aq}⁻), SO₄^{·-}, SO₅^{·-}, superoxide radicals (O₂^{·-}), singlet oxygen (¹O₂) and hydroperoxy radicals (HO₂[·]). The redox potentials of these ROS are listed in Table 11.2. In carbon-based AOP systems, ROS can be different, which are discussed based on the category and property of carbocatalysts in Section 11.4. The formation of ROS can be affected by various factors, such as pH, inorganic anions, and dissolved organic matter.⁵⁹ The main strategies for ROS identification include electron spin resonance (ESR), high-performance liquid chromatography (HPLC), quenching experiments, electron paramagnetic resonance (EPR), kinetic analysis, and transient absorption spectrum.⁵⁹

Table 11.2 Oxidizing capacity of different ROS. Reproduced from ref. ⁵⁹ with permission from Elsevier, Copyright 2020.

Reactive species	Redox potential (V)
Hydroxyl radicals ($\text{HO}^\cdot$)	2.7
Sulfate radicals ($\text{SO}_4^{\cdot-}$)	2.5–3.1
Superoxide radicals ($\text{O}_2^{\cdot-}$)	2.4
Singlet oxygen ($^1\text{O}_2$)	2.2
Hydroperoxy radicals ($\text{HO}_2^\cdot$)	1.7
Peroxymonosulfate radicals ($\text{SO}_5^{\cdot-}$)	1.1
Hydrated electron (e_{aq}^-)	– 2.9
Hydrogen radical ($\text{H}^\cdot$)	– 2.3

Hydroxyl radicals attack organic contaminants mainly through electron abstraction, hydrogen abstraction, and hydroxylation,⁶⁰ while sulfate radicals attack organics mainly through electron transfer.⁶¹ Though $\text{HO}^\cdot$ and $\text{SO}_4^{\cdot-}$ have similar redox potentials, the reaction rate of $\text{HO}^\cdot$ with organics ($10^8\text{--}10^9 \text{ M}^{-1} \text{ S}^{-1}$) is normally higher than that of $\text{SO}_4^{\cdot-}$ ($10^6\text{--}10^7 \text{ M}^{-1} \text{ S}^{-1}$). However, $\text{SO}_4^{\cdot-}$ has greater selectivity than $\text{HO}^\cdot$ toward electron-rich substances. Specifically, $\text{SO}_4^{\cdot-}$ is highly sensitive to the substituent groups of aromatic compounds.⁶² In carbon-based AOPs, $\text{SO}_4^{\cdot-}$ is generated at the ketonic site ($\text{C}=\text{C}=\text{O}$) and some nitrogen-doped sites (pyridinic and pyrrolic N), while $\text{SO}_5^{\cdot-}$ is generated at the $\text{C}-\text{C}-\text{O}^+$ sites to fulfill the redox cycle. In terms of $^1\text{O}_2$, though it has been reported in NG-PMS and MWCNT-PDS processes, there are still controversies regarding the formation pathways of $^1\text{O}_2$ and its scavenging effect by water.^{16,17}

11.3.4 Pollutants

In the last decades, a myriad of trace-level pollutants has been detected in drinking water and natural aquatic systems. Among these organic contaminants, persistent organic pollutants (POPs), which mainly include aromatic hydrocarbons and associated compounds (*e.g.*, phenol, antibiotics,

pharmaceutical and endocrine-disrupting chemicals), exert negative effects and cause environmental concerns. POPs are resistant to the conventional biological, photolytic, and chemical oxidation processes. These contaminants primarily come from sewage, industrial waste, spillage, storm water, and agricultural activities.⁶³ Among the various methods of POP removal, strategies including adsorption, catalytic oxidation, and a combination of the two approaches have been adopted. Persulfate-based AOPs, using PMS or PDS as the oxidants, have demonstrated the capacity of effectively degradation of POPs and other emerging micropollutants (*e.g.*, microplastics).

11.4 Applications of Carbocatalysts in Sulfate Radical-based AOPs

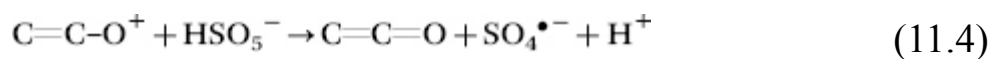
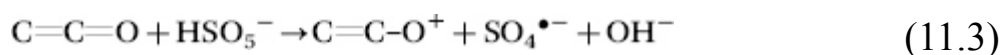
There are various methods utilized for persulfate activation, including external energy activation (*e.g.* ultraviolet, heat and ultrasound), transition metals and oxides, chemical activation (*e.g.* bases, quinines and phenols), and carbocatalysis.^{64,65} However, limitations regarding the economics and infeasibility of SR-AOPs for scale-up hamper the applications of external energy-based activation. Besides, the requirement of an extreme acidic solution pH and metal leaching hinders the practical applications of transition metal-based systems. Carbon-based materials have attracted soaring interests as green persulfate activators in AOPs.

11.4.1 Graphene

11.4.1.1 GO and rGO

Graphene is an ideal electron transfer medium that facilitates the interactions between the oxidant and pollutant. However, the intact sp^2 hybridized structure with a stable π -conjugated system results in the inferior activity of graphene in persulfate activation.^{66,67} Introducing structural defects (edges and vacancies) will create localized π electrons that can improve the activity. GO, which possesses more defects and functional groups than pristine graphene, is expected to exhibit a higher catalytic

efficiency. However, the excessive oxygen groups dramatically deteriorate the performance due to the occupation of defects and reduced conductivity.⁶⁷ Sun *et al.*⁶⁶ and Duan *et al.*⁶⁸ reported that rGO, which retained less functional groups and created new active sites, effectively activated PMS to form $\text{SO}_4^{\bullet-}$ for phenol oxidation. The performance of rGO surpassed GO, MWCNT, and pristine ND (see Figure 11.8). The zigzag edges and $\text{C}=\text{O}$ groups located at the graphene boundaries of rGO were considered to be the active sites. According to density functional theory (DFT), compared with the basal plane, the vacancies and edge sites were more active for persulfate activation with prolonged O–O bonds; the electron-rich carbonyl groups were the most reactive sites among the oxygen functionalities.²¹ The lone pair electrons of $\text{C}=\text{O}$ will weaken the O–O bond *via* the formation of a $\text{C}=\text{O}-\text{H}-\text{O}-\text{OSO}_3$ complex and transfer of electrons *via* hydrogen bonds to PMS to generate $\text{SO}_4^{\bullet-}$. Subsequently, $\text{C}=\text{C}-\text{O}^+$ will capture one electron from PMS to form a monopersulfate radical ($\text{SO}_5^{\bullet-}$) and restore $\text{C}=\text{O}$ (see Figure 11.9). This redox cycle is expressed as eqn (11.3) and (11.4). Due to the positive correlation between the reaction rate and the population of defects, the reaction rates can be tailored *via* rationally controlling the levels of defects and oxygen.²¹ With the exception of phenol, rGO manifested high catalytic activities for degrading 2,4-dichlorophenol (2,4-DCP) and methylene blue (MB).⁶⁶



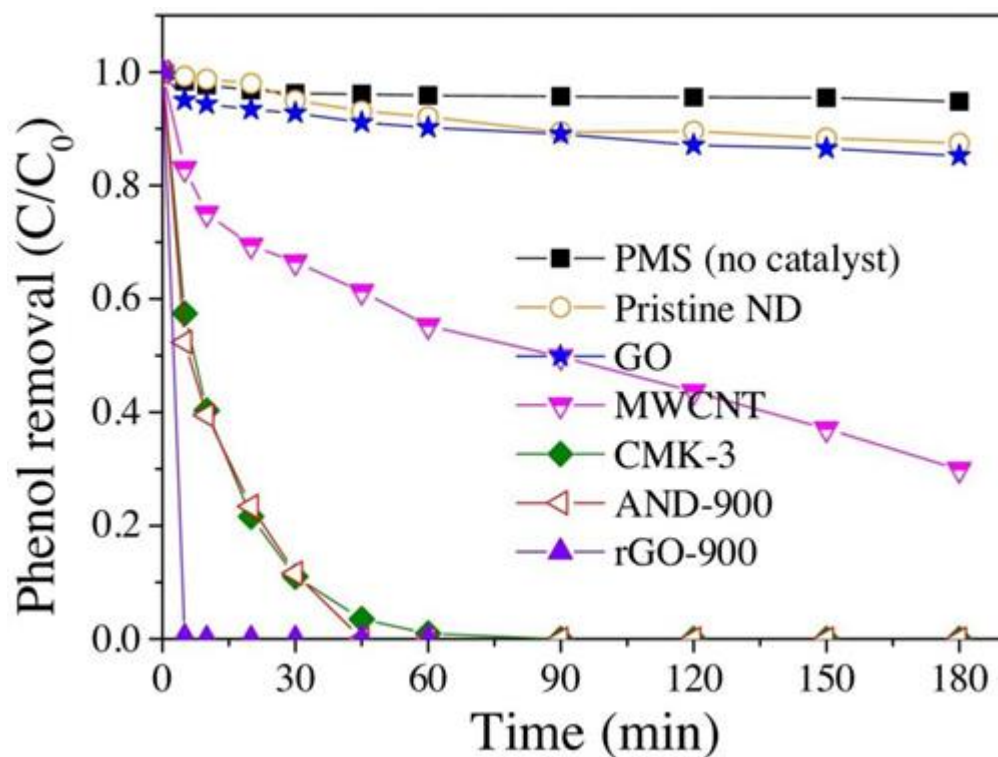


Figure 11.8 PMS activation by different nanocarbons for phenol degradation. Reproduced from ref. ⁶⁸ with permission from Elsevier, Copyright 2016.

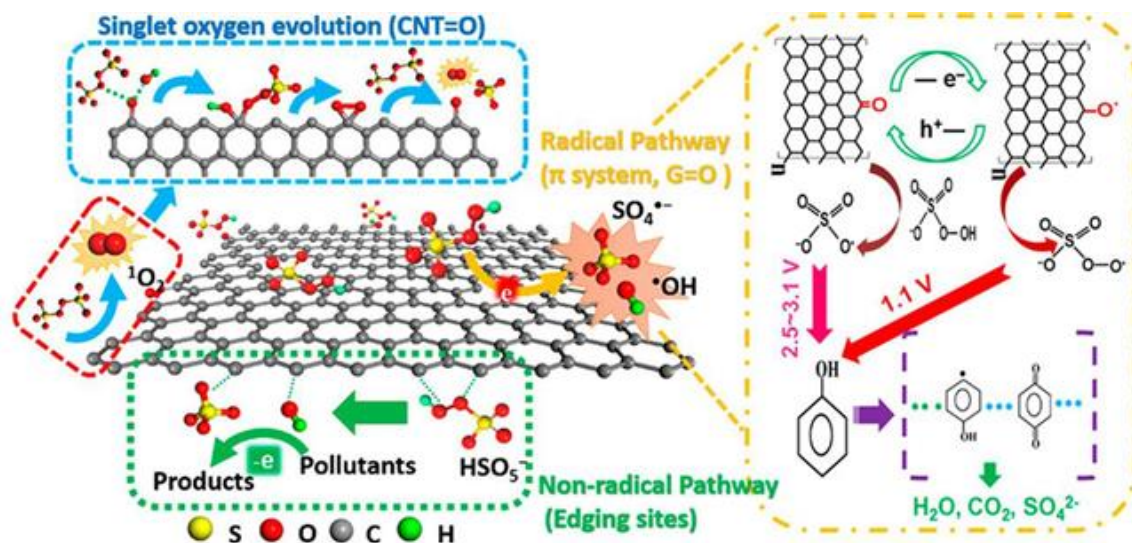


Figure 11.9 PMS activation on carbonaceous materials. Reproduced from ref. ¹⁶ with permission from American Chemical Society, Copyright 2018.

11.4.1.2 *N-doped Graphene*

Among various heteroatoms, nitrogen is the most popular element for enhancing the performance of carbon materials in catalytic processes. Nitrogen doping facilitates the anion exchanging and catalytic activity in redox reactions. Besides, N dopants can enhance the adsorption capacity of carbocatalysts, which will promote the surface enrichment of organics/peroxide at the active sites in nonradical pathways.

Pyridinic N, pyrrolic N, graphitic N (or quaternary N), and nitric oxide are the most common forms of N functionalities (see [Figure 11.10](#)) The type of N dopant is tunable by controlling the synthesis temperature and choosing precursor types due to the distinct thermal stabilities of N doping species. Pyridinic N at the edges or defects can provide one electron to the conjugated π -system, and its lone pair electrons can act as Lewis base sites for peroxide activation. Pyrrolic N at the edge of the 5-membered-ring can provide two electrons and become Lewis basic sites; these two groups demonstrate great potential to produce radicals or singlet oxygen in AOPs. Both pyridinic and pyrrolic N have lone pair electrons that can act as unpaired stable radicals to capture the electrophilic species of peroxides. This is particularly important in radical pathways to generate ROS *via* direct one-electron transfer. Graphitic N substitution of C in the graphitic basal plane will disrupt the charge density of adjacent carbons due to the higher electronegativity of nitrogen compared to carbon. This will result in lower adsorption energy toward O–O bonds in the persulfates and enhance the electron transfer capacity, facilitating the O–O bond activation and cleavage to generate ROS.³¹ Graphitic N is also capable of forming surface-activated PMS through electrostatic bonding, leading to a nonradical pathway.⁶⁹ However, nitric oxide (NO_x) was reported ineffective in carbocatalysis for PMS activation.⁷⁰

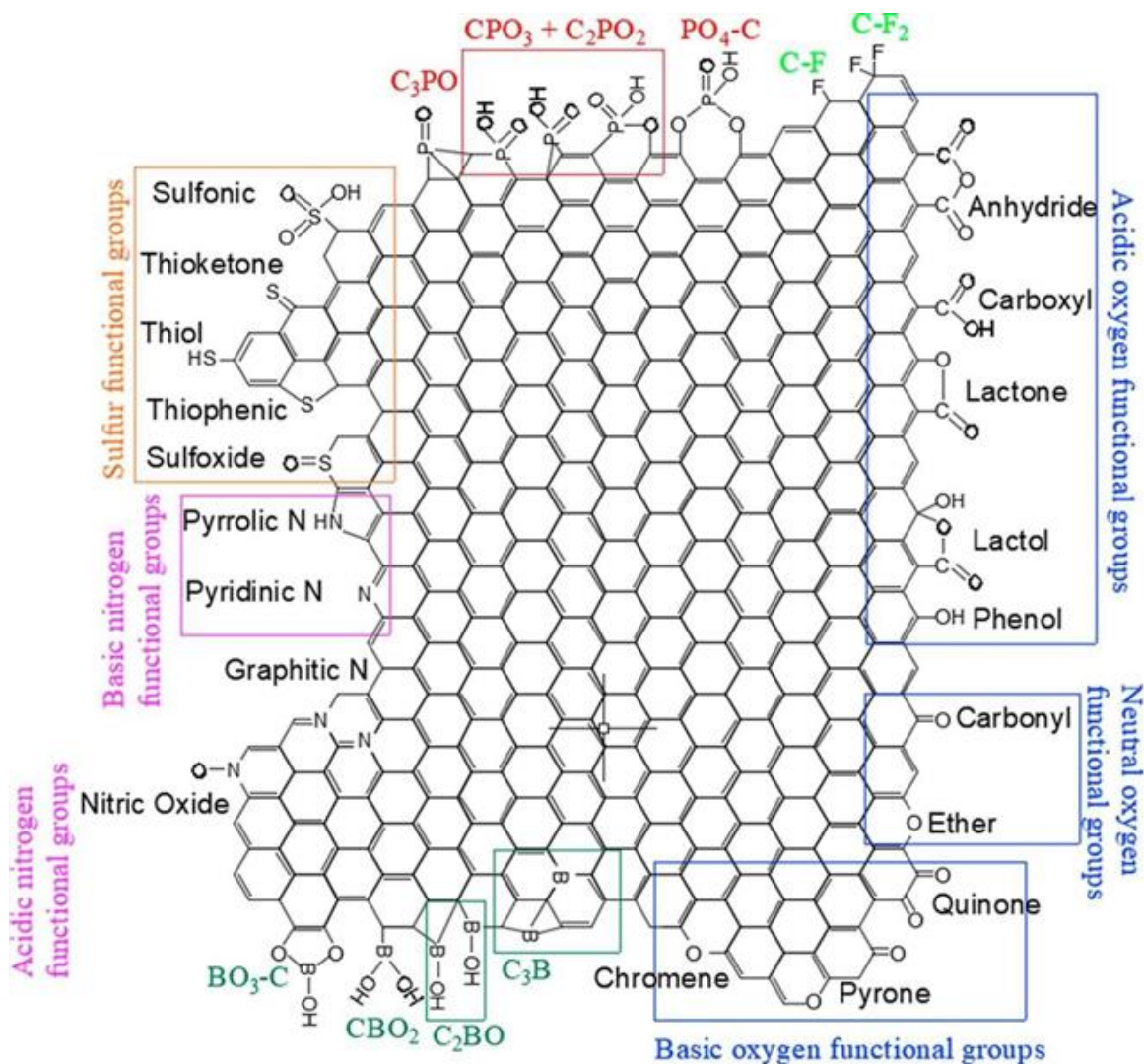


Figure 11.10 Illustration of active catalytic sites on a graphitic carbon network regarding heteroatom doping. Reproduced from ref. ¹⁷ with permission from Elsevier, Copyright 2018.

N-doped graphene (NG350) with a 6.54 at% doping level was developed, whose reaction rate constant was 5.4-fold higher than undoped rGO350 in phenol degradation with PMS.⁷¹ The catalytic performance of N-doped rGO (NG-700) was 80 times higher than the undoped rGO for PMS activation. Notably, the catalytic activity of NG-700 (9.68 at% of N) was even higher than that of Co_3O_4 , the benchmark catalyst for PMS activation (see Figure 11.11).³¹ Additionally, N doping can improve the adsorption

capacity and activation efficiency of PDS for phenols and antibiotic removal.^{72,73}

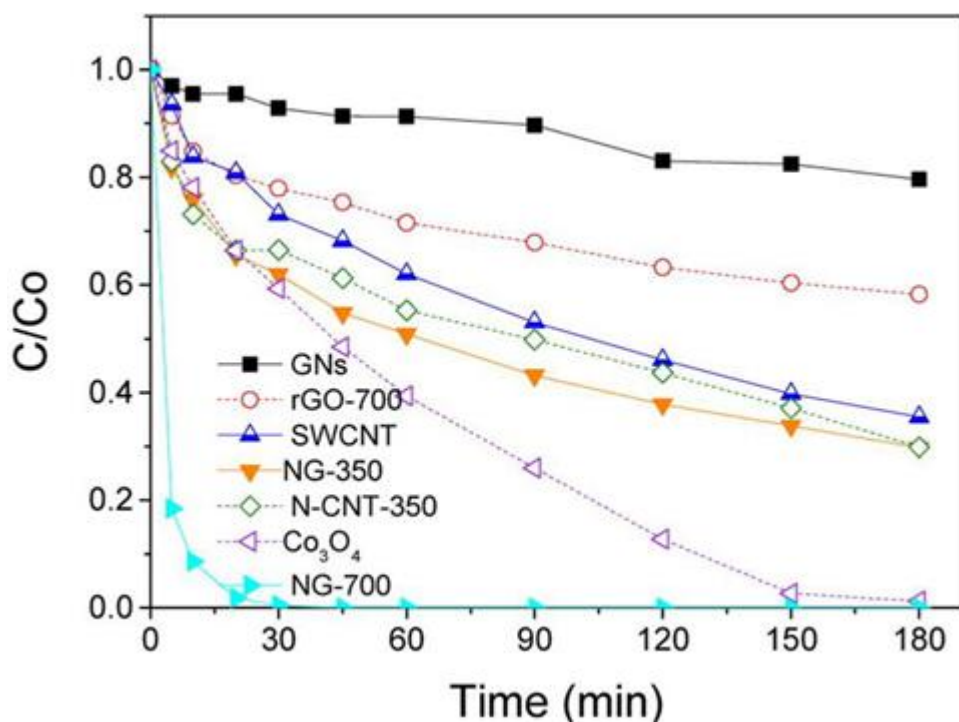


Figure 11.11 Catalytic performance of different functionalized graphenes for phenol removal.

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11.4.1.3 B–N and S–N Co-doped Graphene

Unlike nitrogen species, single doping with B, S, P or I cannot improve the activity for graphene-based AOPs.^{71,74} However, co-doping these elements with nitrogen can promote catalysis. For example, trace amounts of boron doping (0.1 wt%) in N-graphene improved PMS activation. However, excessive boron contents (0.25 wt%) had the reverse effect on phenol oxidation.⁷⁵ In B and N co-doped graphene, the B–C–N heterostructure in the conjugated π network can activate both C and B with a synergistic effect, inhibiting the neutralization of N (electron donor) and B (electron acceptor) at the *ortho* position to preserve both active sites. The B sites will chemically bond with persulfates, while N atoms activate the adjacent

carbon atoms and facilitate charger transfer, synergistically enhancing the persulfate activation.

For S and N co-doped graphene, S atoms can endow the C atoms in adjacent to N with higher electron and spin densities, decreasing the energy barrier to activate PMS. In addition, the synergistic effects of N and S will enlarge the positively charged areas, giving rise to simultaneously promoted adsorption and catalysis. As shown in Figure 11.12, the reaction rate constant of graphene was significantly increased by co-doping with S and N.^{74,76} However, superfluous S contents had a negative effect due to the unfavorable redistribution of electrons/spins and an unbalanced π system.^{74,77}

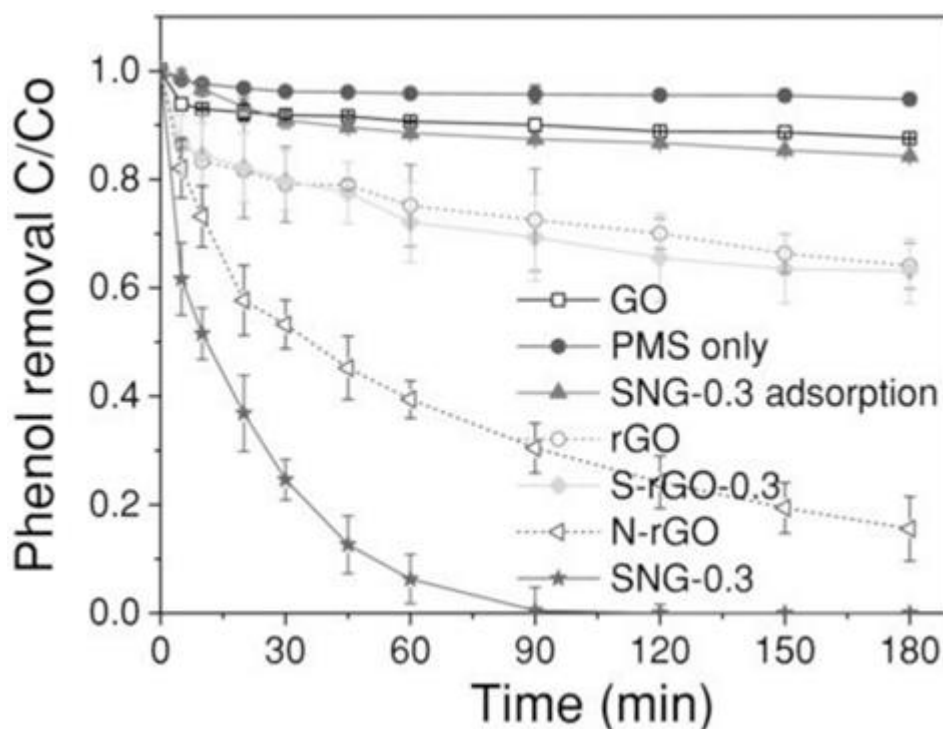


Figure 11.12 Reaction rate constant of different carbocatalysts for phenol removal. Reproduced from ref. ⁷⁴ with permission from John Wiley & Sons, Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

11.4.2 Carbon Nanotubes

11.4.2.1 Pure Carbon Nanotubes

Though CNTs and graphene share the same sp^2 hybridized nanostructure, the differences in dimension, curvature, and surface chemistry lead to different efficiencies in persulfate activation.¹⁷ For example, the dimensionality of carbocatalysts determines the adsorption behavior toward phenolics in the order $0D \ll 1D \leq 2D < 3D$.¹⁵ In addition, the physicochemical properties of CNTs can be influenced by various factors including oxygen groups, defects, chirality, graphitic degree, and wall number, which collectively affect the catalytic behavior.¹⁶

Similar to metal-based catalysts, CNTs can activate PMS *via* a radical pathway at the semiquinone groups. For example, phenol was oxidized by sulfate radicals produced from CNT-C $\square$ O.¹⁴ However, CNTs prefer to react with PDS to form a PDS-CNT complex that will directly oxidize organics *via* a nonradical route. In this process, CNTs act as an electron shuttle between PDS (electron acceptor) and pollutant (electron donor).^{78,79} In the meantime, the activated PDS will oxidize water to produce HO $\cdot$ for organics oxidation.^{15,24} As a result, SWCNTs demonstrated excellent activity for PDS activation and phenol degradation, and outperformed metal oxides such as Fe $_3$ O $_4$, MnO $_2$ and Co $_3$ O $_4$.¹⁵ With the exception of radical-based and direct electron transfer processes, Cheng *et al.*⁸⁰ discovered MWCNTs can activate PDS to produce singlet oxygen rather than radicals for 2,4-DCP oxidation. The C $\square$ O groups on the MWCNTs surface were assumed to be the active site for $^1O_2$ formation.

11.4.2.2 N-doped Carbon Nanotubes

Similarly, nitrogen doping can enhance the activity of CNTs for PMS and PDS activation, but such a modification is not effective for H $_2$ O $_2$.²⁴ It was found that N-SWCNT-PMS-phenol follows a nonradical pathway while N-SWCNT-PDS-phenol follows a radical route. When using PMS as the oxidant, even a tiny amount of N loading (0.8 at%) can significantly convert the process from a radical reaction to a nonradical pathway.^{24,70} In the nonradical process, oxidants firstly bond with the positively charged carbon atoms to form a reactive complex or surface confined radicals. Then, the metastable complex will react with the target pollutant (electron donor)

via electron abstraction through the carbon lattice (electron shutter) or inner-sphere interaction (direct oxidant–organic bonds) as illustrated in Figure 11.13.¹⁶ Thus, nonradical species are prone to oxidize contaminants with a high charge density via electrophilic reactions. However, unlike N–SWCNT, N–MWCNT was reported to be capable of generating sulfate radicals from PMS for phenol oxidation.¹⁴ Pyridinic N and pyrrolic N are more active in PMS activation than C=O on CNTs.¹⁴ So small proportions of pyridinic and pyrrolic N atoms (0.8 at.%) demonstrate higher catalytic activities than pristine CNTs, and the presence of a similar percentage of graphitic N further enhances the efficiency in PMS activation.^{14,70} As a result, N–CNT-700 demonstrated outstanding PMS catalytic performance for phenol removal, and the reaction rate was 57.4-, 6.9- and 15.6-fold higher than that of pristine CNTs, α -MnO₂ and Co₃O₄, respectively.⁷⁰

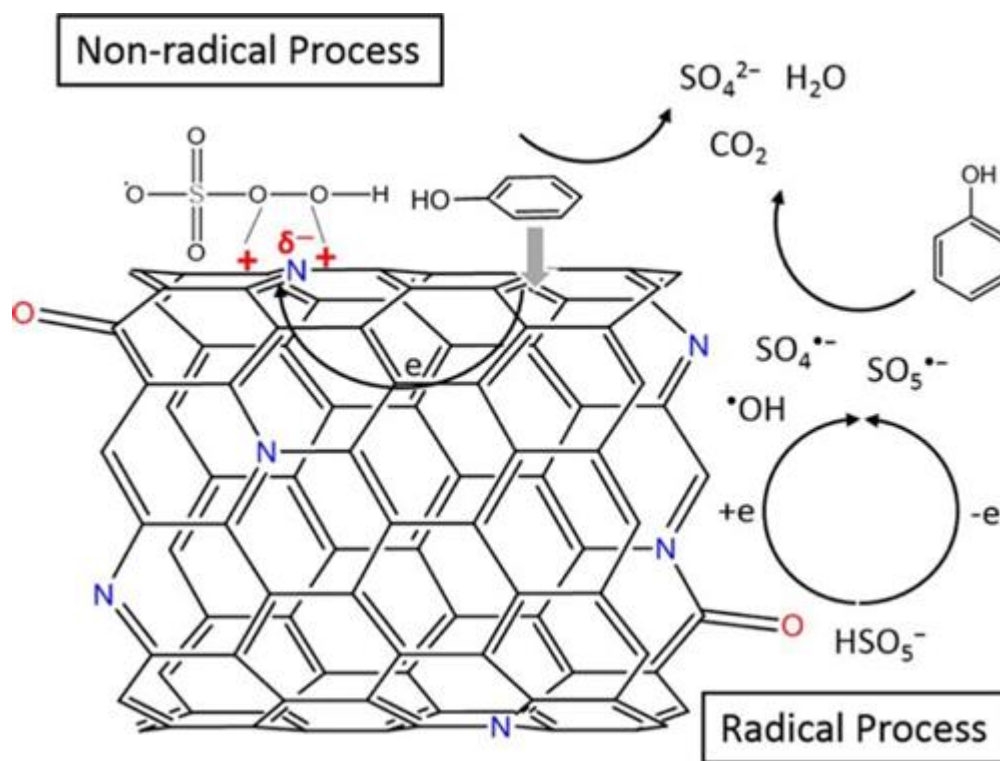


Figure 11.13 Radical and nonradical process of N–CNTs. Reproduced from ref. ⁷⁰ with permission from American Chemical Society, Copyright 2015.

In terms of persulfate activation, N-doping facilitates PDS to directly oxidize adsorbed water to produce HO $\cdot$. In the meantime, non-effective nitrogen functionalities (*e.g.*, nitroxide groups) were capable of replacing the reactive C=O groups and eventually decreasing the catalytic activity of N-CNTs.¹⁴

11.4.3 Nanodiamonds

Pristine NDs with pure sp³ hybridization exhibit low catalytic activity in PMS/PDS-based oxidation. However, thermal annealing at different temperatures can enormously enhance the activities of the derived products toward PMS^{68,81} and PDS⁸² activation (see Figure 11.14). During the thermal annealing process, NDs transform to a core(sp³)–shell(sp²) structure *via* collapse and reformation of the outer sphere of diamond to a strained graphitic layer. This process not only removes the surface amorphous carbon and soot, but also controls the redox ability of the sp² shell for electron transfer, ultimately enhancing its catalytic performance. This graphitized nanodiamond (G-ND, or BND for bulky NDs) can activate PDS *via* the formation of a PDS–NDs complex or confined sulfate radicals on the surface.⁸² The mechanism was further evidenced by Lee *et al.*,⁸³ who reported that BNDs played a role in adsorbing reactants and transferring electrons from the organics to surface activated PDS. Interestingly, for PMS activation, increasing the annealing temperature in a certain range promotes PMS activation of the derived BNDs, but further raising of the temperature over 900 °C will reduce the reaction activity of the derived products (see Figure 11.15). It was discovered that annealing at a higher temperature will fabricate more graphitic shells and transform a radical-dominated reaction to a nonradical process.⁸¹ According to theoretical calculations, the diamond core will endow the graphitic shell (one-layer) with a higher electron density *via* the transfer of electrons through the interfacial covalent bonds, which further facilitates the electron migration to PMS for radical generation.^{81,84} Nevertheless, multiple shells impede the charge transport through multiple graphitic layers, causing a higher adsorption energy of PMS to form a PMS–NDs complex for nonradical oxidation.

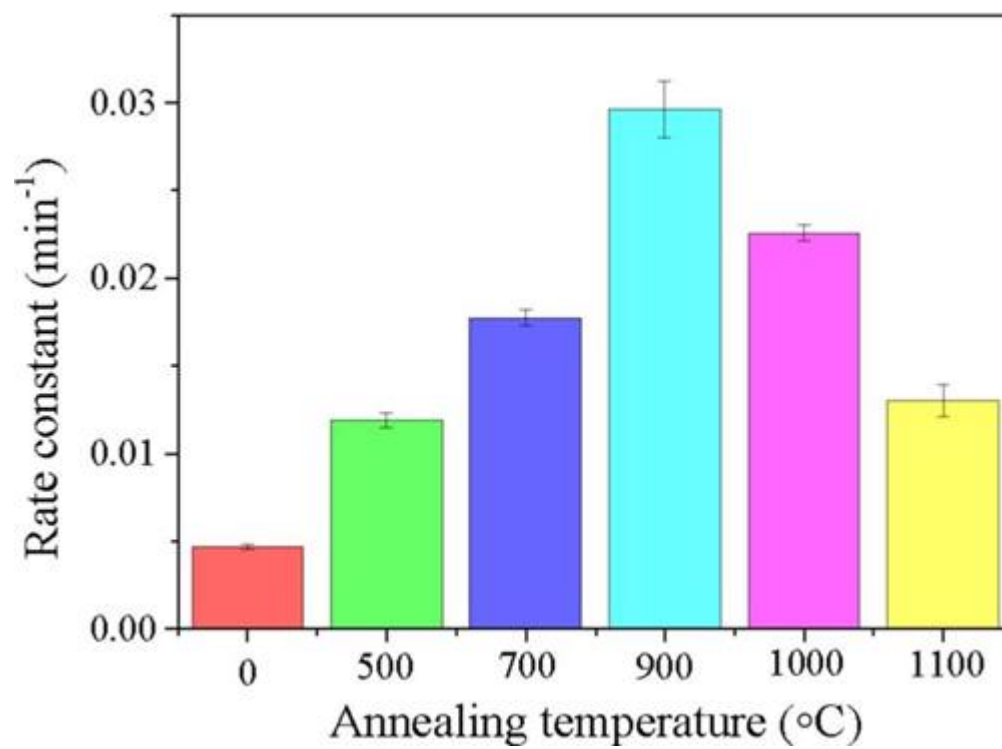


Figure 11.14 Reaction activity of annealed NDs in a PMS–phenol system. Reproduced from ref. ⁸¹ with permission from Elsevier, Copyright 2018.

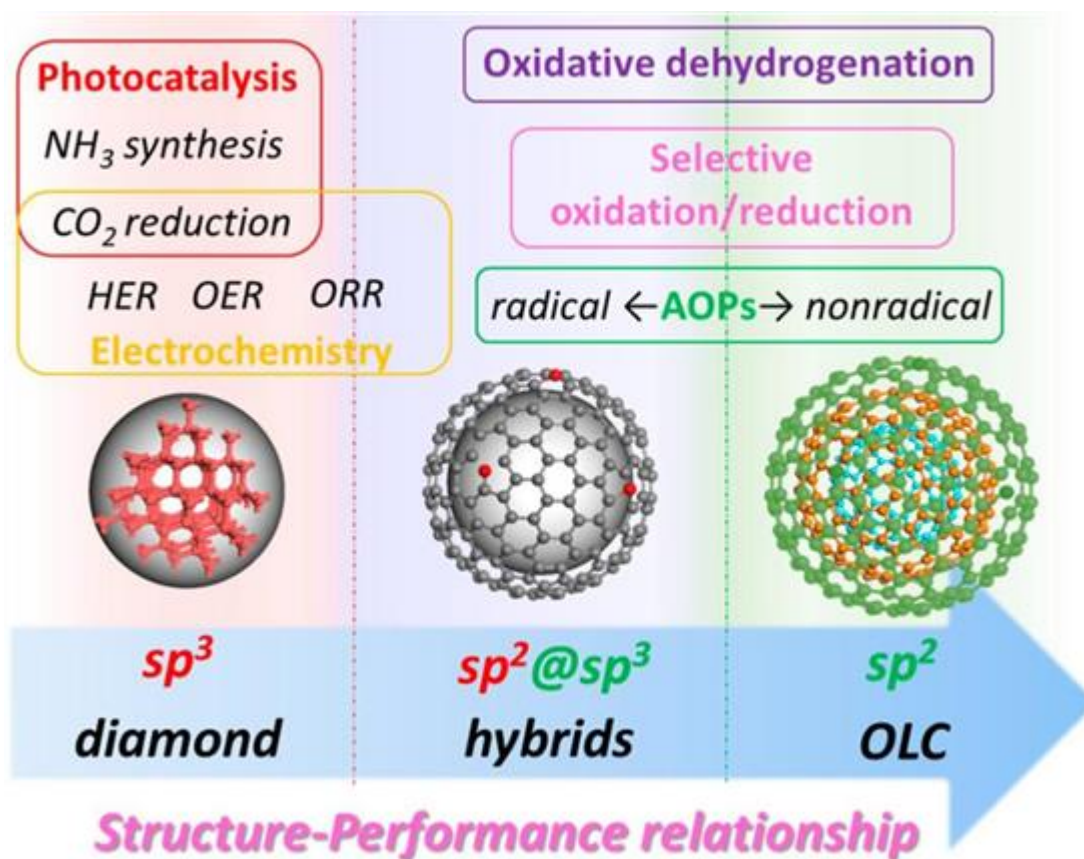


Figure 11.15 Structural transformation after annealing and corresponding applications of NDs.

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In addition to the structural influence of NDs on catalytic performance, heteroatom functional groups have been studied. It was found that the nucleophilic ketonic groups on the ND shell have a high electron density, which demonstrate a high redox potential to activate PMS and generate radicals.⁸⁴ Besides, Duan *et al.*⁸⁴ investigated the effects of N doping on NDs and discovered that the N atoms on the graphitic shell will attract more electrons from the diamond substrate, giving rise to a more reductive surface to promote the generation of $SO_4^{\cdot-}$ and $HO^{\cdot}$.

11.4.4 Metal–Carbon Composites

The incorporation of transition metal-based NPs can remarkably improve the catalytic performance of carbocatalysts in redox reactions. For example,

metal–carbon composites using encapsulation of zero-valent nanocrystals (*e.g.* Fe,⁸⁵ Co⁸⁶ and Ni⁸⁷) into CNTs manifested a better catalytic activity for PMS activation than the sole metal counterparts and CNTs.

In this metal–carbon composite configuration, the wrapped metal clusters/NPs strongly interact with the inner sphere of graphitic carbon. Such a hybrid structure will lead to a decreased local work function of the outer carbon surface for PMS/PDS activation through electrostatic or covalent interactions.⁸⁸ The formation of Me–N–C or Me–O–C bonds facilitates electron transfer from the metal surface to the attached π system, endowing a higher charge density of the outer carbon layers at the interaction domain. Subsequently, this activated region causes O–O bond breakage and charge transfer to generate ROS for organic oxidation. Additionally, N atoms in the carbon lattice play synergistic roles that control the electronic and chemical properties of the carbon sphere for oxidant activation and facilitate electron migration from metal NPs to the carbon.

Except for zero-valent transition metals, other species such as metal carbides (*e.g.* Fe₂C,⁸⁹ Ni₃C⁹⁰) and manganese nitride (MnN₄⁹¹) have demonstrated higher activities in catalytic AOP reactions. This is because the metal–nitrogen–carbon bonding bridge between the metal species and carbon substrate synergistically increases the charge mobility to the outer carbon surface, thus facilitating oxidant activation.

In addition, due to the superior physicochemical properties including diverse material design, large surface area and ultra-high porosity, metal–organic frameworks (MOFs) have attracted much research interest in SR-AOPs. In general, MOFs, their composites, and derived metal oxides tend to coordinate a radical pathway for organic oxidation, while MOF-derived metal–carbon hybrids (especially N-doped carbons) prefer to induce nonradical-dominated routes.⁹²

Additionally, encapsulating metals underneath carbon layers can endow other properties to the carbocatalysts. For instance, metals including Co, Mn, Fe, and Ni can introduce magnetic properties to the carbon substrate, facilitating the separation and recycling of the magnetic hybrid catalysts after use in water. Recently, Kang *et al.*⁹³ successfully synthesized Mn–NCNTs composites to activate PMS for microplastics degradation. On the

other hand, the carbon substrate can in turn protect metals from leaching and corrosion, preventing secondary pollution to the environment.

11.5 Conclusion

Among various water treatment technologies, AOPs demonstrate high performance in the purification of POPs, thanks to the high capability and adaptability. Compared to metal-based catalysts, dimensional carbocatalysts solve the problem of secondary contamination without sacrificing the efficiency and stability in persulfate-based AOPs. Pristine carbocatalysts such as graphene, CNTs and NDs exhibit limited efficacy in PMS/PDS activation. Therefore, considerable progress has been made in the design and modification of the structure and surface chemistry of nanocarbons to improve the catalytic activity. Heteroatom doping (especially nitrogen doping) and construction of nanohybrids greatly enhance carbocatalysis in AOPs *via* creation and tailoring of the active sites and electronic structure of the materials. Metal encapsulation is another effective strategy to boost the performance by reducing the work function of carbon surfaces and promotion of the adsorption of reactants. Carbon configuration, surface chemistry, and defect degree are the critical aspects for the development of desirable carbocatalysts. During organic oxidation, radical- and nonradical-based schemes are discovered in persulfate activation; the two systems can be combined or transformed to each other *via* tuning the structure, heteroatom doping, and defects of the carbocatalysts. Nevertheless, the high cost of mass manufacture of high-quality graphitic nanocarbon materials still render it far from commercial application. Novel strategies are highly encouraged for the mass production of cheap, efficient, and on-demand carbocatalysts in the future.

Abbreviations

0D	zero-dimensional, D for dimensional
2,4-DCP	2,4-diclorophenol
AC	activated carbon
AOPs	advanced oxidation processes

BNDs	bulky nanodiamonds
CNTs	carbon nanotubes
CVD	chemical vapor deposition
DFT	density functional theory
e_{aq}^-	hydrated electron
EPR	electron paramagnetic resonance
ESR	electron spin resonance
GO	graphite oxide
$H^\cdot$	hydrogen radical
H_2O_2	hydrogen peroxide
HMX	octogen
$HO^\cdot$	hydroxyl radicals
$HO_2^\cdot$	hydroperoxy radicals
HPLC	high-performance liquid chromatography
HR-AOPs	hydroxyl radical-based advanced oxidation processes
MB	methylene blue
MOFs	metal–organic frameworks
MWCNTs	multi-walled carbon nanotubes
NDs	nanodiamonds
NPs	nanoparticles
$O_2^{\cdot-}$	superoxide radicals
$^1O_2$	singlet oxygen
O_3	ozone
OLCs	onion-like carbons
PDS	peroxydisulfate
RDX	hecogen
PMS	peroxymonosulfate
POPs	persistent organic pollutants
PS-AOPs	persulfate-based advanced oxidation processes
rGO	reduced graphene oxide
ROS	reactive oxygen species
$SO_4^{\cdot-}$	sulfate radical
$SO_5^{\cdot-}$	monopersulfate radical
SR-AOPs	sulfate radical-based AOPs

SSA	specific surface area
SWCNTs	single-walled carbon nanotubes
TNT	trinitrotoluene

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Chapter 12

Zero Valent Iron-induced Fenton-like Oxidation Towards Water Treatment

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12.1 Introduction

Confronted with the increasingly severe water crisis caused by human activities, the seeking of sustainable water remediation techniques is an urgent task for numerous scientific research workers. Fenton reagents (Fe(ii) salt and hydrogen peroxide (H₂O₂)) and its derived iron-mediated oxidation systems are the most widely studied advanced oxidation processes (AOPs) since it was first discovered by H. J. H Fenton in 1894.¹ Several reactive oxygen species (ROS) can be produced by Fe(iii)/Fe(ii) circularly catalyzed chain reactions to decompose peroxides, including H₂O₂, peroxydisulfate (PDS), and peroxymonosulfate (PMS).² These ROS (*e.g.* hydroxyl radicals ($\cdot\text{OH}$), sulfate radicals ($\text{SO}_4^{\cdot-}$), and ferryl species (Fe(iv))) exhibit high oxidation capabilities for degrading and even mineralizing a wide array of contaminants, meanwhile, the eco-friendly property of iron-based catalysts shows high potential of Fenton and Fenton-like systems for practical use in the field of water treatment.²⁻⁴ However, the extremely fast accumulation of Fe(iii) strongly inhibits the production of ROS by the subsequent Fenton-like reactions.

Zero valent iron (ZVI or Fe⁰) is a very ideal electron donor for accelerating Fe(iii) reduction in Fenton-like reactions. ZVI is also a reactive metal due to the high reducing capability of ZVI ($E^\circ = -0.44$), which can effectively remove a broad array of organic and inorganic contaminants.⁵ Therefore, ZVI and its derived materials are frequently and widely used in studies aimed at water remediation under a variety of conditions, such as groundwater remediation and wastewater treatment. ZVI-based materials are a category of versatile materials that can achieve decontamination by mediating the simultaneous and competitive processes of direct reduction and indirect oxidation. ZVI-induced reduction processes can directly remove some electron-deficient substances (*e.g.* heavy metals, arsenic, nitrate, nitroaromatics, phenols,

chlorinated organic compounds, and dyes) by donating electrons, and ZVI-induced chain reactions can indirectly remove a wide array of organic contaminants by producing ROS.^{5–8}

Resulting from the fourth most abundant form of elemental iron on the earth, the environmentally friendly performance of iron species, and ZVI-induced generation of a mass of ROS (especially hydroxyl radicals) means ZVI-based Fenton-like systems exhibit great potential for practical application in water remediation especially with *ex situ* peroxides. Over the last few years, some review papers about ZVI were published focusing on: 1) groundwater remediation and wastewater treatment;⁵ 2) limitations of applying ZVI;⁶ 3) application of ZVI nanoparticles;⁹ 4) iron characteristics and impact factors;¹⁰ 5) characterization methods;¹¹ 6) surface passivation.^{12,13} However, these review papers mainly summarize the removal of contaminants *via* ZVI-induced direct reduction processes and the strategies for enhancing the reactivity of ZVI, there is still a lack of a comprehensive review that analyses ZVI-based Fenton-like systems. Accordingly, this critical review scrutinizes the ZVI-based water treatment processes in water treatment from the viewpoint of Fenton-like reactions with particular attention focused on: 1) principle of ZVI-induced Fenton-like oxidation; 2) ZVI-based Fenton-like oxidation with *ex situ* peroxides; 3) ROS; 4) the application of ZVI-based Fenton-like oxidation towards industrial wastewater treatment. At the end of the review, barriers to the practical use of ZVI-based Fenton-like oxidation are summarized, and some research gaps such as mechanistic investigations and application explorations are proposed for future studies with advanced and clever strategies.

12.2 Principle of ZVI-induced Fenton-like Oxidation

12.2.1 Rate-limiting Step of Classical Fenton Systems

The classical Fenton chemistry in acid conditions involves chain initiation, chain propagation, and chain termination (Table 12.1).² Due to the rapid consumption of Fe(ii) and its sluggish regeneration, contaminant degradation undergoes two-stage oxidation including the initial fast stage and the subsequent slower stage.¹⁴ The reduction of Fe(iii) is the rate-limiting step of the Fenton system, meanwhile, the poor recovery of Fe(ii) and its induced precipitation of inactive Fe(iii) species (*e.g.* iron (hydroxy)oxides) to form iron cement causes catalyst poisoning, a narrow effective pH range, and slow H₂O₂ decomposition for the production of hydroxyl radicals.¹⁵ Therefore, seeking state-of-the-art and environmentally-friendly methods to promote Fe(ii) recovery has caught the attention of environmental remediation practitioners in recent years.¹⁶ The strategies for enhancing iron-mediated Fenton-like systems mainly focus on acceleration of Fe(ii) regeneration, such as the input of physical stimulations (*e.g.* electricity, light, and ultrasound) and chemical accelerators (*e.g.* chelating and reducing agents).^{17–22} The reducing agents (RAs) directly induce reduction of Fe(iii) to Fe(ii) and brilliantly overcomes the limitations caused by Fe(iii) precipitation, which strongly promotes the oxidation capabilities of the second stage in Fenton-like systems resulting in significant enhancement of the overall decomposition efficiencies of contaminants.^{21–24} The one and only commonality of RAs for enhancing Fenton-like systems is the capacity to reduce Fe(iii) into Fe(ii), rather than other generally physical and chemical characteristics such as structure, solubility, state of matter, molecular weight, *etc.* However, secondary pollution because of the decomposition of RAs may

also cause other environmental risks or require subsequent water treatment processes. From this viewpoint, as an ideal electron donor with high reducing properties, ZVI can continuously accelerate Fe(ii) recovery from Fe(iii) whilst releasing Fe(ii) *via* ZVI corrosion without (or with acceptable) secondary pollution.

Table 12.1 Chain reactions in Fenton systems.

	Reactions	Rate constants ($\text{M}^{-1} \text{s}^{-1}$)		
(1)	$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{Fe(III)} + \text{OH}^-$	40–80 ²⁵	$\cdot\text{OH}$ generation	Chain initiation
(2)	$\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \text{HO}_2\cdot + \text{H}^+$	9.1×10^{-7} ; ³ 10^{-3} – $10^{-1.7}$ ^{25,26}	Fe(ii) regeneration (Rate-limiting step)	
(3)	$\text{Fe(III)} + \text{HO}_2\cdot \rightarrow \text{Fe(II)} + \text{O}_2 + \text{H}^+$	$(0.33\text{--}2.1) \times 10^6$; ³ 3.3×10^7 ²⁷		
(4)	$\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \cdot\text{OH}$	0.5, ³ 10^{25}	Chain propagation	
(5)	$\text{HO}_2\cdot \rightleftharpoons \text{H}^+ + \text{O}_2^{\cdot-}$	$\text{pK}_a = 4.8$ ²⁸		
(6)	$\text{O}_2^{\cdot-} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{OH}^- + \cdot\text{OH}$	0.13, ¹⁶ 10^{25}		
(7)	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O}$	$(1.7\text{--}4.5) \times 10^7$ ²⁵		
(8)	$\text{RH} + \cdot\text{OH} \rightarrow \text{R}\cdot + \text{H}_2\text{O}$	$> 10^8$ – 10^9 ; ²⁷ 10^7 – 10^{10} ²⁹		
(9)	$\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$	10^9 ; ¹⁵ 10^7 – 10^9 ²⁵		
(10)	$\text{Fe(II)} + \cdot\text{OH} \rightarrow \text{Fe(III)} + \text{OH}^-$	$(2.5\text{--}5.0) \times 10^8$; ³ $(2.3\text{--}4.5) \times 10^8$ ³⁰	Chain termination	
(11)	$\text{Fe(II)} + \text{HO}_2\cdot \rightarrow \text{Fe(III)} + \text{HO}_2^-$	$(0.72\text{--}1.5) \times 10^6$ ³		
(12)	$\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$(5.0\text{--}8.0) \times 10^9$ ³		
(13)	$\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$(0.8\text{--}2.2) \times 10^6$; ³ 8.3×10^5 ³¹		
(14)	$\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$(0.66\text{--}1.4) \times 10^{10}$ ^{3,30,32}		
(15)	$\text{R}\cdot + \text{Fe(II)} + \text{H}^+ \rightarrow \text{Fe(III)} + \text{RH}$	/		
(16)	$\text{Fe(III)} + \text{R}\cdot \rightarrow \text{Fe(II)} + \text{R}^+$	/		
(17)	$\text{Fe(II)} + \text{RO}_2\cdot \rightarrow \text{Fe(III)} + \text{RO}_2^-$	/		
(18)	$\text{R}\cdot + \text{R}\cdot \rightarrow \text{R-R}$	/		

12.2.2 Fenton-like Chemistry During ZVI Corrosion

Although the corrosion chemistry of ZVI involves complicated and incompletely comprehended physicochemical processes, it is widely accepted that the electrochemical mechanism is as follows: the oxidation of Fe^0 releases Fe(II) and donates electrons at the anode, followed by the reduction of H^+ and molecular oxygen to produce H_2 (anaerobic conditions) or H_2O_2 (aerobic conditions) at the cathode. Meanwhile, the stepwise oxidation from Fe^0 to Fe(III) during ZVI corrosion continuously donates electrons to induce the chain reactions from oxygen molecules to a variety of ROS (e.g. H_2O_2 , hydroxyl radicals, and superoxide radicals) in aerobic conditions, which exhibit high oxidation capabilities towards the non-selective degradation of a broad array of organic contaminants, such as methanol, ethanol, 2-propanol, benzoic acid, sulfamethazine, carbon tetrachloride.^{33–36} Overall, ZVI corrosion processes involve three stages (see Figure 12.1): 1) ZVI corrosion to release Fe(II) ; 2) ROS generation; 3) formation of iron (hydroxy)oxides (passivation layers).

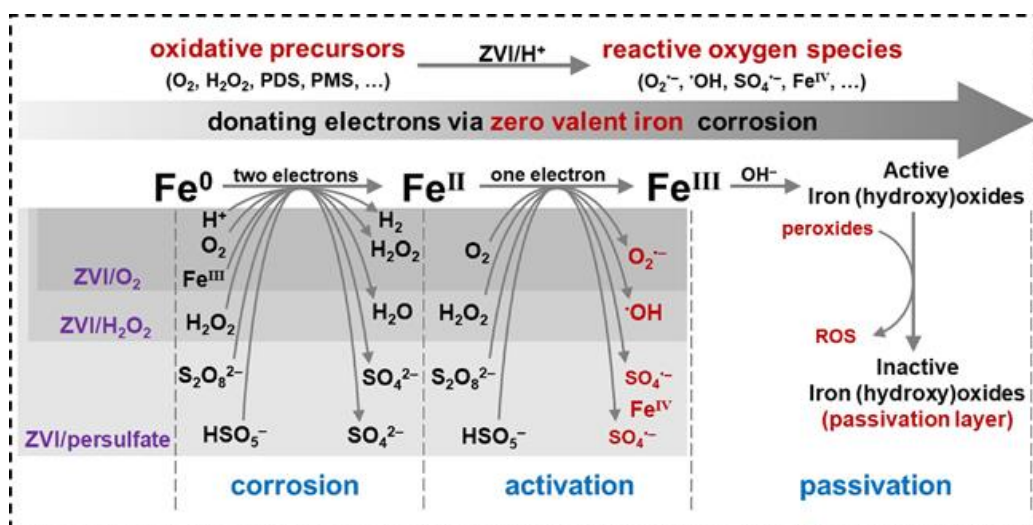
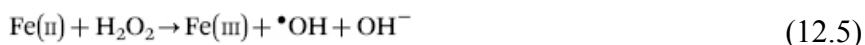


Figure 12.1 Scheme of ZVI corrosion for the production of reactive oxygen species in ZVI-based Fenton-like systems.

ZVI is a very active metal with a high reducing capability that can directly reduce various organic and inorganic compounds in aqueous solution, such as heavy metal ions (*e.g.* Cr(vi), Cu(ii), Pb(ii), Cd(ii)), nitrate, and nitrophenols.^{5,37} Therefore, various matters can start the chain reactions by corroding Fe⁰ to release Fe(ii) (eqn (12.1)–(12.3)).^{33,38} In anoxic conditions, H⁺ can directly corrode ZVI to produce Fe(ii) and H₂ (eqn (12.1)). In aerobic conditions, molecular oxygen is the precursor for oxidizing Fe⁰ to synergistically produce H₂O₂ and Fe(ii) *via* two-electron transfer (eqn (12.2)), then H₂O₂ further accelerates the release of Fe(ii) from Fe⁰ (eqn (12.3)).

Moreover, the *in situ* generated H₂O₂ and Fe(ii) further produce hydroxyl radicals *via* Fenton reaction with the generation of Fe(iii) (eqn (12.5)). Fe(ii) is a reactive species with low stability, which can be easily oxidized by oxidants (*e.g.* O₂, Fe(iii), H₂O₂, H⁺) in water solutions. Thus, the reactivity of Fe(ii) is pH-dependent, Fe(OH)₂ formed by the hydrolyzation of Fe²⁺ ions is the more active Fe(ii) species for decomposing H₂O₂ to produce hydroxyl radicals *via* Fenton reactions.³⁹ Meanwhile, Fe(ii) is also more sensitive to other oxidants (*e.g.* O₂ (eqn (12.7))) with the increase of pH due to the formation of Fe(ii) hydroxides, which inhibits the generation of hydroxyl radicals *via* Fenton reactions.^{40,41} In addition, the aging of ZVI caused by the formation of passivation layers due to the accumulation of Fe(iii) species and consumption of H⁺ will strongly inhibit the reactivity of ZVI, which is the intrinsic drawback of ZVI-based environmental remediation technologies.¹²

12.3 ZVI-based Fenton-like Oxidation with *Ex Situ* Peroxides

12.3.1 Coupling ZVI with *Ex Situ* Hydrogen Peroxide

Hydroxyl radicals are the primary reactive species in the ZVI–O₂ system that oxidatively degrade contaminants, and generate H₂O₂ *in situ* *via* two-electron transfer from Fe⁰ to molecular oxygen is the critical intermediate and the precursor of hydroxyl radicals.⁴² However, the yield of H₂O₂ that relies on electron donation by Fe⁰ is relatively low. The formation of H₂O₂ can be strongly inhibited in the presence of other oxidative substances (*e.g.* heavy metals and nitrate) or in anaerobic conditions, which causes the accumulation of Fe(ii) without generation of H₂O₂. Therefore, the coupling of ZVI and *ex situ* H₂O₂ shows higher oxidation capabilities towards various organic contaminants, such as 4-chlorophenol, polyvinyl alcohol, phycocyanin, rhodamine B, and acesulfame.^{43–47}

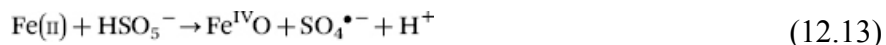
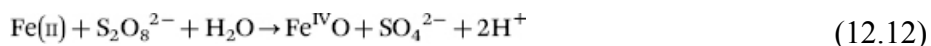
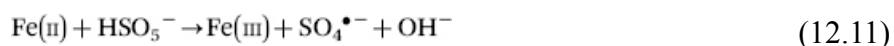
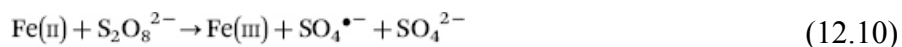
On account of the requirement of higher H⁺ concentration to dissolve the original surface oxide layers (formed during the production⁴⁸) and produce H₂O₂ *in situ*, the high-efficiency pH range of the ZVI–O₂ system is generally located at or near pH 3.0 without a buffer, although some ligands (*e.g.* ethylenediaminetetraacetic acid, oxalate, phosphate ions, citric acid) can expand the effective pH range to a near-neutral pH.^{49–52} As well as acting as the precursor for hydroxyl radicals, the *ex situ* H₂O₂ can also accelerate the corrosion of Fe⁰ to release Fe(ii) (eqn (12.1)) resulting in further enhancement of the Fenton reaction, which can be demonstrated by

the positive correlation between H_2O_2 decomposition and Fe(II) release.⁴⁶ Thus, the ZVI– H_2O_2 system with the *ex situ* H_2O_2 has a wider high-performance pH range from 2.0 to 5.0 for the significant degradation of organic compounds.^{53–55} Nevertheless, the optimal pH of the ZVI– H_2O_2 system is also pH 3.0, which is similar to the classical Fenton system (Fe(II) salt and H_2O_2) and may reveal that the main reactive species for the decomposition of H_2O_2 to produce hydroxyl radicals is also Fe(II) .

In addition to model organic wastewater, the extremely high reactivity and handleability of the ZVI– H_2O_2 system also strongly promotes robust scientific progress of ZVI-based techniques towards practical use. Even more importantly, the ZVI– H_2O_2 system can almost completely degrade organic contaminants and obviously decrease the TOC and COD resulting in a significant increase in biodegradability (BOD/COD) and decreased toxicity of industrial wastewaters.^{56–60} In consideration of the environmentally-friendly properties of ZVI corrosion products, the ZVI– H_2O_2 system is a super-duper pre-treatment for industrial organic wastewater in high concentrations and combined with traditional activated sludge systems.

12.3.2 Coupling ZVI with *Ex Situ* Persulfates

Since the newly-developed persulfates (PDS and PMS) were developed as precursors of ROS, a wide variety of persulfate-based AOPs have promptly accumulated as activators of the peroxide bonds of persulfates over the past ten years, and can substantially degrade a broad array of contaminants.^{61,62} Compared to the H_2O_2 -based AOPs, the persulfate-based AOPs have some superiorities, including a higher yield of ROS, more methods for activating persulfates, stable persulfate salts have lower transport and storage costs. ZVI is also a viable alternative for donating electrons to activate persulfates resulting in the formation of ROS.⁶³



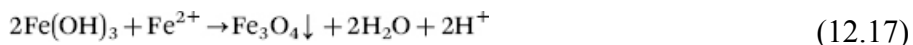
Similar to H_2O_2 , the oxidation process of coupling ZVI and persulfates (both PDS and PMS) also involve the heterogenous corrosion of ZVI and the homogeneous activation of persulfates. The corrosion of ZVI can release Fe(II) via three possible routes: 1) oxidation by H^+ (eqn (12.1)); 2) oxidation by molecular oxygen (eqn (12.2)); 3) oxidation by persulfates (eqn (12.8) and (12.9)).^{64,65} Due to the relatively high oxidation capability, persulfates can directly react with ZVI to accelerate the corrosion of ZVI to release Fe(II) , which is faster than ZVI corrosion by molecular oxygen and H^+ .^{63,65} Following the corrosion of ZVI, *in situ* generated Fe(II)

donates electrons to activate persulfates and produce ROS, which mainly include sulfate radicals ($\text{SO}_4^{\cdot-}$) and ferryl ion species (Fe(IV)). Fe(II) species derived during ZVI corrosion are the primary activator for persulfates, which generally cause the cleavage peroxide bonds of persulfates *via* one-electron transfer to produce sulfate radicals (eqn (12.10) and (12.11)).⁶³ However, some controversies have arisen about the generation of Fe(IV) during the Fe(II) -catalyzed activation of persulfates (eqn (12.12) and (12.13)).^{66–68} Moreover, Fe(II) is, in principle, the basic but not the exclusive activator of persulfates, *in situ*-generated (hydroxy)oxides (*e.g.* Fe_3O_4 and FeOOH) also possess potential capability to decompose persulfates resulting in the generation of ROS.⁶⁹

Although the formation of ROS generated in ZVI–persulfates systems is still inconclusive, ZVI–persulfates systems show high oxidation capability for the oxidation of a wide array of organic contaminants, such as sulfamethoxazole, 4-chlorophenol, cyclohexanoic acid, naphthenic acid, chloramphenicol, tetracycline.^{70–74} Nevertheless, up to now studies of the ZVI-induced activation of persulfates remain in the laboratory. Although the water treatment efficiency for textile industry wastewater using the ZVI–PMS system is even higher than that of the ZVI– H_2O_2 system, the practical application of the ZVI–persulfate system has seen minimal substantive progress resulting mainly from the higher cost and secondary pollution of sulfate ions from the input of persulfates.⁷⁵

12.3.3 pH-dependent Reactivity

The oxidation capability of ZVI-based Fenton-like systems shows significant pH-dependent reactivity caused by the corrosion chemistry of ZVI, involving: 1) the corrosion of ZVI to induce the generation of ROS; 2) the formation of iron (hydroxy)oxides (passivation layers). The acidic water solution favors ZVI corrosion to release Fe(II) , which is the main iron species for activating peroxides to produce ROS; and the optimal pH for the ZVI-based Fenton-like systems ranges from 2.0 to 4.0. As the reaction progresses, Fe^0 will be turned stepwise into Fe(III) ; meanwhile, the solution pH will gradually increase with the consumption of H^+ .^{13,76}



The Fe(III) accumulated during corrosion is extremely susceptible to hydrolysis, which exists in water in the form of aqueous hydroxide species (*e.g.* FeOH^{2+} , Fe(OH)_2^+ , Fe(OH)_3 , Fe(OH)_4^-) at $\text{pH} > 3.0$.^{38,77,78} The iron hydroxide species (mainly Fe(III) hydroxides) formed during ZVI corrosion are further converted to various (hydroxy)oxides (*e.g.* Fe(OH)_3 , FeOOH , Fe_3O_4 , Fe_2O_3) *via* complex interactions with oxidants (*e.g.* O_2 , H_2O_2 , and radicals) and Fe

species. Moreover, these *in situ*-generated (hydroxy)oxides with amorphous or crystal structures will form sediments on the surface of ZVI with the pH increase caused by the consumption of H^+ .^{13,76} Although some *in situ*-generated iron (hydroxy)oxides can further donate electrons to induce the generation of ROS or increase the adsorption capability towards certain contaminants,^{69,79,80} the passivation layers with higher oxidation states hinder electron transfer between Fe^0 and other substances to reduce or even eliminate the reactivity of ZVI.⁸¹

As shown in Figure 12.2, the formation of passivation layers on the surface of ZVI is also a pH-dependent process, a higher pH ($pH > 4.0$) favors the sedimentation of iron ($Fe(III)$ and $Fe(II)$) hydroxides resulting in further formation of iron (hydroxy)oxides. The increase of solution pH due to the consumption of H^+ during ZVI corrosion is beneficial for the generation of iron (hydroxy)oxides. Meanwhile, high concentrations of H^+ at lower pH can also dissolve the surface iron (hydroxy)oxides to expose Fe^0 on the surface of ZVI powders. Therefore, controlling the solution pH at $\sim pH\ 3.0$ by continuously adding acid (e.g. sulfuric acid) can effectively restrain the formation of passivation layers to continuously release $Fe(II)$ via ZVI corrosion, meanwhile, keeping the high reactivity of the $Fe(II)$ species to induce Fenton-like reactions; this is especially true in continuous flow modes of water treatment equipment to reduce the concentration gradients of iron species ($Fe(III)$ and $Fe(II)$). At this condition, the gradual decrease of the size of ZVI powders (such as from microparticles to nanoparticles) may further improve its reactivity to promote Fenton-like oxidation.

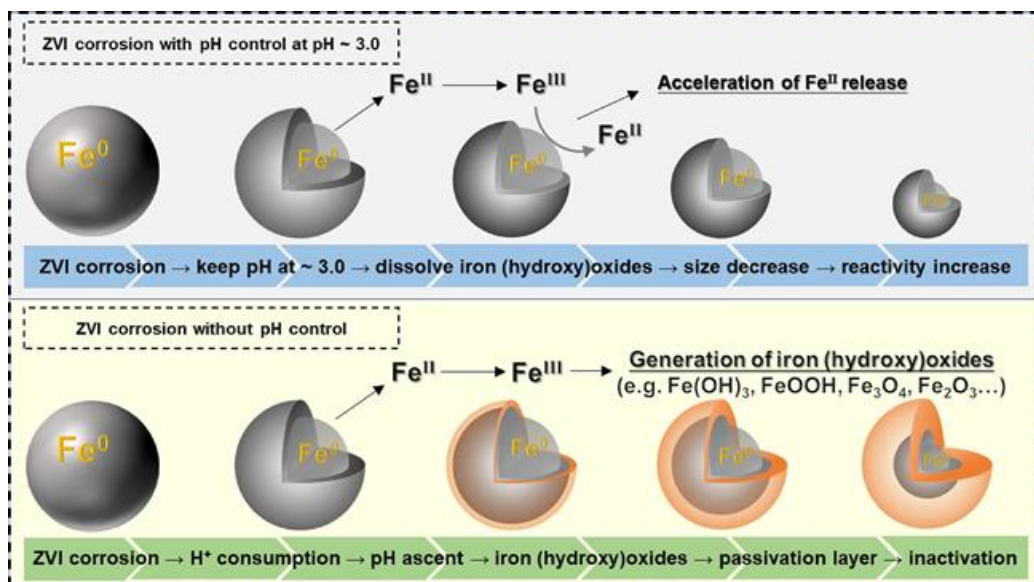


Figure 12.2 Scheme of ZVI corrosion with and without pH control.

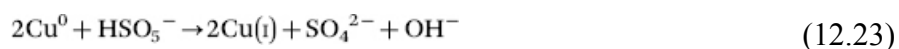
12.3.4 Simultaneously Removing Heavy Metals and Organic Contaminants

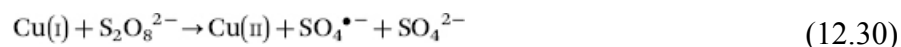
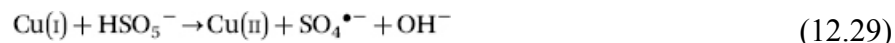
Due to the limitations of ZVI corrosion chemistry, many strategies were attempted to enhance the reactivity of ZVI: 1) pre-treatment of original ZVI powders (e.g. acid washing, ultrasound pre-treatment, H_2 pre-treatment, and liquid nitrogen pretreatment);^{82–84} 2) tailoring the size of ZVI powders (microparticles and nanoparticles);^{9,85} 3) input of chemicals (e.g. organic ligands

and reducing agents) to enhance the reactivity of ZVI powders;^{49,50,86} 4) coupling with energy (e.g. ultrasound, light, electricity, microwave, and magnetic effects);^{87–91} 5) synthesizing ZVI-based bimetallic particles (e.g. ZVI–Cu, ZVI–Co, ZVI–Ni, and ZVI–Ag);^{92–94} 6) simultaneously removing heavy metal and organic contaminants;^{95,96} 7) coupling with other materials (e.g. carbon materials, zeolites, iron oxides, and membranes).^{97–100} Although these physicochemical methods can enhance the reactivities of ZVI, the emergence of new shortcomings with the input of chemicals or energy also limit their practical application, such as higher cost, secondary pollution, and the short-term reactivity recovery of ZVI. Based on our understanding of ZVI-based Fenton-like oxidation, employing ZVI-based materials to simultaneously remove heavy metal and organic contaminants is recommended.

The corrosion of ZVI occurs more rapidly by establishing bimetal catalytic oxidation systems with noble metals (e.g. Co, Cu, Pd, Ni, Pt, Ag).^{92–94} Fe⁰ and surface noble metals can form a galvanic cell to promote both the direct reduction of target contaminants and the indirect oxidation of contaminants *via* Fenton-like reactions. The surface noble metal generally acts as a catalyst to promote ZVI corrosion and release Fe(II) *via* the acceleration of electron transfer from Fe⁰ to the target compounds (e.g. organic contaminants and O₂). Therefore, many ZVI-based bimetal materials were developed and attempts to apply them in water remediation have been reported, such as ZVI–Cu, ZVI–Pd, ZVI–Ag, and ZVI–Ni.^{101–104} These materials were generally prepared using a simple method *via* rapid replacement reactions between Fe⁰ and noble metals (chemical plating).^{101,102} Compared to ZVI powders, these ZVI-based bimetallic particles show significantly higher reactivity for dechlorination, debromination, nitrate reduction, nitrophenol reduction, and oxidative degradation of a wide variety of organic contaminants.^{93,101–107} Nevertheless, the high cost of noble metals and leaching of heavy metals using ZVI-based bimetallic particles results in low potential for practical applications.

However, the existence of heavy metals (e.g. Cu, Pb, and Cr) in industrial wastewater is quite common. The synchronous removal of heavy metals and organic pollutants by ZVI-based technologies can form ZVI-based bimetals to enhance the reactivity of ZVI powders. In these processes, heavy metals (e.g. Cu(II) and Cr(VI)) can accelerate ZVI corrosion to release Fe(II) to enhance Fenton-like reactions, meanwhile, the *in situ*-generated low valent metals (e.g. Cu⁰ and Cr(III)) can further produce ROS *via* low valent metal catalyzed Fenton-like reactions.¹⁰⁸ In recent years, some ZVI-based Fenton-like systems have been reported to remove heavy metals (mainly Cu(II) and Cr(VI)) and organic pollutants, and their overall oxidation efficiencies are higher than those without heavy metals.^{108–111}





As an example, the mechanism for the simultaneous removal of Cu(II) and organic contaminants using ZVI-based Fenton-like systems is shown in [Figure 12.3](#). First of all, ZVI rapidly reduces Cu(II) into Cu⁰ (attached on the surface of ZVI) resulting in the removal of Cu(II) and the release of Fe(II) ([eqn \(12.19\)](#)), thus, Fe(II) further activates peroxides (H₂O₂, PDS, and PMS) to produce ROS. Not only that, our previous literature reports proved that Cu⁰ can also decompose these peroxides to produce ROS ([eqn \(12.20\)–\(12.30\)](#)).^{112,113} Therefore, the surface Cu⁰ is further corroded to release Cu(I) resulting in the generation of ROS *via* Cu(I)-mediated chain reactions. Although Cu⁰ is further oxidized to Cu(II), the concentration of dissolved copper remains at a relatively low level due to the ZVI-induced fast reduction from Cu(II) to Cu⁰.¹¹⁴ Moreover, the dissolved copper is completely removed by increasing the solution pH (approximate pH > 5.0) to inhibit the corrosion of Cu⁰.¹⁰⁸ In addition, some ZVI-derived composites further enhance the capability to synergistically remove heavy metals and organic contaminants, such as bentonite-supported nano-ZVI particles, biochar-supported ZVI particles.^{95,96,115}

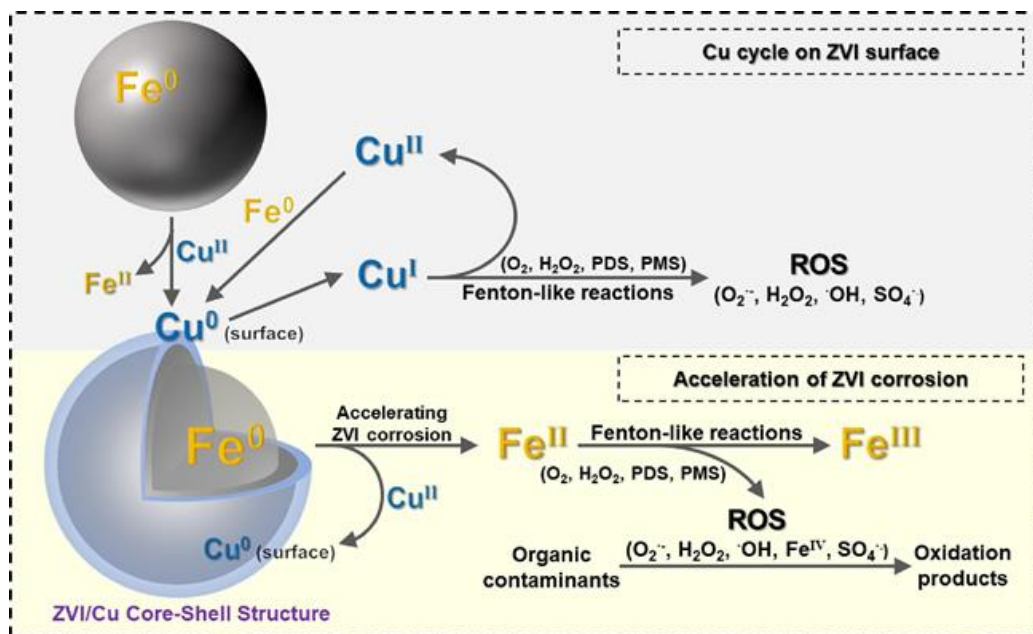


Figure 12.3 Simultaneous removal of Cu(ii) and organic contaminants using ZVI-based Fenton-like systems.

Based on the above analysis, ZVI-based Fenton-like systems show high capabilities for the simultaneous removal of heavy metals and organic contaminants with careful control of the operating parameters leading to decreased concentrations of dissolved heavy metals in effluent water.

12.4 Reactive Oxygen Species

ZVI and its derived iron species can induce chain reactions of oxygen and peroxides (H_2O_2 , PDS, and PMS) to produce a variety of ROS, such as hydroxyl radicals ($\cdot\text{OH}$), sulfate radicals ($\text{SO}_4\cdot^-$), superoxide radicals ($\text{O}_2\cdot^-$), ferryl iron species ($\text{Fe}(\text{iv})$) (Table 12.2). Among these ROS, hydroxyl radicals, sulfate radicals, and $\text{Fe}(\text{iv})$ produced *via* Fenton and Fenton-like reactions are the primary oxidants in ZVI-based Fenton-like systems for the degradation of multifarious organic contaminants, although the generation and contribution of $\text{Fe}(\text{iv})$ are still controversial.¹¹⁶ Some recent papers proposed singlet oxygen ($^1\text{O}_2$) may be produced to oxidize some electron-rich compounds or groups during the activation of persulfate; however, the role of singlet oxygen is still disputed and the involvement of singlet oxygen in the ZVI-induced activation of persulfates is seldom reported.⁶²

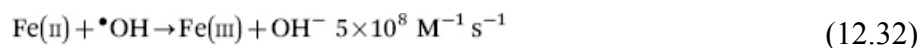
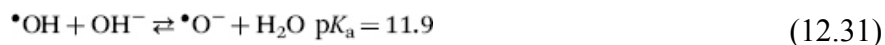
Table 12.2 The main reactive species and their precursors in ZVI-based Fenton-like systems.

	Molecular formula	pK_a	Redox potential vs. NHE	Oxidation property
Redox couple	E° (v)			
Hydrogen peroxide	H_2O_2	11.6–11.8 ^{123,124}	$\text{H}_2\text{O}_2/\text{H}_2\text{O}$ 1.76 ¹²⁵	/

Peroxydisulfate	$\text{S}_2\text{O}_8^{2-}$	-3.5^{126}	$\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$	$2.01-2.08^{127,128}$	/
Peroxymonosulfate	HSO_5^-	$\text{p}K_{a1} = 1.0^{129}$ $\text{p}K_{a2} = 9.4^{130}$	$\text{HSO}_5^-/\text{SO}_4^{2-}$	$1.82-1.84^{131-133}$	/
Hydroxyl radicals	$\cdot\text{OH}/\cdot\text{O}^-$	11.9^{30}	$\cdot\text{OH}/\text{OH}^-$	$1.64-2.74^{30}$	Non-selective oxidant
Sulfate radicals	$\text{SO}_4^{\cdot-}$	/	$\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}$	$2.50-3.10^{63}$	Less selective oxidant (pH dependent)
/	$\text{SO}_5^{\cdot-}$	/	$\text{SO}_5^{\cdot-}/\text{SO}_5^{2-}$	0.81 (high pH) ¹²⁹	Mild oxidant
$\text{SO}_5^{\cdot-}/\text{HSO}_5^-$	$0.95-1.24$ (low pH) ¹²⁹				
Superoxide radicals	$\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$	4.8^{28}	$\text{O}_2/\text{O}_2^{\cdot-}$	-1.6 to -0.59^{134}	Mild oxidant
$\text{O}_2^{\cdot-}/\text{H}_2\text{O}_2$	0.89^{135}				
Fe(IV)	$\text{Fe}^{\text{IV}}\text{O}^{2+}$	/	$\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}$	$1.40-1.80^{136}$ 2.0^{137}	Selective oxidant

12.4.1 Hydroxyl Radicals

The formation mechanism of reactive species seems to have been a permanent debate since the discovery of Fenton reagents according to the opposite results from theoretical calculations and practical chemistry experiments;^{117–120} however, hydroxyl radicals are the most widely accepted reactive oxidant in classical Fenton system as well as in the ZVI–O₂ system and the ZVI–H₂O₂ system in acidic conditions.^{120–122} Due to the pH-dependent hydrolysis with a $\text{p}K_a$ of 11.9, hydroxyl radicals ($\cdot\text{OH}$, 2.7 V) will change into their conjugate base ($\cdot\text{O}^-$, 1.64–1.78 V) in strongly alkaline aqueous solutions (eqn (12.31)), which causes a changeover from electrophile to nucleophile and the relatively slow reaction kinetics of $\cdot\text{O}^-$ -induced oxidation processes.³⁰ Nevertheless, hydroxyl radical maintains relatively high oxidation capability in most ZVI-based AOPs, in view of the strict requirements of acidic conditions for ZVI corrosion chemistry to induce the generation of reactive radicals.



Hydroxyl radicals are a non-selective oxidant with a high standard reduction potential, which can non-selectively degrade almost all organics *via*: 1) hydrogen atom abstraction; 2) single

electron transfer; 3) addition–elimination.⁶² The formation of hydroxyl radicals and their contribution in oxidizing contaminants have been qualitatively and semi-quantitatively investigated using a variety of methods, such as quenching tests with tertiary butanol (TBA) as a quenching agent, electron paramagnetic resonance (EPR) analysis with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) or 5-*tert*-butoxycarbonyl 5-methyl-1-pyrroline *N*-oxide (BMPO) as trapping agents, and detection of hydroxyl radical-induced hydroxylated products with terephthalic acid, benzoic acid, or other aromatic compounds as chemical probes.^{138,139} The second-order rate constants between hydroxyl radicals and organic molecules are almost higher than $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (see Figure 12.4).^{140–147} For this reason, the lower sensitivity of hydroxyl radicals to their chemical surroundings also causes the relatively low efficiency towards the target compounds in solutions of complex substances. For instance, hydroxyl radicals can also rapidly react with coexisting substances in real waters, such as halide ions (*e.g.* Cl^- , I^- , and Br^-), oxyanions (*e.g.* $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$), and dissolved organic matter (*e.g.* humic acid and fulvic acid).^{30,148–151} Moreover, high concentration of hydroxyl radicals can also oxidize Fe(II) with a rate constant of $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in the ZVI– H_2O_2 system to decrease the utilization rates of ZVI and H_2O_2 (eqn (12.32)).¹³⁷

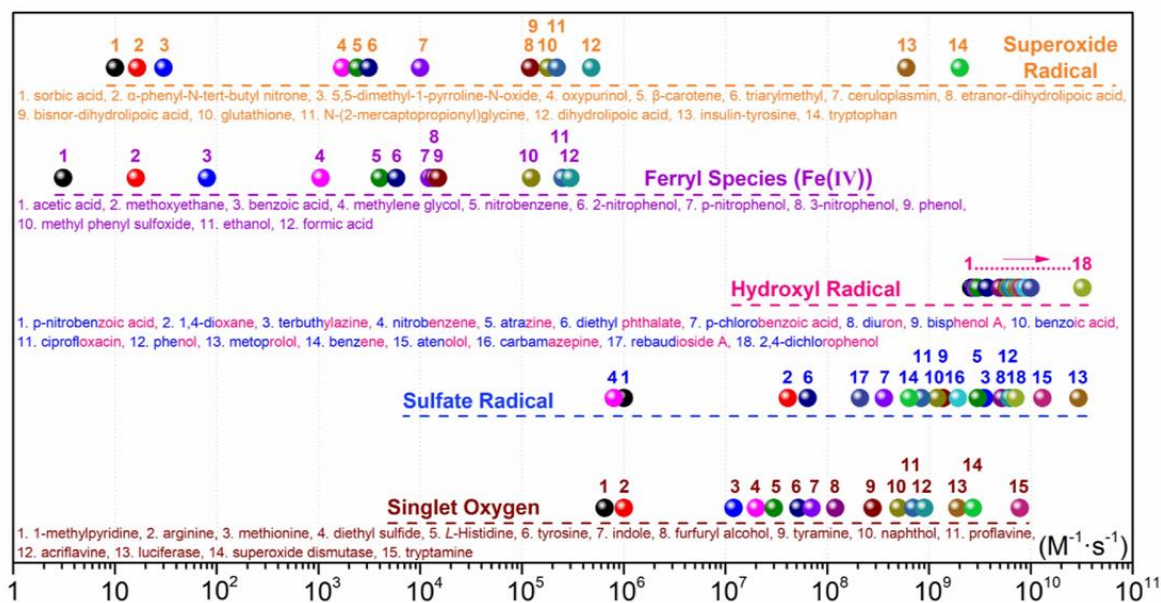
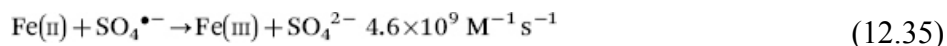
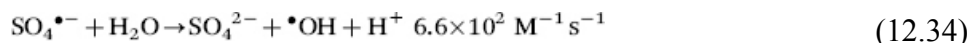
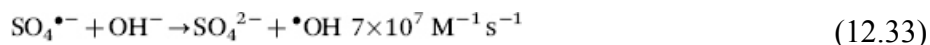


Figure 12.4 The second-order rate constants between organic compounds and reactive species (singlet oxygen, sulfate radical, hydroxyl radical, ferryl species (Fe(IV)), superoxide radical) generated in ZVI-based Fenton-like systems.^{140–147}

12.4.2 Sulfate Radicals

Sulfate radicals are strong oxidants that can also degrade a wide variety of organic contaminants and even cause mineralization at high concentrations. Although sulfate radicals can interconvert to hydroxyl radicals with hydroxide ion or water molecule precursors (eqn

(12.33) and (12.34)), the dominant oxidants are sulfate radicals at pH < 9.0 that changes to hydroxyl radicals at pH > 11.0 due to the requirement for high concentrations of hydroxide ions.¹⁵² Sulfate radicals are more reactive in alkaline conditions, which is different from hydroxyl radicals; however, the ZVI-induced activation of persulfates to produce sulfate radicals mainly occurs in acidic conditions.



The standard reduction potential of sulfate radicals (2.5–3.1 V) is even higher than hydroxyl radicals,⁶³ however, it shows higher substrate-specific reactivity.⁶² As shown in Figure 12.4, different from the universally high second-order rate constants of hydroxyl radical-induced oxidation of organics ($> 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the second-order rate constants between sulfate radicals and organics range from $10^6 \text{ M}^{-1} \text{ s}^{-1}$ to more than $10^9 \text{ M}^{-1} \text{ s}^{-1}$. Sulfate radicals can also degrade these different kinds of organics, but the reaction kinetics of these degradation processes depend on the specific reactivity of the substrates. Sulfate radicals are similar to hydroxyl radicals; the oxidation of organics is possible *via* three pathways: 1) hydrogen atom abstraction; 2) single electron transfer; 3) addition–elimination. The oxidation of aromatic compounds by sulfate radicals primarily undergoes single electron transfer and addition–elimination, but it is extremely sensitive to substituent effects.⁶² For instance, the relatively sluggish kinetics for oxidation of nitrobenzene ($< 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and diethyl phthalate ($6.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) causes low removal ratios in sulfate radical-dominated processes.^{153,154} Therefore, the practical application of ZVI for activating persulfates to produce sulfate radicals should be carefully evaluated with full consideration of the substrate-specific reactivity of wastewater.

12.4.3 Ferryl Ion Species (Fe(iv))

Ferryl ion species (Fe(iv), Fe^{IV}O) are also transient reactive oxidants (1.4–2.0 V) and can also selectively degrade many kinds of organic contaminants.^{136,137} Fe(ii) is the main reactive species for activating peroxides during ZVI corrosion, the generation of Fe(iv) during Fenton-like reactions between Fe(ii) and peroxides is still controversial. Although the changeover of reactive species from hydroxyl radical to Fe(iv) in classical Fenton systems (Fe(ii) and H₂O₂) will partly occur at pH 6–7 (1–10%) both without and with organic ligands (*e.g.* oxalate acid, citric acid, nitrilotriacetic acid),^{120,155} the involvement of Fe(iv) during the corrosion of ZVI without persulfates is almost negligible at a wide pH range (2 to 9) based on chemical probe tests and quenching tests.^{121,156}

Recent literature reports suggest that Fe(iv) is mainly produced during the binary mixture of persulfates and Fe(ii). Wang and co-workers firstly proposed that Fe(iv) is the dominant ROS for degrading contaminants during the Fe(ii)-induced activation of PDS by distinguishing the distinct characteristic products of the reactions between methyl phenyl sulfoxide (PMSO) and sulfate radicals and Fe(iv).⁶⁶ However, in their follow-up study, the organic ligands of Fe(ii) (oxalate acid, citric acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, pyrophosphate,

tetrapolyphosphate) were found to induce mechanistic changeover from Fe(IV) to sulfate radicals in Fe(II) –PDS systems, and this process was not sensitive to solution pH.¹⁵⁵ Afterwards, Dong and co-workers reported that both Fe(IV) and radicals were the reactive species in Fe(II) –PDS systems based on the results of various chemical probe experiments.⁶⁷ And similar arguments persist when Fe(IV) is the main ROS during the Fe(II) -catalyzed decomposition of PMS (the Fe(II) –PMS system).⁶⁸ Although the controversy about the generation of Fe(IV) during the ZVI-induced decomposition of peroxides (especially PDS and PMS) has remained in recent years, Fe(IV) is a vital ROS for the degradation of contaminants in ZVI-based Fenton-like systems. Wang and co-workers systemically investigated the relative contribution of sulfate radicals and Fe(IV) during the ZVI-induced activation of persulfates (both PDS and PMS) with PMSO as the chemical probe, and this report proposed a pathway for the simultaneous generation of sulfate radicals and Fe(IV) : 1) sulfate radicals are produced by heterogeneous electron transfer from Fe^0 to persulfate; 2) Fe(IV) is produced by the homogeneous activation of persulfates by the released Fe(II) during ZVI corrosion.¹¹⁶

As an electropositive species, Fe(IV) is a more selective oxidant with a low oxidizing potential compared to hydroxyl radicals and sulfate radicals (Table 12.2). Although Fe(IV) can't effectively oxidize some electron-deficient compounds and groups, Fe(IV) has two primary merits: 1) the longer lifespan of Fe(IV) increases the contact probability towards target compounds; 2) Fe(IV) selectively reacts with target compounds resulting in high utilization efficiency.^{116,157} As shown in Figure 12.4, the rate constants for the degradation of organic contaminants for Fe(IV) range from 10 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$. To fully take advantage of Fe(IV) , a meaningful strategy is to combine the selective oxidants (e.g. Fe(IV)) and the non-selective oxidants (e.g. sulfate radicals and hydroxyl radicals) to establish more efficient oxidative systems for environmental remediation.

12.5 Promoting the Application of ZVI Towards Industrial Wastewater Treatment

The strict requirements for solution pH, the addition of peroxides, and high concentrations of iron corrosion products present intrinsic drawbacks and limit the practical application of ZVI-based Fenton-like systems in some fields, such as tap water treatment and groundwater treatment. However, ZVI-based materials exhibit great potential for application in the treatment of highly concentrated organic industrial wastewater, and the technical advantages of ZVI-based Fenton-like systems include: 1) high oxidation capability to thoroughly degrade target organic contaminants and significantly decrease TOC and COD; 2) improve biodegradability and reduce the toxicity of wastewater for further biological treatment; 3) less secondary pollution due to the eco-friendly derivatives used during ZVI corrosion; 4) Fe(III) species derived from ZVI can act as the coagulant by mixing with coagulant aids (e.g. polyacrylamide); 5) simple operation with high antijamming capability towards solution temperature.

Due to the harsh demands of solution pH, many efforts were made by researchers to expand the effective pH range, such as: 1) adding organic ligands (e.g. oxalic acid, ethylenediaminetetraacetic acid, citric acid, and tripolyphosphate) to chelate with Fe(III) and Fe(II) to inhibit the formation of surface passivation layers, accelerate the corrosion of ZVI, and promote the generation of ROS *via* Fenton-like reactions;^{49,54,158} 2) adding reducing agents

(e.g. hydroxylamine hydrochloride and ascorbic acid) to accelerate Fe(III) reduction and enhance ROS generation *via* Fenton-like reactions.⁵⁴ Although these methods can expand the effective pH range to higher pH values (neutral or weak alkaline), they also cause secondary organic pollution from the input of organic promoters. Whereas, the extension of the effective pH range of ZVI-based Fenton-like systems is not necessary for treatment of many kinds of industrial wastewater. Based on our practical engineering experience, the treatment cost of per ton of industrial wastewater ranges from 50 RMB to more than 1000 RMB using some frequently-used physicochemical technologies (e.g. iron–carbon micro-electrolysis, catalytic ozonation, and ultrafiltration). Due to the high operating cost of industrial wastewater purification, the expenditure by sustained adjustment of solution pH using sulfuric acid, hydrochloric acid, or nitric acid is acceptable in continuous flow modes of wastewater treatment processes. Meanwhile, the solution pH of wastewater increases with reaction time due to the continuous consumption of H⁺ during the corrosion of ZVI, which accelerates the formation of iron (hydroxy)oxides and surface passivation layers. The continuous adjustment of solution pH can restrain the aging of ZVI powders to maintain their reactivity. Therefore, ZVI-based Fenton-like technologies are worth popularizing towards industrial wastewater treatment.

Previous literature reports depict ZVI-based Fenton-like systems that can effectively treat a wide variety of industrial wastewaters, such as pharmaceutical wastewater, textile industry wastewater, coking wastewater, olive mill wastewater (Table 12.3).^{56–59,75,159–161} Segura and co-workers published some research papers focusing on the pre-treatment of pharmaceutical wastewater using ZVI-induced Fenton-like systems.^{56–58} For example, Segura and co-workers reported that the ZVI–H₂O₂ system removed 80% TOC in pharmaceutical wastewater (initial TOC 4700 mg L^{−1}), meanwhile, the biodegradability was significantly enhanced when the BOD₅/COD increased from 0.18 to 0.6.⁵⁷ Moreover, low-biodegradable wastewater (BOD₅/COD < 0.05) from textile industry was also be effectively purified using the ZVI–H₂O₂ system with a high COD removal ratio of approximately 90% (initial COD 1500 mg L^{−1}) and an increase in biodegradability; in addition, after treatment the effluent was non-toxic⁵⁹ and the ZVI–H₂O₂ system was largely immune to changes in solution temperature.⁵⁹ Moreover, ZVI also shows high reactivity for the activation of persulfates towards industrial wastewaters. Ghanbari and co-workers reported that ZVI–PMS systems and ZVI–PMS–H₂O₂ systems (PMS : H₂O₂ = 1 : 1) have high oxidation capabilities towards textile wastewater compared to ZVI–H₂O₂ systems, with COD and TOC removal efficiencies of the following order: ZVI–H₂O₂ < ZVI–PMS < ZVI–PMS–H₂O₂.⁷⁵ Nevertheless, the accumulation of sulfate ions resulting from the input of persulfates is an intrinsic drawback. Based on these literature reports, ZVI–H₂O₂ systems are the most suitable ZVI-based Fenton-like technology for the treatment or pre-treatment of industrial wastewater.

Table 12.3 Industrial wastewater treatment using ZVI-based Fenton-like technologies.

Wastewater		Effluent characterization	ZVI- derived techniques	Operating conditions	References
Types	Characterization				

Pharmaceutical industry	pH 9.75 TOC 10 021 mg L ⁻¹ BOD ₅ 3754 mg L ⁻¹ COD 49 620 mg L ⁻¹ BOD ₅ /COD 0.08	/	ZVI-H ₂ O ₂	pH 3.0 ZVI 1.2 g L ⁻¹ H ₂ O ₂ 943 mM 60 min	56
Total nitrogen 285 mg L ⁻¹	/				
Pharmaceutical industry	pH 5.5 TOC 4700 mg L ⁻¹ BOD ₅ 2700 mg L ⁻¹ COD 15 000 mg L ⁻¹ BOD ₅ /COD 0.18 SS 790 mg L ⁻¹ Conductivity 70 mS cm ⁻¹ Toxicity 27%	pH 6.0 TOC removal 80% BOD ₅ 900 mg L ⁻¹ COD 1480 mg L ⁻¹ BOD ₅ /COD 0.6 SS 380 mg L ⁻¹ Conductivity 7.5 mS cm ⁻¹	ZVI-H ₂ O ₂	pH 3.0 ZVI 28.2 g L ⁻¹ H ₂ O ₂ 290 mM 120 min 22 °C 0.5 L Air aeration 5 L min ⁻¹	57
No toxicity					
Textile industry	pH 7.2 COD 1500 mg L ⁻¹ BOD ₅ /COD 0.05	/	ZVI-H ₂ O ₂	ZVI 0.247 g L ⁻¹ H ₂ O ₂ 37 mM 300 min	59
High phytotoxicity	Almost no phytotoxicity	15–45 °C			
Textile industry	pH 5.65 TOC 496 mg L ⁻¹ BOD ₅ 280 mg L ⁻¹ COD 1550 mg L ⁻¹ BOD ₅ /COD	/	ZVI-PMS	pH 4.0 ZVI 3.0 g L ⁻¹ PMS 20 mM 150 min	75
		TOC removal 48.1% COD removal 74.6%			
			23–26 °C		

	0.18				
Textile industry	pH 9.1 TOC 324 mg L ⁻¹ BOD ₅ 189.6 mg L ⁻¹ COD 875 mg L ⁻¹ BOD ₅ /COD 0.22 Conductivity 12.76 mS cm ⁻¹ Toxicity 60% Absorbance at 660 nm, 1.8	pH 6 TOC 93 mg L ⁻¹ BOD ₅ 87.9 mg L ⁻¹ COD 208 mg L ⁻¹ BOD ₅ /COD 0.42 Conductivity 12.76 mS cm ⁻¹ Toxicity 20%	0.5 L ZVI-H ₂ O ₂	pH 3.0 ZVI 2.0 g L ⁻¹ H ₂ O ₂ 24.5 mM 60 min 25 °C 50 mL 400 rpm	159
Coking industry	pH 9.1–9.3 COD 7500–8400 mg L ⁻¹ Total phenol 1700–1900 mg L ⁻¹ Ammonium 400–480 mg L ⁻¹ Cyanide 7.5–8.5 mg L ⁻¹	 COD removal 44–50% Total phenol removal 95% / /	ZVI-H ₂ O ₂	ZVI 3.0 g L ⁻¹ H ₂ O ₂ 300 mM 60 min 25 °C 300 mL	160
Olive mill wastewater	pH 5.2 COD 19 g L Total polyphenol 672 mg L ⁻¹ BOD ₅ /COD 0.14	150 rpm / COD removal 92% / BOD ₅ /COD 0.53	ZVI-H ₂ O ₂	pH 2–4 ZVI 20 g L ⁻¹ H ₂ O ₂ 0.95 M 24 h	161
Dinitrodiazophenol industry wastewater	pH 5.7 BOD ₅ 0 mg L ⁻¹ COD 1250 mg L ⁻¹	25 °C / BOD ₅ 94 mg L ⁻¹ COD removal 78%	ZVI-air-Fenton-ZVI-air	pH 2.0 ZVI 40 g L ⁻¹ H ₂ O ₂ 2.5 mM	162

	BOD ₅ /COD 0	BOD ₅ /COD 0.27		3 h	
				25 °C	
		Air aeration 1.5 L min ⁻¹			
Ammunition wastewater	pH 5.7 BOD ₅ 10.4 mg L ⁻¹ COD 518 mg L ⁻¹ BOD ₅ /COD 0.02	/ BOD ₅ 15.7 mg L ⁻¹ COD 28 mg L ⁻¹ BOD ₅ /COD 0.56	ZVI–air– Fenton– ZVI–air	pH 2.0 ZVI 40 g L ⁻¹ H ₂ O ₂ 2.5 mM 3 h	163
				25 °C	
		Air aeration 1.5 L min ⁻¹			
Delay explosive wastewater	pH 6.5 BOD ₅ 1110 mg L ⁻¹ COD 5862 mg L ⁻¹ BOD ₅ /COD 0.19	/ BOD ₅ 1640 mg L ⁻¹ COD removal 50% BOD ₅ /COD 0.56	ZVI–air– Fenton– ZVI–air	pH 2.5 ZVI 10 g L ⁻¹ H ₂ O ₂ 10 mM 4 h	164
Cr 1.61 mg L ⁻¹	Pb 2.46 mg L ⁻¹ Pb not detected	Pb not detected Air aeration 1.0 L min ⁻¹		30 °C	

Moreover, as an example of practical project cases, our group first established a three-stage treatment process by combining a ZVI–O₂ system and a Fenton system (ZVI–air–Fenton–ZVI–air), which showed high-efficiency for the treatment of industrial wastewater (*e.g.* dinitrodiazophenol industry wastewater, ammunition wastewater, delay explosive wastewater);^{162–164} some successful engineering examples of the ZVI–air–Fenton–ZVI–air system towards industrial wastewaters are shown in Figure 12.5. Due to the separation between ZVI corrosion and Fenton reaction, the ZVI–air–Fenton–ZVI–air system synergistically removed heavy metals (*e.g.* Pb and Cr) and organic contaminants in wastewater *via* ZVI reduction.¹⁶⁴ At present, this patented technology is promoted to treat a wider variety of industrial wastewater by combining with subsequent activated sludge systems, such as pharmaceutical wastewater and explosive wastewater. Based on the above analysis, the study of ZVI should not stay in the laboratory, researchers should be encouraged to boldly promote the practical use of ZVI, especially towards industrial wastewater treatment.

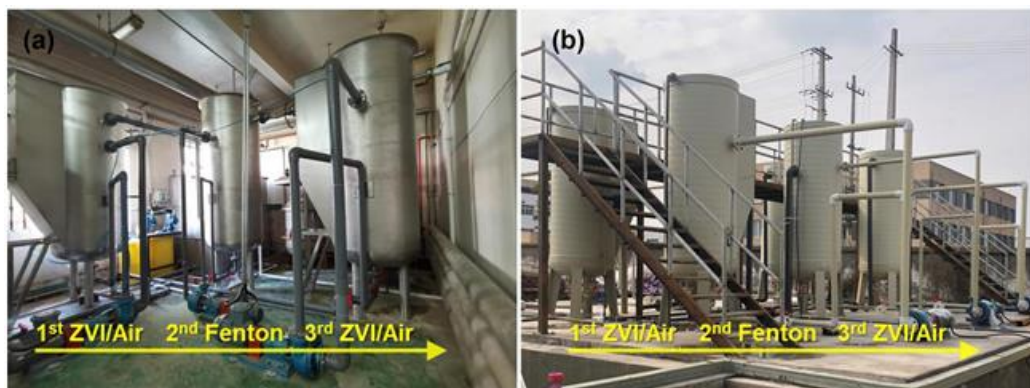


Figure 12.5 The cases of practical engineering applications of the ZVI–air–Fenton–ZVI–air system towards (a) ammunition wastewater and (b) delay explosive wastewater.

12.6 Conclusions and Prospects

ZVI-based materials have been demonstrated as a class of promising materials for water remediation. From the viewpoint of Fenton-like oxidation, ZVI is an ideal electron source to donate electrons and induce the production of ROS without (or with acceptable) secondary pollution. A variety of ROS with different characteristics are produced during ZVI-based Fenton-like systems, but hydroxyl radicals, sulfate radicals and Fe(IV) are the primary oxidants for the degradation of organic contaminants. In general, the pH-dependent reactivity of ZVI caused by aging and inactivation is the primary barrier for the practical use of ZVI. Seeking proper strategies to continuously release Fe(II) during ZVI corrosion is critical to maintain the reactivity of ZVI powders, which inspired a mass of studies mainly aimed at synthesizing new ZVI-based materials and developing novel or ingenious methods to improve their reactivities, such as input of chemical promoters and physical stimulations. In our opinion, controlling the formation of passivation layers (iron (hydroxy)oxides) by continuously adjusting the solution pH (near pH 3.0) may be the best way to treat industrial wastewater up to now; this can induce continuous corrosion to release highly reactive Fe(II) for Fenton-like reactions. Moreover, ZVI-based materials also exhibit high abilities for the synergistic removal of heavy metals and organic pollutants. ZVI-based Fenton-like technologies significantly decrease the COD, TOC, and toxicity of many kinds of industrial wastewaters, such as pharmaceutical wastewater, textile industry wastewater, coking wastewater, olive mill wastewater; meanwhile, they strongly enhance the biodegradability of these wastewaters. Therefore, ZVI-based Fenton-like oxidation is a great pre-treatment (for subsequent biological treatment) or treatment method. Therefore, we strongly recommend researchers daringly promote the practical application of ZVI-based Fenton-like technologies in industrial wastewater treatment.

Although ZVI-based Fenton-like technologies have great potential to be applied in the field of wastewater treatment, there are still some technical obstacles:

- (1) Designing specific reactors to achieve the fluidization of ZVI powders in water (especially micro-ZVI powders).
- (2) Thorough removal of ZVI corrosion products from water.

- (3) Seeking feasible methods to harmlessly dispose or regenerate iron cements.
- (4) Establishing mathematical relationships between operating conditions and inflow water quality indexes (*e.g.* TOC, COD, and BOD).
- (5) Designing specific water treatment process and equipment to take full advantage of both the reducing and oxidizing capabilities of ZVI. For example, the three-stage treatment process (ZVI–air–Fenton–ZVI–air) established by our group separates the release of Fe(ii) during ZVI corrosion and Fenton reactions between Fe(ii) and H₂O₂, which greatly decreases the unproductive consumption of ZVI by ROS.^{162–164}

Moreover, there are some theoretical obstacles for the practical use of ZVI-based Fenton-like technologies, which were rarely mentioned in previous literature reports:

- (1) ZVI-based Fenton-like systems involve various ROS (hydroxyl radicals, sulfate radicals, and Fe(iv)) with different reactivities. The mechanism of ROS formation should be meticulously investigated to regulate and control the type and proportion based on the properties of specific wastewaters.
- (2) Establishing a properly stoichiometric analysis method of corrosion chemistry to evaluate electron utilization.
- (3) Establish whether ZVI can directly activate peroxides (H₂O₂, PDS, and PMS) *via* heterogeneous Fenton-like reactions. Peroxides can also react with ZVI to accelerate its corrosion, but it is still unclear whether ROS were produced in these processes, if not, it may cause electron and peroxide waste.
- (4) Solution pH is regarded as the main factor that affects the formation of iron (hydroxy)oxides. The formation mechanism of *in situ*-generated surface layers of ZVI powders with the variation of solution pH is also suggested to be further explored using emerging analysis technologies, such as *in situ* Raman spectroscopy, *in situ* Fourier transform infrared spectroscopy, and Mossbauer spectrometry. Based on this, evaluating the reactivity of *in situ*-generated, renascent, amorphous, and crystalline iron (hydroxy)oxides (*e.g.* Fe(OH)₂, FeOH²⁺, Fe(OH)₂⁺, Fe(OH)₃, FeOOH, Fe₃O₄, Fe₂O₃) during ZVI corrosion is beneficial in adjusting solution pH more economically.
- (5) Carefully investigating the changeover from micro-ZVI particles to nano-ZVI particles and their induced change of reactivity.
- (6) The effects of intermediates derived from organic precursors in highly concentrated industrial organic wastewater, such as complexation and reduction of Fe species. For example, previous literature reports suggest that quinones generated during the oxidation of aromatic compounds can act as electron shuttles to promote the Fe(iii)/Fe(ii) cycle and enhance Fenton-like oxidation.^{165,166}
- (7) Evaluating potential conflicts of ZVI-induced reduction and oxidation during treatment of specific industrial wastewaters. The complex nature of reduction and oxidation involved in ZVI-based Fenton-like systems is universal. For instance, ZVI-based Fenton-like oxidation commonly acts as the pre-treatment process for activated sludge systems by increasing the biodegradability of industrial wastewater; however, ZVI can also reduce nitrate nitrogen into ammonia nitrogen, which is not conducive to subsequent biological treatment.¹⁶⁷

After hurdling these theoretical and applied barriers, we believe that the application of ZVI will greatly improve the processes of water remediation.

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Chapter 13

Photocatalysis for Water Treatment: From Nanoparticle to Single Atom, From Lab-scale to Industry-trial

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13.1 Introduction

For decades, photocatalysis has been studied as a potential technology for wastewater treatment, due to its advantages of moderate reactions conditions (ambient temperature and pressure), hardly any secondary pollution and direct utilization of solar energy *etc.* Its main role is the conversion of solar energy into reactive oxygen species (ROS), and it has been proven that photocatalysis is especially effective at dealing with several typical pollutants *e.g.* pathogenic bacteria, antibiotics/antibiotic resistant genes and heavy metals. However, as a new technology mainly in the research and development stage, photocatalysis also faces several challenges *e.g.* low efficiency for the utilization of solar energy, sluggish dynamics for ROS generation and less attention on the development of devices *etc.* Therefore, there is a long way to go before photocatalysis can

be widely used in real waste water treatment, as both basic scientific issues and appropriate devices/technology need to be carefully considered.

In this regard, this chapter provides a timely summary of recent progress both in basic research and industrial trials of photocatalysis in water treatment. Firstly, the mechanism of photocatalytic environmental remediation is briefly introduced. Then, typical photocatalytic nanomaterials and crucial surface/interface processes for photocatalytic water treatment are summarized and discussed. Moreover, emerging single-atom photocatalytic materials for water treatment are introduced and discussed in detail. Thereafter, several excellent examples from industrial trials of photocatalysis for water treatment are summarized, mainly about devices and technology. Finally, some suggestions and outlook for photocatalytic water treatment in the future are also raised and briefly discussed.

13.2 Basic Processes and Mechanism for the Photocatalytic Degradation of Pollutants

Photocatalysis is a branch of heterogeneous catalysis, which is a catalytic reaction that uses light energy. Light energy absorbed by photocatalysts can be converted into chemical energy for storage or be used to degrade harmful pollutants into harmless inorganic small molecules. The essence of photocatalysis is the combination of photochemistry and catalytic chemistry, and the photochemical reaction mainly occurs on the surface of semiconductor photocatalysts.

Figure 13.1 presents a typical photocatalytic mechanism.^{1,2} The photocatalytic degradation process mainly consists of four processes. Firstly, when the photon energy $h\nu$ is greater than or equal to the energy of semiconductor photocatalysts E_g , the electrons in the conduction band (CB) of the photocatalysts are excited to the valence band (VB) of the photocatalysts to produce photogenerated electrons, forming photogenerated holes in the original location of the electrons (Figure 13.1 I). Secondly, the excited electrons and holes transfer to the surface of the photocatalyst. Thirdly, photogenerated electrons react with O_2 adsorbed on the surface of the photocatalyst to form $\cdot O^{2-}$, photogenerated holes convert

H_2O or OH^- adsorbed on the surface of the photocatalyst into $\cdot\text{OH}$. Ultimately, reactive species (RS), such as $\cdot\text{OH}$, $\cdot\text{O}^{2-}$, h^+ , attack pollutants and achieve their purification and mineralization (Figure 13.1 V). However, owing to positive and negative charges, the recombination of photogenerated electrons and holes is inevitable (Figure 13.1 II), which dissipates the input energy through the form of heat or emitted light, and is not conducive to the degradation of pollutants. Moreover, in addition to the photogenerated electrons and holes for reduction and oxidation processes (Figure 13.1 III and IV), a portion of the photogenerated electrons and holes are trapped in metastable surface states (Figure 13.1 VI and VII), restraining their participation in redox reactions. According to the photocatalytic mechanism of semiconductors, the recombination of photogenerated electrons and the holes is detrimental to the photocatalytic degradation of pollutants. In order to obtain higher photocatalytic efficiency, the photogenerated carriers should be efficiently separated and rapidly transferred to the surface/interface to inhibit the recombination.

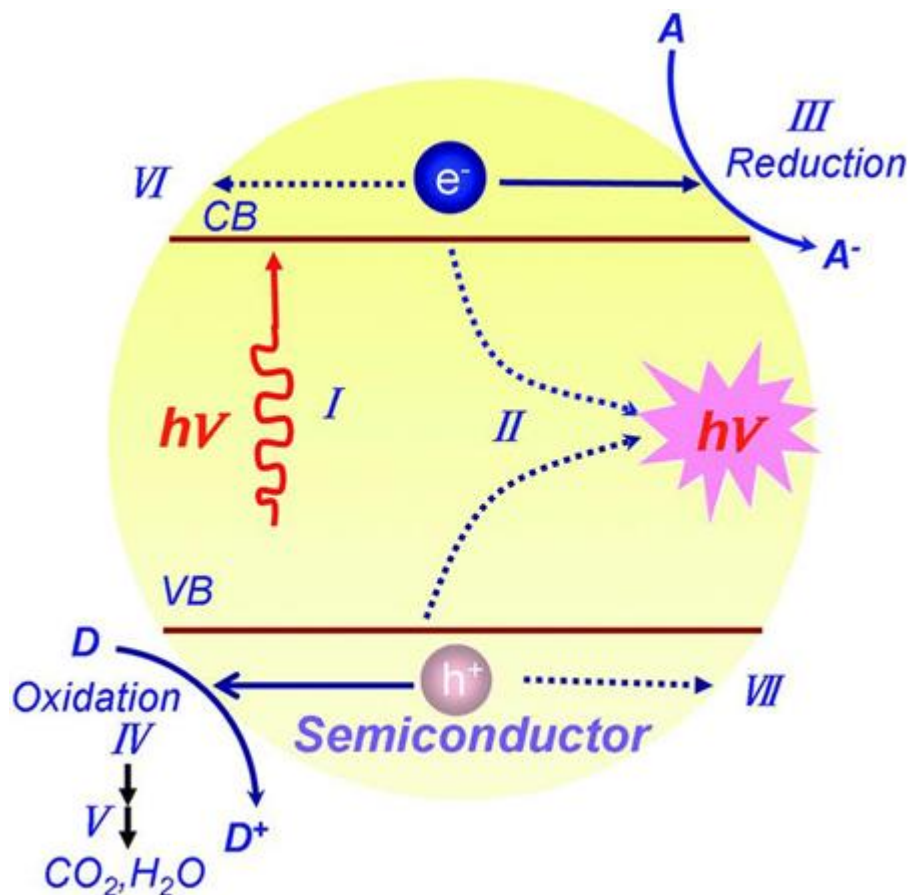


Figure 13.1 Photocatalytic degradation mechanisms: (I) the formation of photogenerated electrons and holes; (II) the recombination of photogenerated electrons and holes in semiconductor photocatalysts; (III) the reduction process *via* photogenerated electrons migrating to the surface; (IV) the oxidation process *via* photogenerated holes migrating to the surface; (V) the mineralization process of pollutants; (VI) photogenerated electrons trapped by a dangling bond; (VII) photogenerated holes trapped on the surface of the semiconductor. Reproduced from ref. ² with permission from the Royal Society of Chemistry.

In the presence of photocatalysts, organic pollutants can be degraded into water, carbon dioxide, nitrogen dioxide and other substances under light radiation. Photocatalysis has far-reaching significance in environmental pollution treatment. In fact, in the process of photocatalytic degradation of pollutants, the degradation of most pollutant molecules often needs multi-step chemical reactions. In practical application, we still have to consider the cost-effectiveness and other issues. Therefore, in the photocatalytic degradation of pollutants, we need to study the key physical parameters,

such as degradation rate, kinetic equations, mineralization rate and degradation pathways. These physical quantities reflect whether the degradation of organic compounds is efficient or not.

In photocatalytic reactions for environmental cleaning, organic pollutants can be oxidized by ROS. ROS can be produced through redox reactions of photogenerated electrons and holes with H_2O and O_2 . As illustrated in Figure 13.2, both oxidation and reduction process take place concurrently in photocatalysis. Typically, the stepwise oxidation of H_2O sequentially generates ROS of $\cdot\text{OH}$, H_2O_2 , $\cdot\text{O}_2^-$, and $^1\text{O}_2$. Simultaneously, the stepwise reduction of O_2 produces $\cdot\text{O}_2^-$, H_2O_2 , and $\cdot\text{OH}$.³

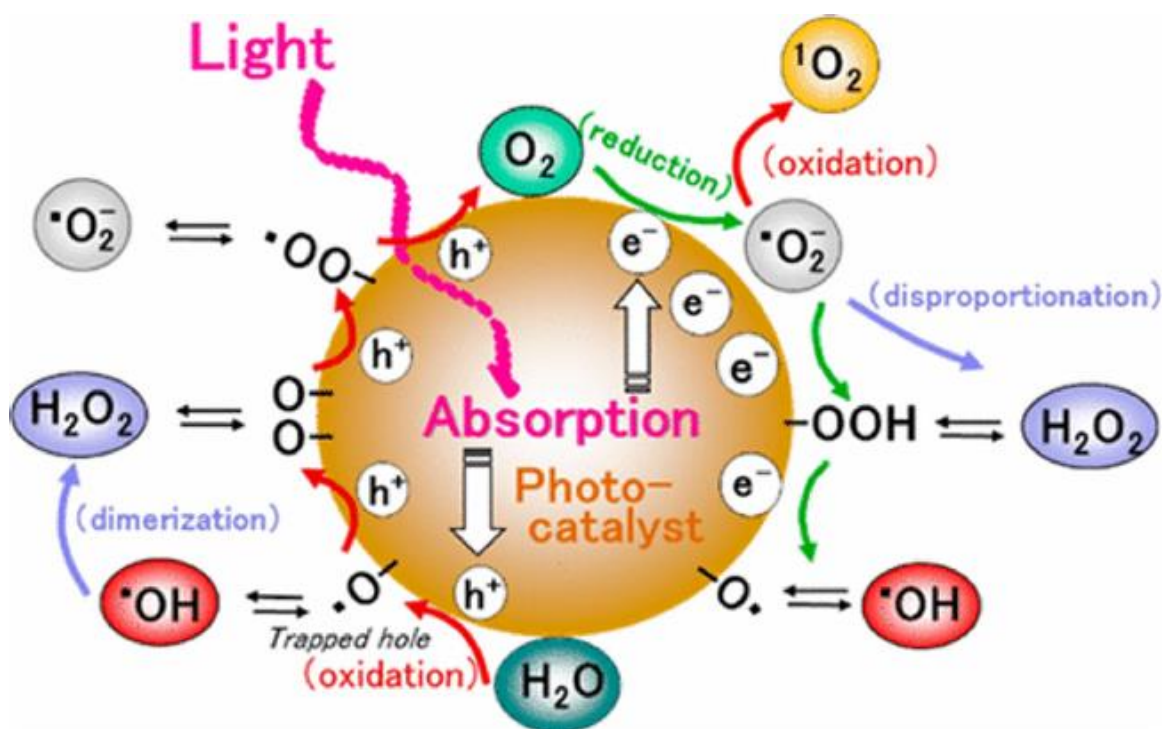


Figure 13.2 Reactive oxygen species generation from oxygen and water. Reproduced from ref. ³ with permission from American Chemical Society, Copyright 2017.

13.3 Typical Photocatalytic Nanomaterials for Environmental Remediation

In the field of photocatalysis, nanomaterials have become one of the most commonly applied photocatalysts due to their special photocatalytic properties. Typically, according to research progress concerning photocatalytic materials, environmental nanomaterials are mainly divided into metal oxides,^{4–6} metal sulfides,^{7–9} Bi-based photocatalysts,^{10–12} Ag-based photocatalysts,^{13–15} g-C₃N₄,^{16–18} elemental semiconductor photocatalysts,^{19–21} metal–organic frameworks (MOFs)^{22–24} and covalent organic frameworks (COFs).^{25–27} These photocatalytic nanomaterials still have some defects in terms of light absorption, stability or selectivity, but research into the preparation, modification, mechanism and application of these photocatalysts is continuously developing.

13.3.1 TiO₂

In 1972, Fujishima and Honda found that the photocatalytic splitting of water could produce hydrogen using sunlight for the first time.²⁸ Since then, photocatalysis has become one of the key technologies for the conversion of solar energy to chemical energy. Among many semiconductor materials, TiO₂ was one of the earliest semiconductor materials used in the field of photocatalysis. In nature, TiO₂ usually has three different crystal structures: anatase, rutile and brookite. Besides, some new structures appeared, such as TiO₂ (B), but this is quite a rare structure only reported in a few studies. Among the three typical structures, rutile is the most stable crystal, anatase titanite can be transformed into rutile at high temperatures. Different crystal structures of TiO₂ usually show different morphologies and properties. Therefore, the methods and conditions required for the synthesis of the crystal structures of nano-TiO₂ materials are respectively different. For example, anatase nano-TiO₂ is usually obtained using solution synthesis or low-temperature vapor deposition, while rutile was often produced using high-temperature deposition and even heating reactions. Due to its excellent photocatalytic activity, many efforts have focused on TiO₂ to degrade various pollutants and achieve environmental remediation. For example, Shi *et al.* synthesized a Bi₂O₃-sensitized TiO₂ hollow photocatalyst successfully. Due to the synergistic effect of p–n

heterojunctions and the hollow structure, the $\text{TiO}_2\text{-Bi}_2\text{O}_3$ photocatalyst showed excellent photocatalytic degradation performance and structural stability (Figure 13.3). Under visible light irradiation ($\lambda > 420$ nm), antibiotics could be completely degraded (100%), overcoming the challenging issue of incomplete removal of antibiotics among almost all visible-light catalysts reported.²⁹ The results revealed that both photogenerated h^+ and $\cdot\text{O}_2^-$ played an important role in the photocatalytic degradation process of tetracyclines (TC).

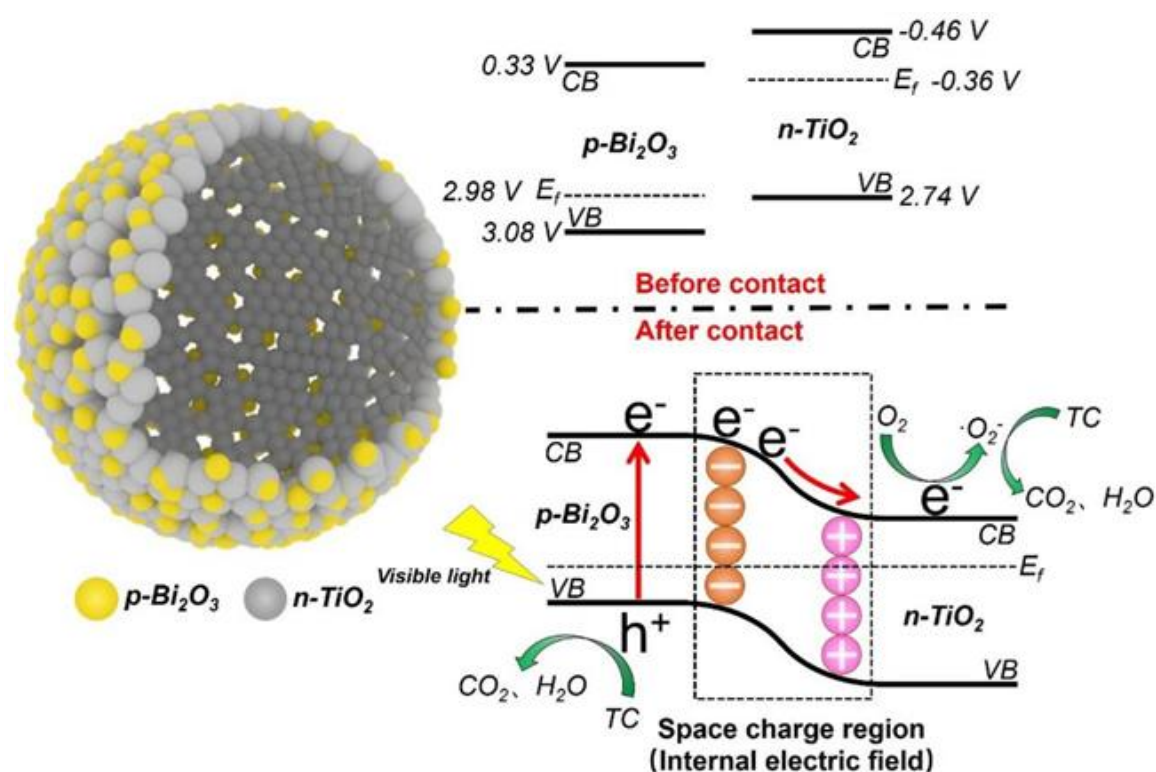


Figure 13.3 Photodegradation mechanism of TC over hollow $\text{TiO}_2\text{-Bi}_2\text{O}_3$ (HTB) under visible light. Reproduced from ref. ²⁹ with permission from American Chemical Society, Copyright 2020.

13.3.2 g- C_3N_4

Since g- C_3N_4 was first reported to decompose hydrogen under visible light in 2009,³⁰ more and more attention has focused on it. g- C_3N_4 is composed

of carbon and nitrogen atoms. The carbon atoms and nitrogen atoms are sp^2 hybridized and form a π -conjugated electronic structure, the layers are bound by van der Waals forces. g- C_3N_4 is a typical non-metallic polymer semiconductor material, which responds to visible light. Its band gap energy band value is 2.7 eV, and the energy positions of the conduction band and valence band are -1.1 eV and 1.6 eV, respectively (vs. NHE).³¹ The preparation method for g- C_3N_4 is simple, low-cost, and it is visible light-responsive. At present, research in the field of photocatalysis is very active. For example, Gao *et al.* synthesized perylene diimide (PDI)-g- C_3N_4 N-N heterojunctions for the inactivation of *Staphylococcus aureus* cells.¹⁷ The (PDI)-oxygen-doped g- C_3N_4 N-N heterojunction photocatalyst was prepared using an electrostatic *in situ* assembly method. The π - π interaction between self-assembled PDI and O-CN led to electron delocalization and promoted electron migration. The self-assembled PDI broadened the visible response range of O-CN and produced more photogenerated carriers. In addition, O-CN matched the band structure of the self-assembled PDI to form an embedded electric field, which promoted the separation of interfacial charge. In addition, PDI-O-CN can accumulate a variety of active species (H^+ , $\cdot O_2^-$ and $^1O_2$) to improve its oxidation ability. The best PDI-O-CN could kill 96.6% of *Staphylococcus aureus* cells in 3 h, while O-CN could only kill 62.2%. In addition, the degradation rate of phenol using PDI-O-CN-40% and the amount of oxygen released in 2 h were 3.6 and 1.8 times higher than that of O-CN, respectively.

13.3.3 Metal–Organic Frameworks (MOFs)

MOFs are a kind of zeolite material with porous structures composed of metal ions or clusters as nodes and organic ligands as linkers. They are not only organic–inorganic hybrid materials but also coordination polymers, which have the advantages of both organic and inorganic materials. In particular, MOFs are photo-reactive and can interact with incident light and exhibit semiconductor properties. With ligand–metal charge transfer and/or direct metal–oxygen cluster excitation, MOFs can photocatalyze various photochemical redox reactions. In recent decades, MOFs have been shown to have unique advantages in photocatalysis due to their special structure

and some properties of organic and inorganic materials. Firstly, the specific surface area of MOFs is larger than that of other materials, which provides the basis for full contact between a large number of active sites and reactants. Secondly, there are a large number of pores in MOF materials, and the arrangement of these pore structures is orderly, so the reaction substrate can easily enter these pores and react with the active sites. Finally, this kind of material can achieve specific catalytic reactions by changing structure and composition, which provides high flexibility. For example, Chen *et al.* synthesized platinum nanoparticle-encapsulated UiO-66-NH₂ (Pt-UiO-66-NH₂) for the photocatalytic degradation of phenol.³² The formation of the MOF played a variety of important roles, including binding with Zr clusters, promoting the dispersion of Pt, and playing a regulatory role in the construction of the MOF. In addition, the phenol removal rate of Pt-UiO-66-NH₂ was more than 70% in the presence of light and H₂O₂. At present, great progress has been made in the degradation of organic pollutants,^{33,34} but the poor water stability of these materials also limits their application in the field of photocatalysis.

13.3.4 Perovskite Photocatalytic Materials

Titanate, ferrite, tungstate, molybdate, vanadate, niobate, tantalate and other perovskite materials have been found to have photocatalytic activity. The application of layered perovskite in photocatalysis is related to their properties and structural characteristics. As photocatalytic materials, they have the following advantages: first, the materials have good light absorption, which lays the foundation for the effective use of solar light; second, the layered structure becomes an important guarantee for efficient transport and separation of photo-generated carriers; third, perovskite materials have diverse structures and high adjustability, which can be changed by structural regulation, results show that the band gap of the material can achieve specific redox reactions; fourth, the energy band position can meet different photoinduced reactions; fifth, some materials have piezoelectric, ferroelectric and other special properties that promote photocatalytic reactions. For example, niobium-doped titanate nanoflakes (TNFs) were synthesized by Liu *et al.* to degrade IBP. The TNFs were

prepared using a one-step hydrothermal method; Nb doping affects the bending of the titanate nanosheets, resulting in the formation of nanosheets.³⁵ In addition, the photo-adsorption properties of the original titanate were changed by adding Nb⁵⁺ between the [TiO₆] layers. The band gap of Nb TNFs was reduced to 2.85 eV, and that of the pure titanate nanotubes (TNTs) was 3.4 eV. Enhanced visible light absorption significantly enhanced the visible light-driven activity of the Nb TNFs for IBP degradation. The quasi first-order kinetic constant of the Nb TNFs was calculated to be 1.04 h⁻¹, but there was no obvious removal effect on TNTs. Photogenerated holes (h⁺) and ·OH were the main reasons for the degradation of IBP.

13.3.5 Ag₃PO₄

In 2010, Yi *et al.* applied Ag₃PO₄ to photocatalytic oxygen generation and the degradation of organic compounds, and since then Ag₃PO₄ has attracted substantial interest from many scholars.³⁶ Ag₃PO₄, with an indirect band gap of 2.36 eV and a direct band gap of 2.43 eV, is a photocatalyst with excellent photogenerated charge separation efficiency under visible light due to its unique electronic structure. Ag₃PO₄ has a body-centered cubic structure with a *P*4(3)/*n* spatial structure group and a 0.6004 nm lattice parameter and can exhibit high photooxidation ability under visible light. For example, Santos *et al.* synthesized visible light-driven Ag₃PO₄–NiO through *in situ* precipitation to degrade rhodamine B (RhB).³⁷ The photocatalytic activity of the composite material was much higher than pure Ag₃PO₄, owing to the effective interaction between Ag₃PO₄ and NiO, and 96% of RhB was degraded in only 15 min under visible light.

13.3.6 Elemental Semiconductor Photocatalysts

In recent years, scientists have made great efforts to develop efficient and inexpensive semiconductor photocatalysts. In addition to research on metal-based and non-metal-based compound semiconductor materials, some elemental semiconductor materials, such as P,³⁸ S,³⁹ Si⁴⁰ and C,⁴¹ have attracted more and more attention due to their abundant reserves and

absence of secondary pollution. Phosphorus is abundant in the earth's crust. Red phosphorus (RP) is one of the most common allotypes of phosphorus, and its chemical state is relatively stable. Red phosphorus is one of the most widely used elemental materials in the fields of organic synthesis, pyrotechnic manufacture, pesticide synthesis, semiconductor compound preparation and semiconductor material dopants. In 2014, Shen *et al.* efficiently synthesized a single crystal submicron fiber phosphorus material with particle diameters of about 150 nm to 2 μm *via* chemical vapor deposition and prepared type II phosphorus submicron rods by changing the reaction parameters.⁴² Under visible light, the degradation efficiency of RhB was 46.4% and 28.8% in 6 h for single crystal submicron fiber phosphorus material and type II phosphorus, respectively ([Figure 13.4](#)).

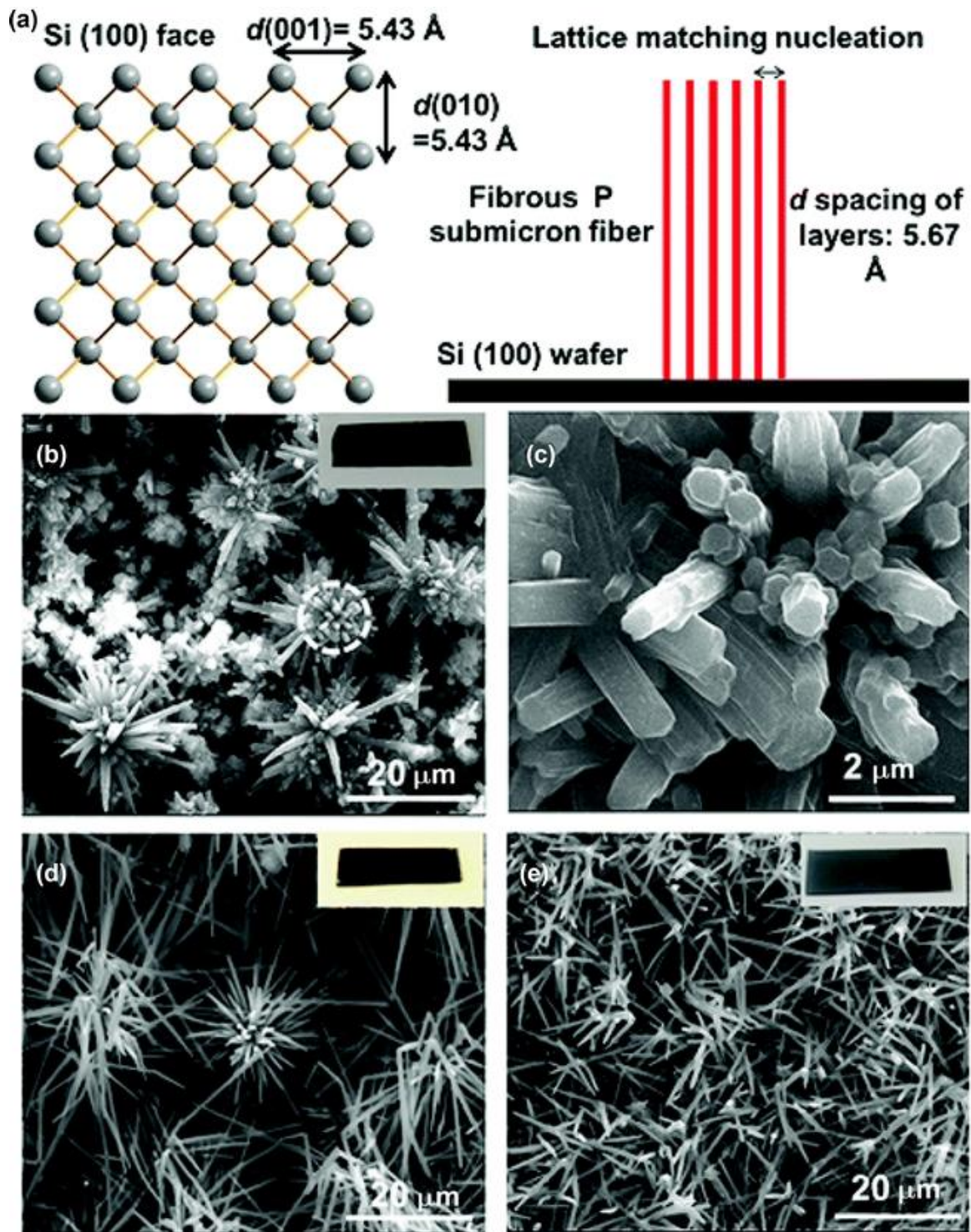


Figure 13.4 (a) Illustration of the lattice matching effect of fibrous phosphorus submicron fibers vs. p-Si (100) nanowires wafer. Red phosphorus submicron materials obtained on (b, c) p-Si (111) nanowire wafers, (d) n-Si (100) nanowire wafers and (e) bare p-Si (100) wafers at -0.06 MPa , 100 mg red phosphorus and $550 \text{ }^{\circ}\text{C}$. Image (c) shows the

highlighted zone in (b). “P”: phosphorus. Reproduced from ref. ⁴² with permission from The Royal Society of Chemistry.

It can be seen from the research and experimental reports of photocatalytic environmental treatment that photocatalytic nanomaterials have good degradation efficiency for organic compounds, the photocatalytic materials have good reuse rates, and the photocatalytic performance is not significantly reduced after repeated use, which proves once again that photocatalytic materials have the advantages of no secondary pollution and high degradation efficiency, and show great potential in water treatment.

13.4 Modulation of Crucial Surfaces and Interface Processes for Nano-photocatalysts

Surface and interface processes are crucial for the photocatalytic activity of photocatalysts. The process of regulating surfaces and interfaces mainly involves inhibition of the adverse recombination of photogenerated electrons and holes and enhancement of the adsorption and activation abilities of the surface for reaction species, so that more photogenerated electrons and holes reach the surface to efficiently participate in the redox reaction.

In the environment, the concentration of pollutants is relatively low. For example, the total bacterial colony in secondary effluents of a sewage plant is 3.1×10^3 CFU per mL. The resistant genes were detected at 10^4 copies per L ($< 1 \text{ ng L}^{-1}$). The TOC value of a printing and dyeing biochemical effluent is 90–110 mg L^{-1} . In heterogeneous photocatalytic degradation processes, the diffusion rate of pollutants is relatively low according to Fick's law. Moreover, as the degradation proceeds, the diffusion rate will decline with the decrease of concentration, and the number of pollutants arriving at the interface between the solution and photocatalyst per unit time will continue to decrease, resulting in the decrease of degradation rate according to the characteristics of pseudo first-order photocatalytic degradation kinetics. This has become an important factor restricting the photocatalytic degradation efficiency of pollutants. In addition, the adverse recombination of interfacial charge also restricts the photocatalytic performance.

In recent years, many efforts have focused on improving the hydrophilicity of catalysts, designing electrostatic adsorption layers and weak interaction adsorption layers, which can improve the diffusion process of pollutants, achieve the enrichment of pollutants at the solution and photocatalyst interface, effectively accelerating the reaction kinetics of pollutants at the interface between the solution and photocatalyst, and greatly improving the photocatalytic degradation efficiency. For example, commercial red phosphorus produces ROS under light excitation. However, due to its surface being a hard layer containing trace carbon, poor hydrophilicity and low wettability, it has almost no activity for the inactivation of *Escherichia coli* in water under visible light. Xia *et al.* developed a metal-free elemental photocatalyst through the purification of commercial red phosphorus via a hydrothermal method and applied it to inactivate *Escherichia coli* under visible light.⁴³ Through hydrothermal treatment of commercial red phosphorus, the hard layer on the surface was stripped and the surface was weakly oxidized. The hydrophilicity of the hydrothermally treated red phosphorus was greatly improved and high interfacial wettability was achieved. *Escherichia coli* was enriched at the water and photocatalyst interface. The photocatalytic activity for the bacterial inactivation of *Escherichia coli* using hydrothermally treated red phosphorus was 2–3 times higher than that reported at that time. The results showed $\cdot\text{O}_2^-$ derived from the combination of dissolved O_2 and photogenerated electrons played a major role in the photocatalytic bacterial inactivation of *Escherichia coli*. RhB is a dye wastewater simulant with positive charge. Zhang *et al.* prepared chlorine-doped hydrothermal carbonation carbon (Cl-HTCC) with negative charge for the degradation of RhB.⁴⁴ RhB was enriched at the solution and Cl-HTCC interface using electrostatic adsorption, and the adsorption isotherm was a Langmuir monolayer adsorption (maximum adsorption $Q_m = 62.8241 \text{ mg g}^{-1}$), higher than that of undoped hydrothermal carbonation carbon (HTCC, $Q_m = 1.4377 \text{ mg g}^{-1}$). The 2 wt% Cl-HTCC revealed the best photocatalytic activity and stability for the degradation of 10 ppm RhB, 4.53 times that of HTCC. It was also found that the strong adsorption and coating of RhB on the surface of Cl-HTCC hindered the conversion of dissolved O_2 and H_2O

into ROS by photogenerated electrons and holes, and the main active species was h^+ . In the HTCC system with weak adsorption, the main active species was $\cdot OH$. The concentration of antibiotic resistant genes (ARGs) in water was very low ($< 1 \text{ ng L}^{-1}$); however, it still had the ability to amplify and transfer. The degradation of ARGs is very important but difficult. Zhou *et al.* designed Ag–TiO₂–graphene oxide (GO) (STG) to degrade ARGs, which were rich in amino- and five-membered rings containing carbon.⁴⁵ The hydroxyl groups of GO could form hydrogen bonds with the amino groups in the ARGs, and the continuous six-membered ring structure of GO could form van der Waals force interactions with the five-membered rings containing carbon in ARGs. In the degradation process of secondary effluent containing resistant genes ($10^4 \text{ copies L}^{-1}$), due to the existence of the weak interaction layer of GO, the STG could efficiently enrich the ARGs at the interface, and the degradation efficiency was 99.95% in 60 min, the mineralization rate was more than 60%, and biological activity was lost. In the simulated ARGs solution excluding all background substances, 99% of ARGs could be degraded by STG in only 7 min. The degradation rate was about 50% in 7 min for the control samples without weak interaction adsorption layers, and the residual ARGs could still be amplified.

In addition, Zhu *et al.* synthesized amorphous SnO_x-modified BiOCl (Sn–BiOCl) through a solvothermal method. The introduction of Sn regulated the growth of BiOCl, which formed ultrathin nanosheets with surface oxygen vacancies.⁴⁶ Meanwhile, the interfacial internal electric field *via* charge redistribution between the BiOCl and SnO_x interface induced by the surface modification of SnO_x accelerated the photogenerated charge separation. The photocatalytic activities were enhanced by interfacial internal electric fields and surface oxygen vacancies synergistically. The photocatalytic degradation efficiency of Sn–BiOCl for phenol was 14 times higher than that of the pure BiOCl under full spectrum irradiation. $\cdot O_2^-$ was the main active species in the photocatalytic process of Sn–BiOCl both under ultraviolet (UV) light and visible light.

Li *et al.* synthesized polymeric carbon nitride (CN)–carbon quantum dot (CQD) nano frame heterojunctions *via* a facile bottom-up strategy.⁴⁷ The

CN–CQD nanoframes displayed two kinds of heterogeneous interfaces through building seamlessly stitched, two-dimensional in-plane domains. These two heterojunctions effectively enhanced the charge separation and transfer in different directions. In addition, the hollow double-decked porous CN–CQD nanoframe with a high specific surface area ($296.74 \text{ m}^2 \text{ g}^{-1}$) had more exposed active sites. The photocatalytic activity was evaluated using the degradation of TC and RhB. The degradation rate constant of the CN–CQD nanoframe was approximately 11 and 29 times higher than that of pristine CN. Due to the special coupled heterogeneous interface and hierarchical porous structure, the excitons easily dissociated and the charge was transferred to the active sites rapidly, which improved the intrinsic catalytic activity of CN.

Wang *et al.* designed a novel AgI–BiSbO₄ heterojunction using a hydrothermal–precipitation method. The heterojunction structure promoted the formation of hydroxyl and superoxide radicals and effectively degraded organic pollutants.⁴⁸ The photocatalytic efficiencies of the optimal sample for degradation of ARG and TC were 10 and 1.6 times higher than those of pure AgI, respectively. The results showed that a strong interfacial charge transfer existed between the interlayer in AgI and BiSbO₄ through the formation of Ag–O bonds, which allowed the O atoms to obtain rich free electrons from the Ag atoms of AgI, thus forming an ultrahigh electron transfer tunnel, and ultimately accelerating the separation of photoinduced electrons. In addition, a small amount of Ag⁰ NPs were formed during the photocatalytic process, which enhanced visible light absorption due to their surface plasmon resonance (SPR) effects and further promoted photogenerated carrier separation.

13.5 Emerging Single Atomic Photocatalytic Materials for Water Treatment

Photocatalytic reactions include three key steps: light collection, charge generation and separation and catalytic reaction. In this way, the total efficiency of the photocatalytic system depends on the thermodynamic and kinetic equilibrium of these three key reaction steps. Therefore, in the past few decades, a large number of research studies have been devoted to

exploring advanced photocatalysts with excellent light collection ability, high charge carrier separation efficiency and effective catalytic reactivity. However, so far, the conversion efficiency from solar energy to chemical energy and the selectivity of photocatalytic target products are not satisfactory. Therefore, it is important to find suitable photocatalyst materials to meet these standards.

Nowadays, single-atom photocatalyst has shown remarkable potential and has become the most active research direction in the field of photocatalysis due to their unique advantages in enhancing light capture, charge transfer kinetics and surface reactions of photocatalytic systems. At present, some research studies have provided a deeper understanding of monatomic photocatalysts, and advanced characterization technologies and important theoretical research is further deepening our understanding of these monatomic photocatalysts with excellent performance, so that we can accurately predict their working mechanisms and applications in photocatalysis.

Since Zhang *et al.* first put forward the term in 2011, single-atom catalysts (SAC) have become one of the most innovative and high energy research fields in the whole heterogeneous catalysis field.⁴⁹ SACs have attracted so much attention due to the following remarkable advantages over their nanoclusters, nanoparticles and bulk clusters: (I) high activity and selectivity due to unsaturated coordination sites and unique electronic structure; (II) greatly reduced use of catalytic metals due to maximum atom utilization; (III) single atoms as active sites mean the reaction mechanism is easy to determine, and (IV) providing suitable conditions to understand the relationship between atomic size and activity.

According to the definition of SACs, the valence of an isolated single atom on a support surface should be zero. However, this is not the case. These individual metal atoms are usually connected with atoms or ligands near the support surface. It should be noted that these metal ions can be reduced to metal atoms by photogenerated electrons in the photocatalytic reaction. They are stabilized through covalent coordination or ion interactions.

From the perspective of coordination chemistry, SACs act as bridges between homogeneous and heterogeneous catalysts when the support is a

rigid ligand. Therefore, we can expect that the interdisciplinary study of SACs from the perspectives of homogeneous catalysis, heterogeneous catalysis and coordination chemistry will make important contributions to the development of catalysis.

From the point of view of photocatalysis, the introduction of SACs can significantly affect the three key reaction steps according to the interaction between metal atom and support. Generally, the band structure and electronic structure of a single atom embedded in a light collection carrier can be modified to adjust its light absorption behavior and charge transfer kinetics. In addition, the surface structure of single-atom photocatalysts can be easily customized through different metal–support interactions to enhance the adsorption and activation ability of the photocatalyst towards reactants.

Therefore, the advantages of SACs provide an unprecedented opportunity to improve photocatalytic activity. For example, Wang *et al.* studied monoatomically dispersed Ag-supported ultrathin g-C₃N₄ (AgTCM–UCN) photocatalysts to enhance the visible light photocatalytic degradation of sulfamethazine (SMT) in the presence of persulfate (PMS)⁵⁰. AgTCM–UCN was synthesized using a simple copolymerization of dicyandiamide, silver trichloromethane (AgTCM) and NH₄Cl. Under UV, visible and simulated sunlight irradiation, AgTCM–UCN–PMS showed better photocatalytic degradation efficiency for SMT than AgTCM–UCN, UCN–PMS and g-C₃N₄–PMS. The enhanced photocatalytic activity may be due to the synergistic effect from the SPR of Ag, high surface area of UCN and efficient charge separation of PMS. Electron spin resonance (ESR) and RS capture experiments show that SO₄^{•−} is produced after adding PMS, while O₂^{•−} and h⁺ are the main causes of SMT degradation. Based on mass spectrometry analysis and theoretical calculations, three degradation pathways of SMT were deduced, including the decomposition of sulfonamide bonds, the removal of SO₂ and the oxidation of aniline. The photocatalytic mechanism is shown in Figure 13.5: under visible light irradiation, light with wavelengths of less than 499 nm is absorbed by UCN resulting in photoinduced electrons (e[−]) and holes (h⁺). Due to the SPR effect of Ag, it can capture photons with wavelength greater than 499 nm,

thus promoting the formation of electron–hole pairs. Photoinduced electrons may migrate down from UCN to Ag through the Schottky barrier, thus inhibiting the electron–hole recombination rate. In the presence of PMS, the photoinduced Ag resident electrons are trapped by PMS to produce $\text{SO}_4^{\cdot -}$, which effectively improves the efficiency of photogenerated electron–hole separation. In addition, photogenerated electrons may also be trapped by O_2 , leading to the formation of $\text{O}_2^{\cdot -}$. Because the value of the valence band is 1.69 eV, which is lower than the redox potential of $\cdot\text{OH}/\text{OH}^-$ (+ 1.99 eV), $\cdot\text{OH}$ is generated from $\text{O}_2^{\cdot -}$ and $\text{SO}_4^{\cdot -}$ instead of H^+ and OH^- . Due to the high specific surface area of UCN and the π – π interactions between UCN and SMT, SMT is easily adsorbed on the surface of UCN. Subsequently, active substances, including $\text{O}_2^{\cdot -}$, H^+ , $\cdot\text{OH}$ and $\text{SO}_4^{\cdot -}$ may attack SMT molecules, leading to their decomposition and eventually mineralization into CO_2 and H_2O .

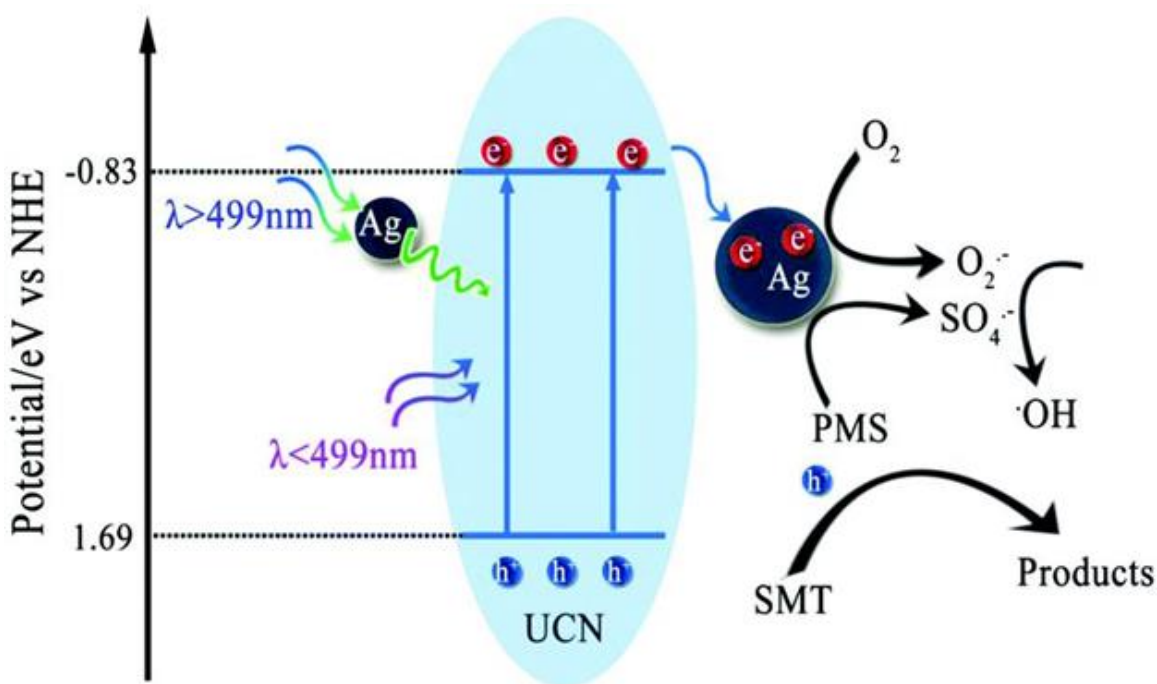
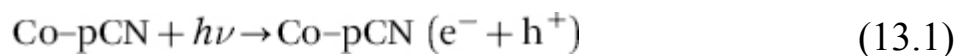


Figure 13.5 Schematic illustration of the photocatalytic mechanism of AgTCM–UCN–PMS under broad-spectrum light. Reproduced from ref. ⁵⁰ with permission from the Royal Society of Chemistry.

Yang *et al.* studied single-atom cobalt grown *in situ* on polymerized carbon nitride (PCN) with bidentate ligands for the photocatalytic degradation of oxytetracycline (OTC)⁵¹. The results showed that single atom cobalt was successfully anchored on PCN, and the interaction between single-atom cobalt and PCN was strengthened by the formation of Co–O bonds and Co–N bonds. The single-atom cobalt catalyst effectively broadened light absorption, increased electron density, promoted charge separation and transfer, and promoted OTC degradation. As the best sample, Co (1.28%)–PCN showed a significant OTC degradation rate constant (0.038 min^{−1}) under visible light irradiation, which was about 3.7 times that of PCN. ESR tests and RS capture experiments showed that ¹O₂, h⁺, [•]O₂[−] and [•]OH played important roles in OTC degradation. Under visible light irradiation (λ > 420 nm), Co–PCN are excited to generate electrons (e[−]) and holes (h⁺) (eqn (13.1)). The CB (− 0.65 vs. NHE) of Co (1.28%)–PCN is lower than the O₂/[•]O₂[−] redox potential (− 0.33 vs. NHE), and the photogenerated electrons of CB are captured by molecular oxygen to form [•]O₂[−] (eqn (13.2)). In addition, the [•]O₂[−] reacts with h⁺ to form ¹O₂ (eqn (13.3)), and reacts with e[−] and h⁺ to form [•]OH (eqn (13.4) and (13.5)). The resulting active species (¹O₂, h⁺, [•]O₂[−] and [•]OH) react with OTC molecules to degrade them (eqn (13.6)).



Ling *et al.* studied the photocatalytic ozonation assisted by highly dispersed Ag–g-C₃N₄ hybrids for rapid the mineralization of

acetaminophen (ACE).⁵² The Ag-g-C₃N₄ hybrid with high dispersion was prepared using a simple calcination method. The results showed that silver exists in the form of metallic silver and is highly dispersed in the matrix of the g-C₃N₄ nanosheets. The apparent mineralization rate constant of solar light-4% Ag-g-C₃N₄-O₃ in 120 min was almost twice that of solar light-g-C₃N₄-O₃. In this system, Ag is not only a good photogenerated electron acceptor for photocatalysis, but also a beneficial decomposition center for O₃. In the solar light-4% Ag-g-C₃N₄-O₃ system, both holes and hydroxyl radicals contributed to the mineralization of ACE. It had a good synergistic effect in the mineralization of ACE, with a synergistic index of 5.3. In addition, the effects of different pH values and silver content on ACE mineralization were studied, and the degradation pathway of ACE in the 4% Ag-g-C₃N₄ photocatalytic ozonation system was proposed. The mechanism of photocatalytic ozonation of 4% Ag-g-C₃N₄ is shown in Figure 13.6, under sunlight, 4% Ag-g-C₃N₄ is excited to generate photogenerated electrons and holes ($\text{g-C}_3\text{N}_4 + h\nu \rightarrow \text{e}^- + \text{h}^+$). As an effective decomposition site of O₃, electrons are transferred to monatomic silver atoms to react with O₃ ($\text{e}^- + \text{O}_2 \rightarrow \cdot\text{O}_3^-$). O₃ undergoes a series of reactions to produce a large amount of $\cdot\text{OH}$ ($\text{H}^+ \rightarrow \text{HO}_3\cdot$, $\text{HO}_3\cdot \rightarrow \text{O}_2 + \cdot\text{OH}$); meanwhile, the consumption of photogenerated electrons leads to more photogenerated holes on g-C₃N₄, which can also oxidize ACE. Finally, the generated $\cdot\text{OH}$ and h^+ contribute to the degradation of ACE.

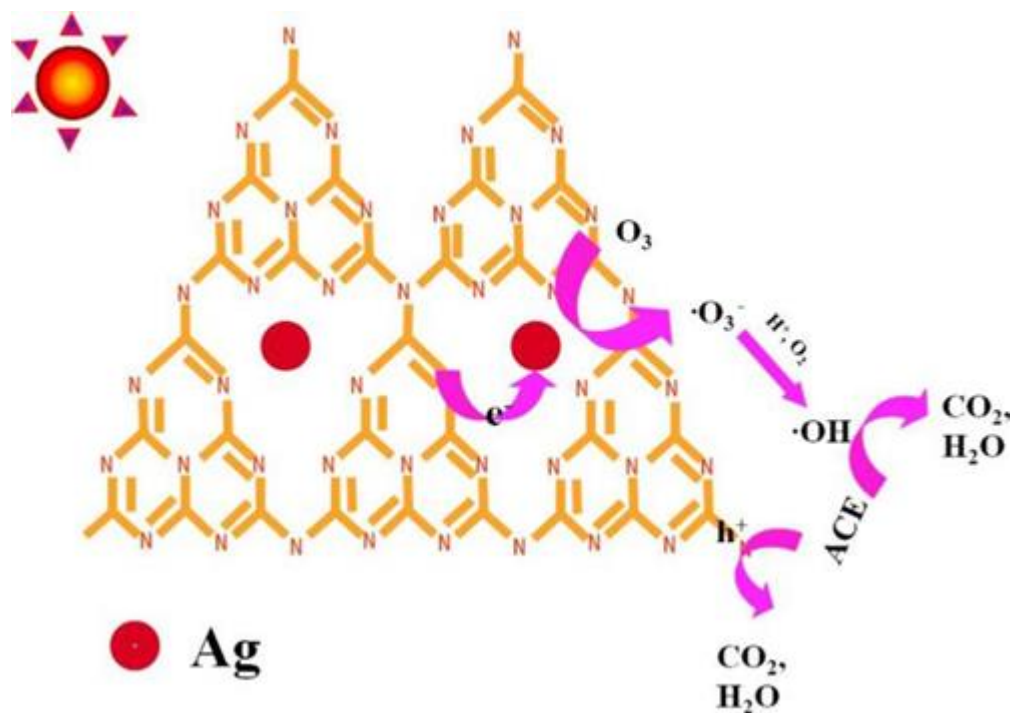


Figure 13.6 Mechanism of ACE photocatalytic ozonation using 4% Ag-g-C₃N₄. Reproduced from ref. ⁵² with permission from Elsevier, Copyright 2019.

Wang *et al.* studied ultrathin g-C₃N₄ containing atomically co-dispersed silver and carbon quantum dot (SDAG-CQDs-UCN) ternary photocatalysts for the degradation of naproxen (NPX)⁵³. SDAG-CQDs-UCN was prepared using a simple thermal polymerization. It exhibited a highly enhanced light response and broad-spectrum (UV, visible and near-infrared) photocatalytic activity. The results showed that the reaction rate of 1.0 wt% CQDs and 3.0 wt% Ag was ten times higher than that of UCN under visible light irradiation. The improvement of the broad-spectrum photocatalytic performance may be related to the surface plasmonic resonance effect of Ag, the up-conversion fluorescence properties of CQDs, the band gap narrowing, and the electron separation and transfer ability of Ag and CQDs. ESR technique and RS capture experiments indicated that ¹O₂ and O₂^{·-} were the main active species for NPX degradation. The product identification and reaction site predictions indicated that the photocatalytic degradation of NPX included decarboxylation, hydroxylation and naphthalene ring cracking. Mineralization experiments showed that NPX

and its degradation products were eventually converted to CO_2 and H_2O . SDAG–CQDs–UCN reacts well in different water substrates and can be effectively used for the degradation of NPX in ambient water. The photocatalytic mechanism of SDAG–CQDs–UCN under broad-spectrum light irradiation is shown in Figure 13.7: Under sunlight irradiation, photogenerated electron–hole pairs are generated on the surface of UCN *via* the absorption of UV and visible light at wavelengths of less than 473 nm. Due to the effect of Ag and CQDs, the accumulation of electrons is promoted, and the Fermi energy level of UCN decreases significantly, so that the light absorption of UCN increases from 473 nm to 504 nm. In addition, the SPR effect of Ag further improves the light capture ability at wavelengths greater than 500 nm. Meanwhile, due to the up-conversion photoluminescence properties of CQDs, long wavelengths of larger than 550 nm can be up-converted to shorter wavelengths, which are subsequently absorbed by UCN. Because Ag and CQDs have good charge transfer characteristics, the photogenerated electrons in CB are captured, thus separating electrons and holes effectively. As the work function of Ag (4.2 eV) is lower than that of CQDs (4.7 eV), the light energy from electrons in UCN tend to be transferred first to Ag and then to terminal reservoir CQDs. The electrons on the CQDs then combine with oxygen molecules to form O_2^- , which reacts with h^+ to form $^1\text{O}_2$. In addition, O_2^- reacts with h^+ to form $\cdot\text{OH}$, this is the reason for the low content of $\cdot\text{OH}$. Because the VB position of SDAG–CQDs–UCN is more negative than the standard redox potential of $\text{OH}^-/\cdot\text{OH}$, h^+ cannot oxidize OH^- and H_2O to form $\cdot\text{OH}$; and due to the large surface area of SDAG–CQDs–UCN and π – π interactions between NPX and SDAG–CQDs–UCN, NPX is easily adsorbed by SDAG–CQDs–UCN. Finally, NPX is attacked by RS (O_2^- , h^+ , $^1\text{O}_2$, $\cdot\text{OH}$), and then decomposes and mineralizes.

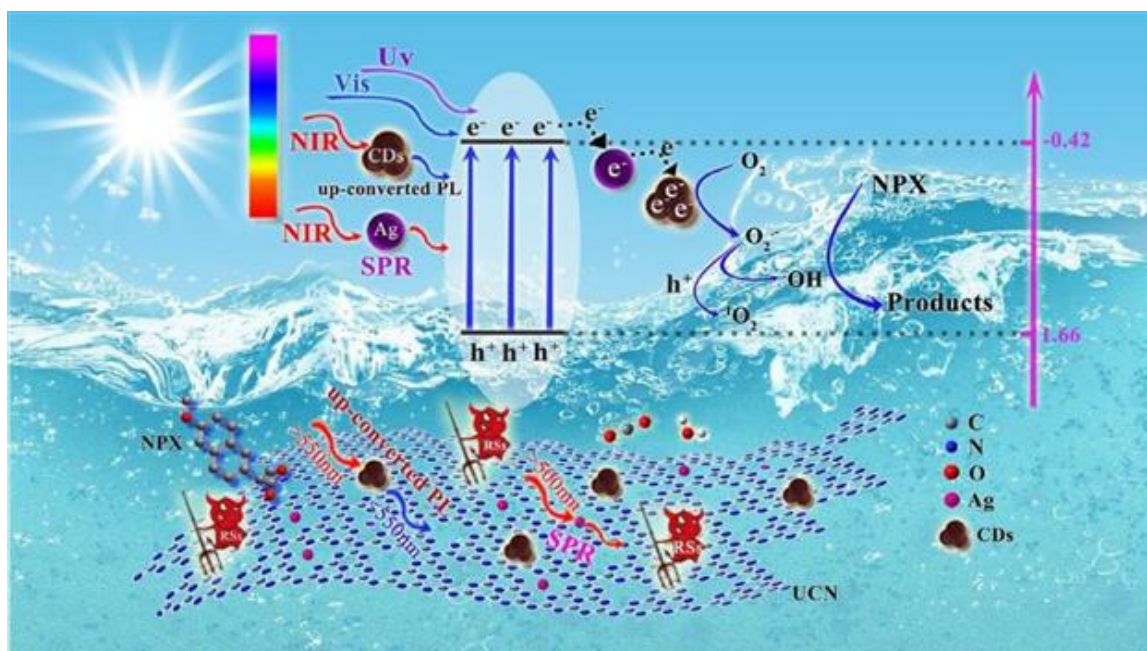
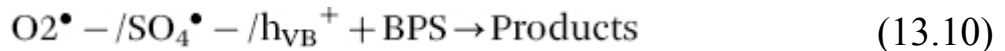
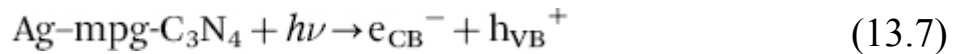


Figure 13.7 Photocatalytic mechanism of SDAG CQDs–UCN under broad-spectrum light irradiation. Reproduced from ref. ⁵³ with permission from Elsevier, Copyright 2017.

Wang *et al.* studied monatomically dispersed Ag mesoporous g-C₃N₄ hybrids for the catalytic degradation of bisphenol A (BPA) in the presence of peroxymonosulfate (PMS) under visible light.⁵⁴ Atomically dispersed Ag-modified mesoporous graphitized carbon (Ag–mpg-C₃N₄) hybrids were prepared using a co-polycondensation method. In the presence of PMS, Ag–mpg-C₃N₄ showed excellent BPA degradation performance. Under visible light irradiation ($\lambda > 400$ nm), 100% BPA was degraded within 60 min and the TOC removal rate was 80% when the concentration of catalyst and PMS was 0.1 g L⁻¹ and 1 mM, respectively. The synergistic effect of single-atom Ag and mpg-C₃N₄ may be the reason for the performance improvement. On the one hand, introducing Ag can capture more visible light; on the other hand, the existence of PMS improves the separation efficiency of photogenerated electron–hole pairs. ESR and radical capture experiments showed that the main ROS were SO₄⁻, O₂⁻ and h⁺, while the role of ·OH was not obvious in this process. The visible light capture ability of Ag–mpg-C₃N₄–PMS was improved by the introduction of

single-atom Ag, which was due to the SPR absorption of single-atom Ag. Therefore, under visible light irradiation, there is more photoelectron generation (e_{CB}^-) and hole generation (h_{VB}^+) in Ag-mpg-C₃N₄ (eqn (13.7)). The SPR effect of single-atom Ag can increase the local electric field, thus speeding up the generation rate of e_{CB}^- and h_{VB}^+ . The Schottky barrier is generated by the matched energy levels of Ag and g-C₃N₄, which minimizes the recombination of e_{CB}^- and h_{VB}^+ . In the presence of PMS, e_{CB}^- can be captured by PMS to produce $SO_4^{\bullet-}$ (eqn (13.8)), which promotes the separation of electrons from holes. In addition, e_{CB}^- reacts with O₂ to generate $O_2^{\bullet-}$ (eqn (13.9)) and $O_2^{\bullet-}$ and h^+ oxidize BPA. The potential of the conduction band edge (V_{CB}) of Ag-mpg-C₃N₄ is lower than the redox potential of OH⁻/[•]OH, and h^+ cannot oxidize OH⁻ to form [•]OH. In addition, the pH rapidly drops to about 3 with the addition and generation of PMS, so that the reaction between $SO_4^{\bullet-}$ and OH⁻ to produce [•]OH is inhibited. In conclusion, $O_2^{\bullet-}$, $SO_4^{\bullet-}$ and h_{VB}^+ are the main oxidizing species, while [•]OH has no significant degradation effect on BPA (eqn (13.10)).



Xu *et al.* studied the implantation of single-atom Pt into nano porous TiO₂ membranes for the degradation of *o*-ethoxy benzoic acid amide.⁵⁵ The experimental results show that the single-atom Pt photocatalyst has remarkable performance and good stability for the degradation of *o*-methoxybenzamide using vacuum ultraviolet (VUV) and UV photocatalysis. Under VUV radiation, the initial concentration was 500 ppb and 100 ppb, and the residence time was 0.5 min. The removal rate of *o*-methoxybenzamide reaches 94.52% and 100%, respectively. The

photocatalytic degradation rate was 2.19 and 3.98 times that of the nano porous TiO₂ films, respectively, and the energy consumption was only 0.46 kW h m⁻³, which was about 28% of that of the original nano porous TiO₂ films. Under UV irradiation, the degradation efficiency of *o*-methoxybenzamide was 84.44% when the initial concentration was 500 ppb and the residence time was 24 min. The nanopore on the surface of the TiO₂ film accelerated the eddy current diffusion and the Pt single atom promoted the molecular diffusion of trace pollutants, effectively overcoming the low concentration mass transfer resistance. The photocatalytic mechanism is shown in [Figure 13.8](#): in the prepared 0.1 Pt nano porous TiO₂ film, the implantation of Pt single atoms significantly increased the number of surface-active sites. On the one hand, each Pt atom implanted on the surface of the catalyst can be used as an electron capture center, which effectively proves the separation efficiency of photogenerated carriers and prolongs the life of the surface holes in the photocatalytic reaction process. The photogenerated holes tend to migrate towards the {001} plane with a low positive potential, while the photogenerated electrons tend to migrate towards the {101} plane with a high positive potential. As the electron capture center on the {001} plane, Pt single atoms are conducive to the conversion of hydroxyl on the surface to $\cdot\text{OH}$ by hole oxidation, which greatly promotes the photocatalytic degradation of *o*-ethoxy benzoic acid amide. On the other hand, the photogenerated electrons that migrate to the {101} plane are eventually captured by the Pt single atom in the {101} plane, and then the electrons on the Pt single atom combine with oxygen molecules to form O₂⁻, O₂⁻ further reacts with h⁺ to form $\cdot\text{OH}$. Therefore, the implantation of Pt single atoms can effectively reduce the concentration of pollutants on the surface, increase the concentration difference between the catalyst surface and the solution, and significantly promote the molecular diffusion of trace organic pollutants. Combined with the accelerated vortex diffusion of nanopores on the surface of the TiO₂ film, the mass transfer resistance at low concentration was effectively overcome. Finally, low concentrations of *o*-methoxybenzamide were effectively photocatalytically degraded through porous TiO₂ membranes implanted with single-atom Pt.

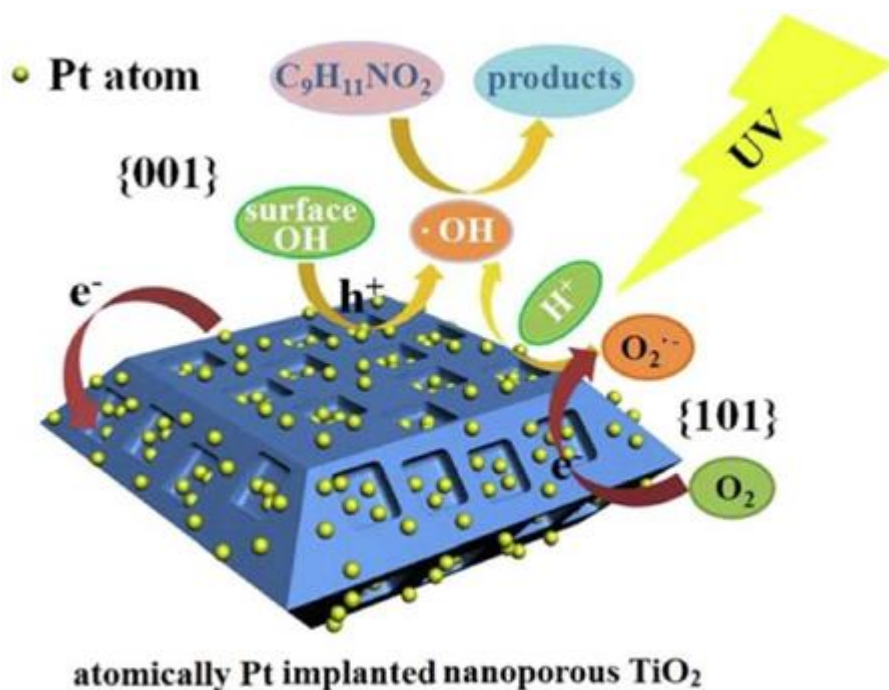


Figure 13.8 Photocatalytic mechanism of nano-porous TiO₂ films implanted with single-atom Pt with {001} exposed surfaces under UV irradiation. Reproduced from ref. ⁵⁵ with permission from Elsevier, Copyright 2019.

Zhao *et al.* studied single-atom silver-induced amorphous hollow tubular g-C₃N₄ for the visible light-driven photocatalytic degradation of NPX.⁵⁶ By forming tubular supramolecular layers, the silver ions are isolated by the nitrogen atoms in the melamine and nitrate anions, hindering agglomeration during thermal polymerization. The high density of atomically-dispersed silver (up to 11.6% atomic ratio) selectively breaks the hydrogen bonds in the layered g-C₃N₄, resulting in a completely amorphous structure. The Ag-induced total amorphism not only enhanced the visible light absorption of g-C₃N₄, but also accelerated the charge transfer, so that the photocatalyst prepared with the best Ag content was 52 times more active than pure g-C₃N₄ at removing NPX. Density functional theory (DFT) calculations and spatial effects were used to explain the degradation pathway of NPX. The toxicity of NPX can be reduced by adequate irradiation. Through studying the degradation mechanism of NPX, it was found that O₂^{·-} and holes played a leading role in the degradation process.

Li *et al.* constructed an active center of CuS₄ atomic clusters on the surface of ZnIn₂S₄.⁵⁷ Compared with the unmodified ZnIn₂S₄ and CuS_{3.6} clusters, CuS₄ had the best energy for O₂ adsorption and electron transfer processes in water, so the generation efficiency of ROS was the highest. The O₂ activation on CuS₄ clusters was dominated by single electron transfer to form $\cdot\text{O}_2^-$ (> 90%), and a small amount was converted to $\cdot\text{OH}$ *via* the H₂O₂ pathway. In the liquid-phase photocatalytic reaction, the degradation rate constant of 20 ppm TC catalyzed using CuS₄-ZnIn₂S₄ (CuS₄-ZIS) was twice and six times as much as that catalyzed using the unmodified ZnIn₂S₄ and CuS_{3.6} clusters, and the mineralization rate reached 77.8%. The photocatalytic degradation mechanism of CuS₄-ZnS for TC is shown in [Figure 13.9](#): The electrons in the VB of CuS₄-ZnIn₂S₄ are excited to CB to produce photogenerated electrons under illumination, forming photogenerated holes in the original position of the electrons. Afterward, photogenerated electrons reacted with O₂ to form $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ was generated according to the pathway: $\text{O}_2 \rightarrow \cdot\text{O}_2^- \rightarrow \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH}$. Ultimately, TC can be degraded by $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and h^+ to CO₂ and H₂O.



Figure 13.9 Proposed photocatalytic degradation mechanisms of TC in the presence of CuS₄-ZIS clusters. Reproduced from ref. ⁵⁷ with permission from Elsevier B.V. Copyright 2020.

So far, great strides have been made in the field of single-atom catalysts, but their development in the field of photocatalysis is still in its infancy. Therefore, this emerging field of research requires the special attention of the multidisciplinary research community in order to further advance its basic understanding and application to achieve effective degradation under solar energy.

13.6 Industrial Application Cases of Photocatalytic Water Treatment

Photocatalysis technology is widely used in wastewater treatment due to the advantages of mild reaction conditions and easy operation. Photocatalysis is the conversion of light energy existing in nature to generate photogenerated

electrons and holes with extremely strong redox abilities and their transfer to the surface of semiconductor photocatalysts where direct or indirect driven oxidation–reduction reactions to achieve complete pollutant elimination in water. Remarkable achievements have been made in the textile, dye, coking, and pharmaceutical industries as well as in other fields.

13.6.1 Photocatalytic Wastewater Treatment Devices

Many researchers have carried out numerous works on improving existing photocatalytic reaction devices and studying new photocatalytic reaction devices, which better solve the practical issues of water pollution. Zhou *et al.* designed and invented a photocatalytic wastewater degradation device that can realize the efficient treatment of wastewater.⁵⁸ Multiple tower plates were arranged between the water inlet and the water outlet and filled with porous ceramic spheres loaded with modified nano-TiO₂ films, with the application of a UV light source. In addition, the light reflective coating applied to it improved the utilization rate of light, and the modified nano-TiO₂ film with strong photocatalytic ability loaded on porous ceramic spheres not only increased the surface area, but also increased the contact area between the photocatalyst and improved the photocatalytic degradation of organic wastewater. The wastewater treatment units could be flexibly connected in series or parallel according to different wastewater treatment volumes, thereby improving wastewater treatment efficiency. Later, Zhou *et al.* made a complete improvement of this device based on this idea.⁵⁹ The new device used three-dimensional printing rapid prototyping technology to quickly print composite materials with catalytic properties into a new structure of photocatalytic degradation devices (Figure 13.10). The photocatalyst was creatively mixed with the raw materials of the preparation reaction device, with the cooperation of a UV lamp to achieve excellent catalytic effects, which not only killed the micro-organisms in the water, but also decreased the organic matter and heavy metal ions in the water redox reaction, and realized sterilization and purification effects on the water. In addition, the device had a simple structure and unit assembly structure, and could be assembled according to the technical requirements of water treatment and was easy to disassemble and maintain.

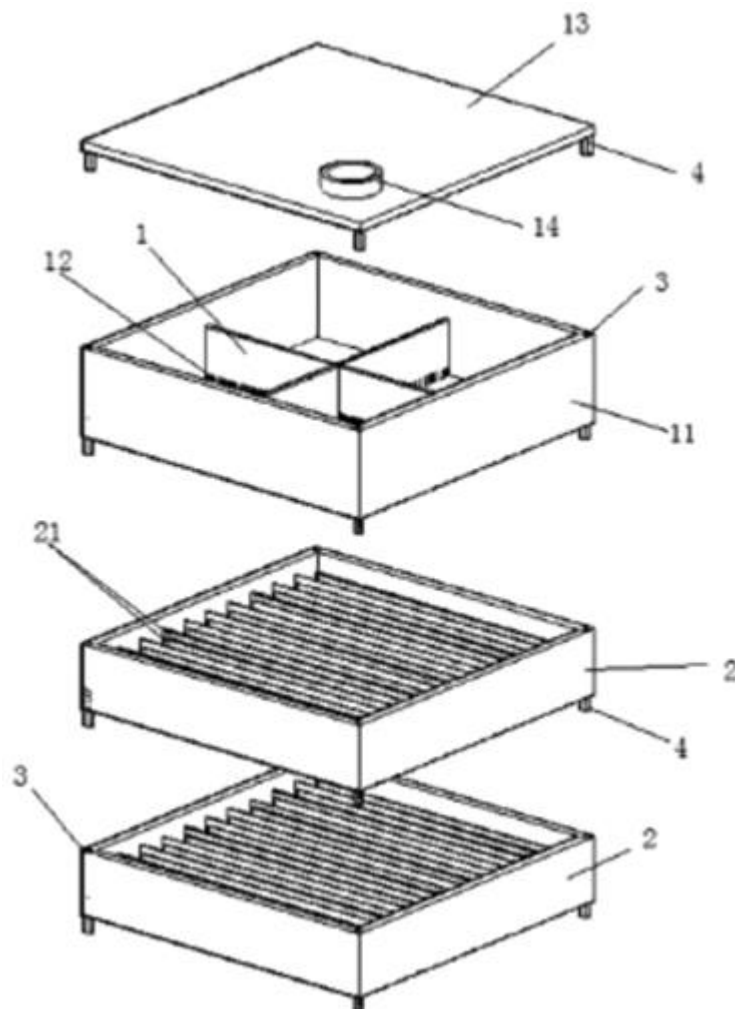


Figure 13.10 Photocatalytic degradation device for wastewater treatment. (1: filter plate, 2: box, 3: groove, 4: pin, 11: square box, 12: filter hole, 13: seal cover, 14: water inlet, 21: baffle.)⁵⁹

In the early 2010s, Bian *et al.* also invented a plate-type photocatalytic reaction device that could be modularized and assembled⁶⁰. This device used solar photovoltaic power generation, electric water lifting circulation, an increased oxygen and natural light and solar energy synergistic environmentally-friendly treatment technology without electrical charge and had the practical characteristics of simple structure, convenient assembly, energy saving and high efficiency. A pneumatic lifting liquid was used as the cyclic power, which not only saved energy, but also agitated the liquid, accelerated renewal of the media-contacted reaction surface,

increased the number of oxygen molecules involved in the reaction and improved oxidative degradation effects. The folded mesh constructed using the catalyst carrier made it easier for the catalyst to adhere to the mesh substrate and the photocatalytic reaction interface was larger and more uniform. The device was not only suitable for industrial and agricultural water treatment, but also suitable for wastewater purification in environmental protection, aquatic products and green landscape waters. In addition, Wei *et al.* invented a photocatalytic wastewater degradation reaction device equipped with a photothermal catalytic device and a photovoltaic photothermal component.⁶¹ It used different wavelengths of sunlight to partially excite the photocatalyst, excite the crystalline silicon solar panel, and increase the system temperature. Through synergistic photothermal and electrocatalytic effects, the efficiency of the photocatalytic reaction was greatly improved. In addition, this device had a simple structure and was low cost, suitable for solar light sources, and was size-adjustable according to need. In practical applications, the reactor could be used as a basic unit, which can be combined in series and parallel to form an array that can be applied to different wastewater treatment requirements.

Lv *et al.* designed and invented a wastewater treatment device and method using synergistic photocatalysis–microbial degradation technology.⁶² The photocatalytic fiber fabric in the device floats on the surface of the water body, using sunlight as the driving force that greatly reduced energy consumption; using the affinity of the photocatalytic fiber material and organic pollutants, the organic pollutants are efficiently catalyzed and degraded and the suspended filler adsorbs and degrades organic pollutants in the water. The organic content in the wastewater was significantly reduced, which not only improved the cleanliness and reduced the COD and BOD5 of the wastewater, but also greatly reduced the total content of nitrogen and phosphorus. Yao *et al.* invented a wastewater treatment system using photocatalytic degradation membrane separation.⁶³ The photocatalyst supported on ceramic membrane tubes had good catalytic performance (Figure 13.11), it can effectively promote the generation of hydroxyl radicals, and had the advantages of non-selectivity, fast reaction rate and complete degradation of high concentrations of refractory organic

wastewater. In addition, the degradation of pollutants *via* photocatalytic reactions reduced the pollution index of the wastewater and improved the anti-pollution and service life of the ceramic membrane.

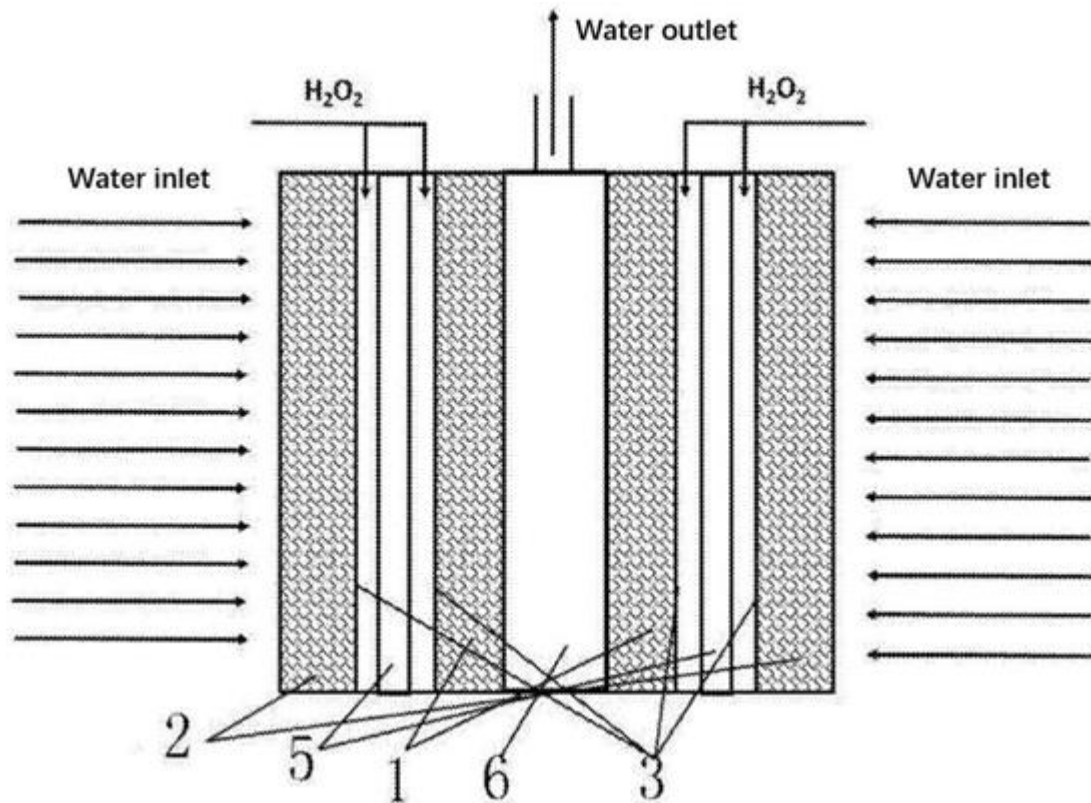


Figure 13.11 Wastewater treatment device using synergistic photocatalysis–microbial degradation technology. (1: Double-layer tubular ceramic membrane inner membrane, 2: double-layer tubular ceramic outer membrane, 3: photocatalyst layer, 5: UV lamp, 6: outlet pipe.)⁶²

Xu *et al.* invented an all-weather visible light photocatalytic wastewater degradation device.⁶⁴ In this device, a supported TiO_2 catalyst with good response to visible light was synthesized. At the same time, it was pumped into a transparent spiral coil to degrade the wastewater. Through sunlight or xenon light irradiation, the continuous and all-weather efficient degradation of organic pollutants in wastewater, especially PPCPs (pharmaceuticals and personal care products), was realized (Figure 13.12). In addition, the device could be used alone or in series, greatly improving the degradation capacity. *Via* the solution pump and the use of the loaded materials such as

attapulgite, diatomite and other materials with smaller density and larger specific surface area, the recovery and reuse of the catalyst was realized to avoid secondary pollution and save energy. The device covers a small area and has a long hydraulic retention time, so it was suitable for laboratory research and aquaculture wastewater treatment.

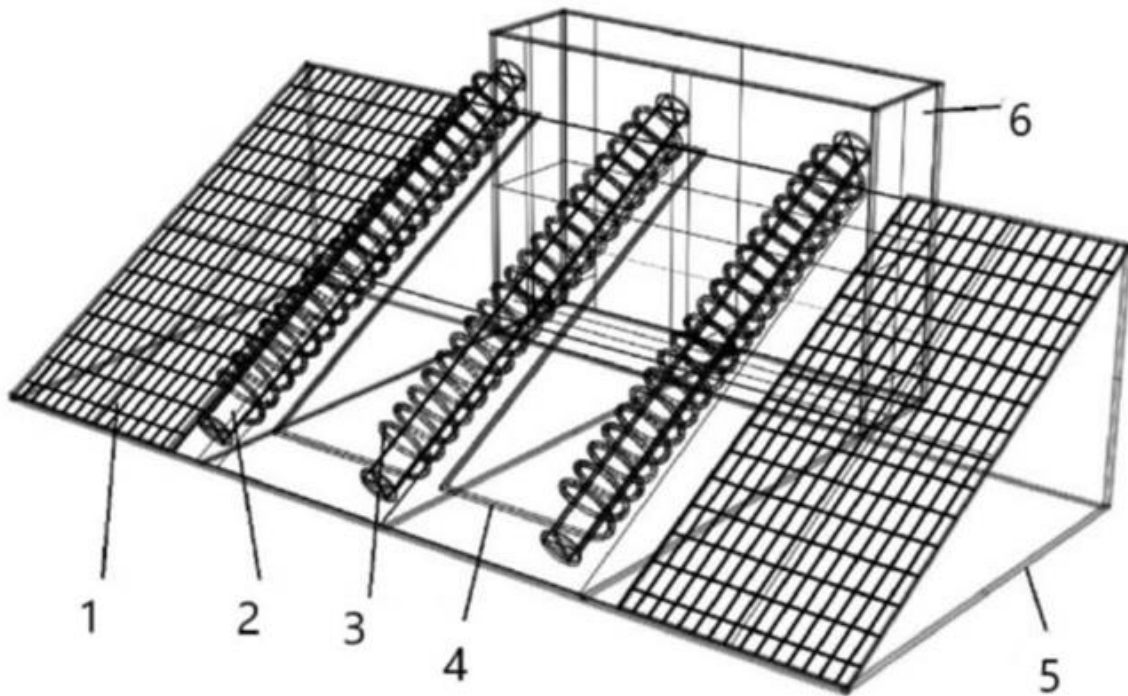


Figure 13.12 All-weather visible light photocatalytic wastewater degradation device. (1: solar panel, 2: xenon light source, 3: coil tube, 4: PVC straight tube, 5: bracket, 6: water storage tank.)⁶⁴

Wang *et al.* designed a restaurant wastewater treatment device.⁶⁵ The catering wastewater treatment device was easily moved, realized on-site treatment and adopted photocatalytic oxidation technology to efficiently and quickly remove COD (chemical oxygen demand) in wastewater (Figure 13.13). Through the combination of modules, it could not only treat catering wastewater discharged from various hotels, restaurants, canteens, *etc.*, but was also applied to independent micro-catering service systems. The catering wastewater was transported to the slag–liquid separation tank in the catering wastewater treatment device through the inlet pipe and the

residues in the catering wastewater were filtered according to particle size and removed step-by-step using the filter screen of the slag–liquid separation tank to obtain residue-free wastewater. The residue-free wastewater was pressurized and transported to an oil–water separator using the water pump on water delivery pipe 1 and the upper oil and the lower water were obtained by layered separation. The upper oil was pumped using the oil pump external to the negative pressure de-oiling pipe; and the lower water was transported to water pipe 2. The photocatalytic reaction was carried out in the photocatalytic reactor to remove COD of the wastewater and obtain purified water. The processing system achieved the technical effects of a high degree of automation, simple operation, small footprint and low operating costs.

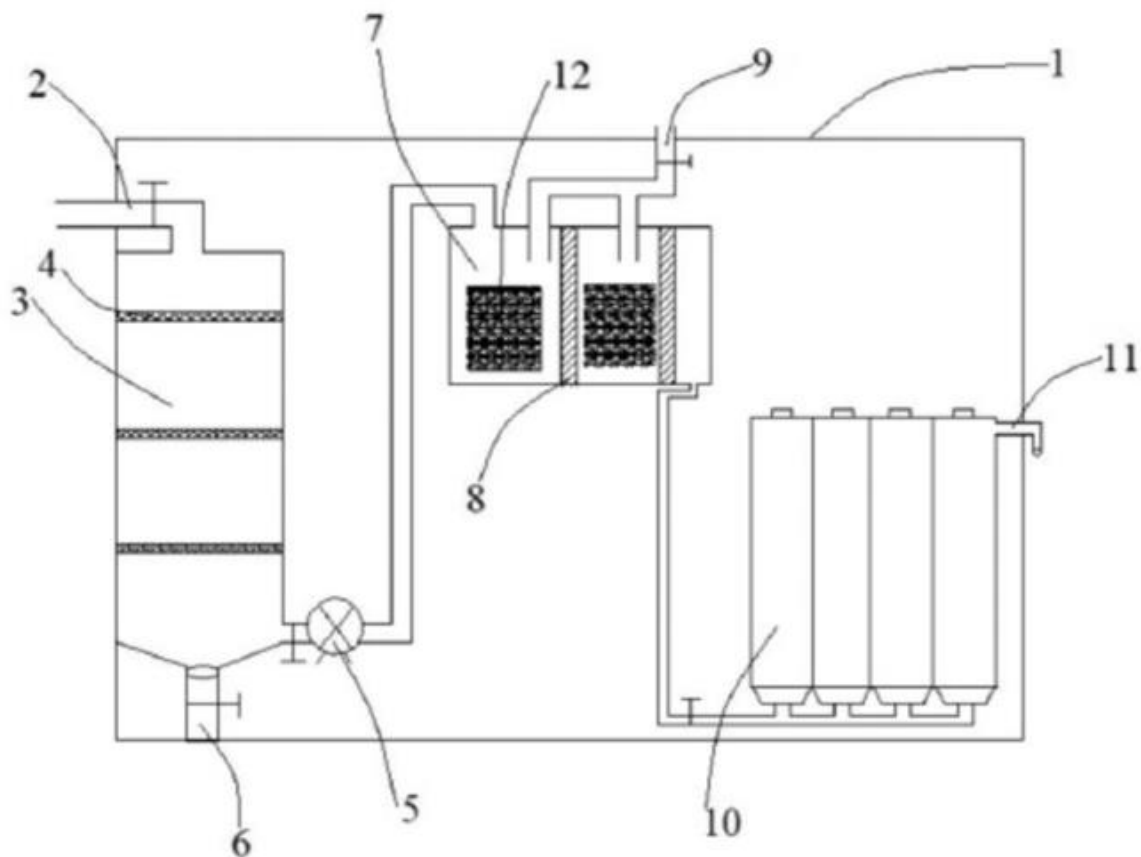


Figure 13.13 Restaurant wastewater treatment device. (1: Shell, 2: inlet pipe, 3: slag–liquid separation tank, 4: filter screen box, 5: water pump, 6: residue pipe, 7: oil–water

separator, 8: polymer unidirectional membrane, 9: negative pressure oil removal pipe, 10: photocatalytic reactor, 11: drain pipe, 12: fixed frame.)⁶⁵

An *et al.* invented a method and equipment for the synergistic purification of industrial resources and deep oxidation.⁶⁶ This device used a gas collecting hood to collect industrial VOCs (volatile organic compounds), and realized the rapid capture and enrichment of VOCs through the adsorption unit in the resource recovery device; it then used hot air to blow off the VOC-containing adsorbent and recovered it through the condensation unit in the resource recovery device; then, the remaining VOCs entered the photocatalytic reaction device and were decomposed or mineralized under the action of the photocatalyst, which completed the purification of industrial VOCs. This device effectively ensured the treatment effects and long-term stability for the complete removal of VOCs; the average removal efficiency of the equipment used to treat the VOCs was more than 95%. At the same time, the equipment realizes the recycling and reuse of high value-added products such as VOCs while achieving the purification and emission of VOCs.

13.7 Conclusion and Outlook

Since the discovery of the photocatalytic effect in 1972, there has been great progress in photocatalytic water treatment. However, as a technology with an age of more than 50 years, the industrial application of photocatalytic remediation is far from satisfactory nowadays. Even worse, its efficiency and engineering cost has been widely criticized. However, with the world now facing a serious energy crisis, modern water treatment plants based on fossil fuels have also come across great challenges. Therefore, it is still quite valuable to further study photocatalytic water treatment methods that can directly use solar energy. Several opinions that might be beneficial for its development in the future are listed as follows:

- 1) It is necessary to contentiously develop new photocatalytic materials with a wide response range to the solar light spectrum, good conductivity and reaction stability. In particular, they should not release harmful species during the remediation process.

2) Further study of single-atomic photocatalysts offers significant potential. Although the characterization of single sites is still difficult and expensive, the fabrication of single-atomic photocatalysts is relatively simple. Moreover, sometimes, its cost is even lower than those of their nanosized counterparts, due to the lower quantities required. Some useful issues to consider include: the fabrication method of high loading single-atomic sites, the development of binary and even polynary single-atomic sites (*e.g.* three kinds or more metal single sites) and more examples of cost-effective single metal sites, *e.g.* transition metals.

3) Industrial trials of photocatalytic nanomaterials should be expanded. Small-sized devices and related technologies for specific pollutants are greatly encouraged.

4) It is valuable to consider the results of other disciplines *e.g.* physics or materials chemistry for the development of photocatalytic water treatment, in order to further promote its efficiency and reduce its cost. For example, the photo-thermal effect could greatly accelerate the reaction dynamics. The application of novel optical focusing technologies might allow solar light to take the place of UV light in future.

Abbreviations

ROS	reactive oxygen species
CB	conduction band
VB	valence band
RS	reactive species
MOF	metal–organic framework
COF	covalent organic framework
RhB	Rhodamine B
RP	red phosphorus
ARGs	antibiotic resistant genes
TC	tetracycline
SPR	surface plasmon resonance
SAC	single-atom catalyst

ESR	electron spin resonance
OTC	oxytetracycline
ACE	acetaminophen
NPX	naproxen
PMS	peroxymonosulfate
BPA	bisphenol A
DFT	density functional theory

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Chapter 14

The Potential Applications of MOF-based Materials in Wastewater Treatment

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14.1 Introduction

Metal–organic frameworks (MOFs), also known as porous coordination networks or porous coordination polymers, have attracted increasing interest,¹ considering their versatile structures, ultrahigh specific surface area, controllable pore, and abundant active sites.^{2,3} Also, it is easy to clarify the relationship between the properties and structures of MOFs as it is possible to obtain MOFs with accurate single crystal structures. Up to now, MOFs were widely investigated in the fields of gas adsorption/separation,^{4,5} catalysis (including photocatalysis),^{6–8} luminescence,^{9,10} drug delivery,^{11,12} energy,^{13,14} water capture^{15,16} and so on.^{17,18}

Just recently, MOFs have aroused tremendous interest from researchers in the field of environmental remediation *e.g.*, water purification^{19,20} and air

pollution control.^{21,22} In 2016, Wang and Ho proposed the research trends of MOF applications in environmental remediation based on a bibliometric analysis of the global research situation over the years 1995–2014.²³ In 2020, Zeng and co-workers clarified the research situation of MOF application in the field of environmental remediation ranging from 1999 to 2018,²⁴ which echoed the research trends predicted by Wang and Ho in 2016. In the research field of water purification, MOFs can not only act as detecting sensors to qualitatively or/and quantitatively determine pollutants, but also eliminate the pollutants as they are efficient adsorbents or catalysts. In addition, some MOFs and their composites can achieve anti-microbial and algae growth inhibition *via* the slow release of some metal ions like Ag^+ or Cu^{2+} or advanced oxidation process (AOP) like photocatalysis. In this chapter, a state-of-the-art review is presented to summarize the development of MOFs, MOF composites and MOF derivatives in the field of water purification. In addition, the perspectives of this research field are proposed in this chapter.

14.2 Detection of Pollutants in Water *via* Luminescent Sensing

Luminescent metal–organic frameworks (LMOFs), as a rapidly growing subclass of MOFs, are attracting increasing attention due to their potential applications in sensing fields.²⁵ LMOFs exhibit photon emission after the absorption of radiative excitation energy,²⁵ which became a research hotspot of luminescent sensing owing to their longer luminescence lifetime, higher quantum yield, higher sensitivity and selectivity toward targets.²⁶ The various possibilities leading to the emission of LMOFs are illustrated in Figure 14.1, which clarifies the different processes involved in both the absorption and emission of light.²⁷

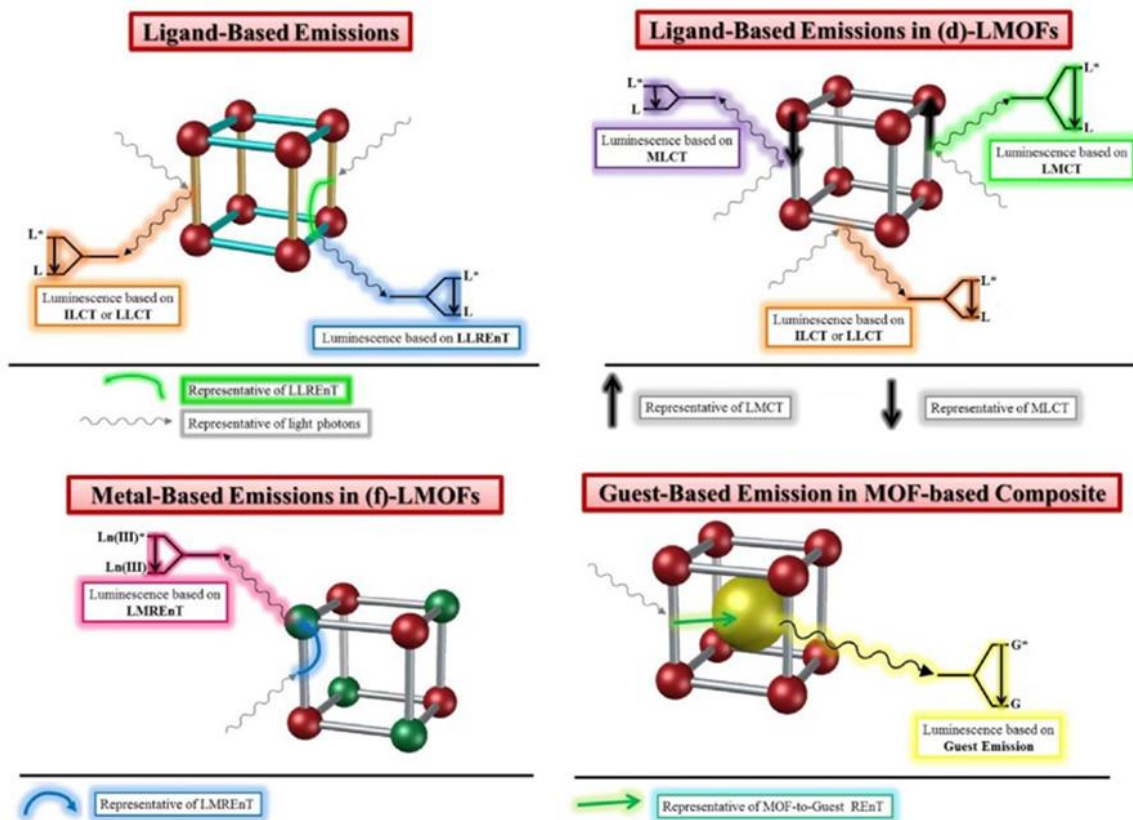


Figure 14.1 Schematic illustration of the emissive processes in LMOFs. ILCT (intra ligand charge transfer), LLCT (ligand-to-ligand charge transfer), LLREnT (ligand-to-ligand resonance energy transfer), MLCT (metal-to-ligand charge transfer), LMCT (metal-to-ligand charge transfer), LMREnT (ligand-to-metal resonance energy transfer), REEnT (resonance energy transfer). “L” stands for organic ligand, Ln(iii) stands for the lanthanide metal ion and “G” stands for guest molecules. Reproduced from ref. ²⁷ with permission from Elsevier, Copyright 2020.

Recently, LMOFs were adopted as sensors to accomplish luminescent detection of various pollutants in water environments due to the following advantages. (i) The active sites in the framework of MOFs can achieve highly selective recognition of the targeted molecules or ions; (ii) the high porosity and regular channel in LMOFs can facilitate the adsorption and desorption of the targeted samples.²⁸ That's to say, LMOFs can act as both the pre-concentrator and detector of the targeted pollutants. Up to now, three mechanisms including fluorescence quenching (turn-off), fluorescence enhancement (turn-on) and ratiometric fluorescence were involved in the detection processes,²⁹ in which fluorescence quenching (turn-off) was

mostly used for practical detection. Generally, if the LMOFs can be adopted as sensors to detect the pollutants in the water sample, they should possess some characteristics like: (i) some special alterations are produced upon the interactions between the LMOF and the targeted pollutants; (ii) the signals resulting from the above-mentioned alteration can be detected; and (iii) the formation of response signals should be a reversible process.³⁰ Up to now, LMOFs were applied to detect various pollutants in water samples, including but not limited to explosives, inorganic cations, inorganic ions, toxics (H_2S , CN^- , organic amine, pharmaceuticals and personal care products, *etc.*) and volatile organic compounds (VOCs).²⁵

Ghosh and coworkers reported a porous LMOF UiO-67@N (1 , $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{L})_6$, $\text{L} = 2$ -phenylpyridine-5,4'-dicarboxylic acid) with high water stability, in which the targeted molecules can easily enter inside the framework of **1** due to the pore sizes (1.5 Å and 23 Å) of UiO-67@N being larger than the sizes of the targeted molecules.³¹ Guest-free UiO-67@N (**1'**) was used to accomplish high selectivity toward 2,4,6-trinitrophenol (TNP) over other nitro analytes. A quick and obvious fluorescence quenching up to 73% was observed with increasing concentrations of TNP, in which the fluorescence quenching occurred at TNP concentrations as low as 2.6 mM. However, all other nitro compounds did not exert significant fluorescence quenching toward **1'**. Upon the irradiation of light, the excited electrons were transferred from the conduction band (CB) of the electron-rich **1'** to the lowest unoccupied molecular orbitals (LUMO) of TNP to result in fluorescence quenching. Soon afterward, more and more LMOFs were developed to achieving selective and sensitive detection of various nitro explosives.²⁵ Li and coworkers synthesized highly stable BUT-12 and BUT-13 to detect trace antibiotics like nitrofurazone (NZF) and nitrofurantoin (NFT) as well as organic explosives like TNP and 4-nitrophenol (4-NP) in aqueous solutions.³² Up to now, various LMOFs were produced to test other organic pollutants like aniline,^{33,34} organophosphorus^{35,36} and mycotoxin^{37,38} in water.

Yan and coworkers reported a Tb(III) -functionalized cadmium LMOF ($\text{Tb}^{3+}@\text{Cd-MOF}$, $\text{Cd-MOF} = \{[(\text{Me}_2\text{NH}_2)_2] \cdot [\text{Cd}_3(5\text{-tbip})_4] \cdot 2\text{DMF}\}_n$, $5\text{-tbipH}_2 = 5\text{-tert-butylisophthalic acid}$),³⁹ which was adopted as a fluorescent

probe to selectively sense Fe^{3+} with a detection limit (LOD) of 0.010 mM and $\text{Cr}_2\text{O}_7^{2-}$ with a LOD of 0.012 mM through fluorescence quenching.⁴⁰ Generally, the fluorescence quenching of LMOFs resulting from metal cations can be attributed to three mechanisms: (i) destruction of the crystal structure,⁴¹ (ii) ion interchange between metal cations of LMOFs and the targeted cations,⁴² and (iii) interactions between targeted cations and organic linkers in the LMOFs.⁴³ In Yan's work, the high selectivity toward Fe^{3+} of $\text{Tb}^{3+}@\text{Cd-MOF}$ resulted from (i) the exchange between Fe^{3+} and Tb^{3+} in the framework of $\text{Tb}^{3+}@\text{Cd-MOF}$ and (ii) the interaction between Fe^{3+} and the 5-*tbip*²⁻ linker. Also, the fluorescence quenching of $\text{Cr}_2\text{O}_7^{2-}$ to the $\text{Tb}^{3+}@\text{Cd-MOF}$ might contribute to the competition of the energy absorption between $\text{Cr}_2\text{O}_7^{2-}$ and 5-*tbip*²⁻ linker in $\text{Tb}^{3+}@\text{Cd-MOF}$, which almost overlapped with the $\text{Cr}_2\text{O}_7^{2-}$ in a DMF solution.

Wang and co-workers designed and synthesized an LMOF $[\text{Eu}_2(\text{clhex})\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$ (BUC-69, H_6clhex = 1,2,3,4,5,6-cyclohexanehexacarboxylic acid) for the purpose of selectively and sensitively detecting *p*-arsanilic acid (*p*-ASA) in water.⁴⁴ BUC-69 can accomplish accurate fluorescence sensing of trace *p*-ASA (10^{-6} M) with a LOD of 1.81 μM in wastewater simulated using real lake water, indicating fluorescence sensing of BUC-69 can overcome the influence of co-existing ions. The obtained results were comparable to the ones determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The fluorescence quenching can be ascribed to competitive absorption of UV light (200–300 nm) between *p*-ASA and BUC-69. Additionally, some other metal ions like K^+ , Al^{3+} , MnO_4^- , Mn^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Ag^+ , Eu^{3+} , Tb^{3+} , Hg^{2+} can be detected *via* fluorescence over LMOFs.^{25,45–47}

Some LMOFs and their composites were developed to detect some inorganic ions like PO_4^{3-} , CO_3^{2-} , ClO_4^- , SCN^- , $\text{N}(\text{CN})^{2-}$, I^- , CN^- .^{46,48} Li and coworkers modified Eu^{3+} into BUC-14 (a MOF synthesized by Wang and co-workers) to obtain $\text{Eu}@\text{BUC-14}$, which was adopted as fluorescence probe to detect the PO_4^{3-} in water samples with a LOD of 0.88 μM .⁴⁹ $\text{Eu}@\text{BUC-14}$ displayed high selectivity sensing toward PO_4^{3-} ions *via*

fluorescence quenching without interference from the co-existing 15 anions and 11 metal cations, as Eu@BUC-14 prefers to adsorb PO_4^{3-} ions with an adsorption capacity of 57.9 mg P g^{-1} .

Up to now, more and more LMOFs were developed to detect various pollutants in water. However, there is a big gap between practical application in real water samples and lab-scale research based on simulated water samples from pure water. In practical applications, some interferences from co-existing ions, chroma and turbidity should be overcome. In addition, some devices fabricated using LMOFs can be developed to detect pollutants in real wastewater *via* naked eyes, which will further push the development of LMOFs as sensor materials.

14.3 Adsorptive Removal of Pollutants in Water

As a class of porous materials constructed from metal templates and organic ligands, MOFs are widely used as efficient adsorbents to remove different pollutants in water, owing to their huge porosity, suitable geometric configuration, abundant functional groups and surface charge.⁵⁰ The adsorption activity of the MOFs can be further boosted by the introduction of unsaturated coordination sites, modification to the organic linkers and fabrication of composites.⁵¹ Recently, the influences of the instinct structure, hydrophobicity, surface area, functional group, porosity size and distribution toward the adsorption behaviors like kinetics, capacity, thermodynamic and adsorbent regeneration were investigated and clarified.⁵² It was deemed that the electrostatic interactions, hydrogen bonding interactions, acid–base interactions, weak coordination interactions to the unsaturated coordination nodes, π – π stacking interactions, and hydrophobic interactions contributed to the adsorption of organic pollutants over MOFs. The electrostatic interactions, ion exchange and weak coordination might result in the adsorptive interactions between MOFs and heavy metals, radioactive metal ions along with other inorganic ions (see Figure 14.2).⁵³

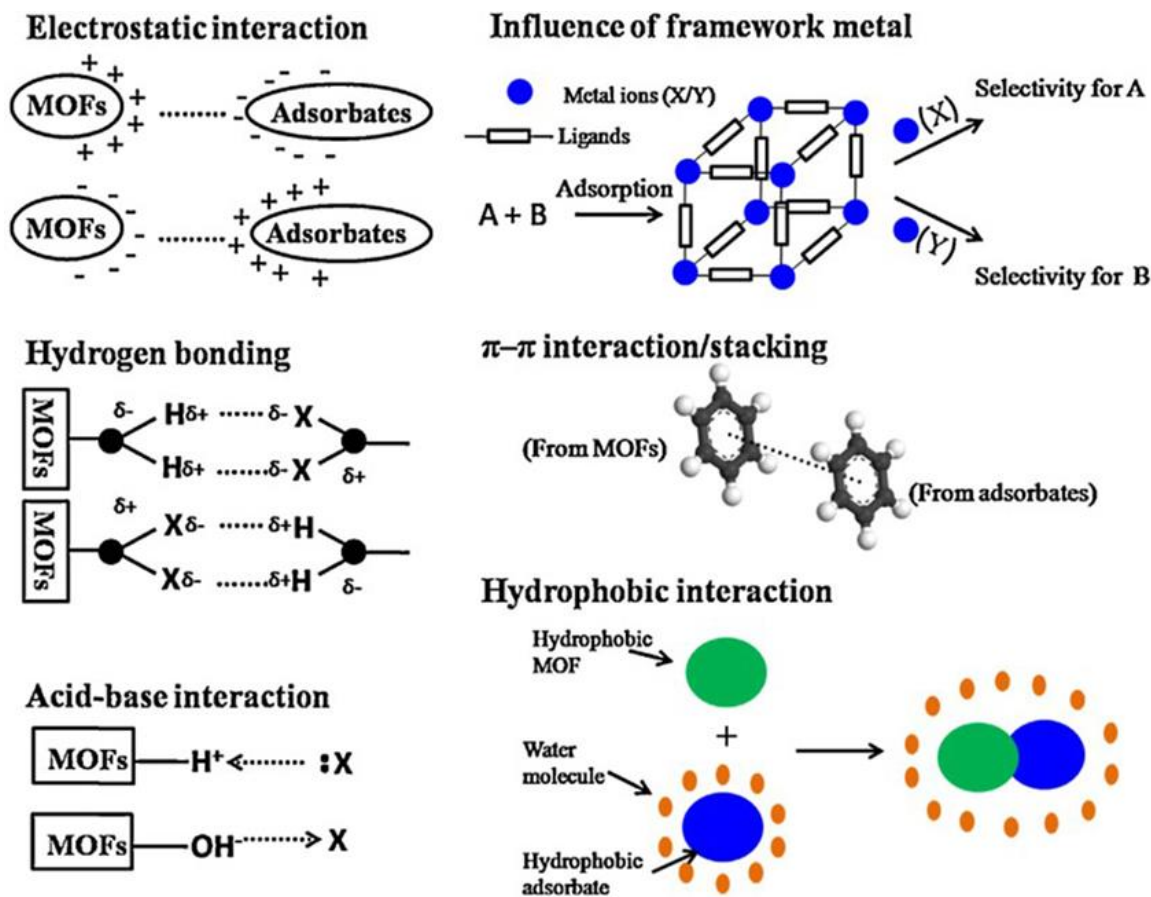


Figure 14.2 Possible mechanisms for the adsorptive removal of pollutants over MOFs.

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Wang and co-workers yielded high-throughput ZIF-67 (2-methylimidazole cobalt salts) *via* electrochemical deposition and used the as-prepared ZIF-67 as an adsorbent to remove 21 organic dyes including four cationic dyes (Rhodamine B, Methylene blue, Basic brown 1 and Acriflavine hydrochloride), 16 anionic dyes (Xylene cyanol FF, Coomassie brilliant blue R-250, Naphthol green B, Orange G, Eriochrome blue black R, Reactive red 120, Orange II, Remazol brilliant blue R, Methyl orange, Metanil yellow, Acid chrome blue K, Congo red, Red MX-5B, Mordant blue 13, Cotton blue, Fuchsin acid) and one neutral dye (Sudan III).⁵⁴ The zeta potentials of ZIF-67 are positive in the pH range 7.0–10.0, which facilitated the adsorption of the anionic dyes *via* strong electrostatic interactions. The open Co(II) sites outside ZIF-67 might be occupied by –

OH from water dissociation, which can be partially replaced by some stronger Lewis bases like the $-\text{SO}_3^{2-}$ group in Methyl orange. In addition, the $-\text{OH}$ on the outside of ZIF-67 might form strong H-bonding interactions with the $-\text{NH}_2$ group in some dyes like Basic brown 1 and Acriflavine hydrochloride. Furthermore, the π - π stacking interactions between the imidazole ring in ZIF-67 and the benzene ring in the dyes would further enhance the adsorption performances. However, ZIF-67 displayed different adsorption activities toward various organic dyes due to their different charge, molecular size, and functional groups. Considering that MOFs like ZIF-67 and BUC-17 displayed preferential adsorption of some organic pollutants, Wang and co-workers fabricated a solid phase extraction (SPE) column with these MOFs to efficiently separate the organic dye matrix, which provided the possibilities of MOF application in the concentration and separation of organic pollutants in real environmental samples.^{54,55} Up to now, increasing amounts of MOFs have been used to achieve adsorptive removal of different emerging organic pollutants like pharmaceutical and personal care products (PPCPs),^{56,57} veterinary drugs,^{58,59} pesticides,^{60,61} perfluorinated compounds (PFCs)⁶² and oil⁶³ in water.

Wang and co-workers designed and prepared mesoporous cationic SCU-8 (a thorium-based MOF), which contained channels with inner diameters of 2.2 nm and possessed a high surface area of $1360 \text{ m}^2 \text{ g}^{-1}$.⁶⁴ The SCU-8 can accomplish effective uptake of anions ReO_4^- (0.26 nm) and $\text{Cr}_2\text{O}_7^{2-}$ (1.34 nm) along with anionic organics like methyl blue (1.98 nm) and perfluorooctane sulfonate (PFOS, 1.7 nm). Up to 88% and 96% of the anionic PFOS with initial concentrations of 1 mg L^{-1} can be removed over SCU-8 crystals within 30 s and 2 min, in which the adsorption performance of SCU-8 was superior to other counterpart adsorbents like activated carbon and anion-exchange resins. The co-existing inorganic ions like NO_3^- , Cl^- , CO_3^{2-} , and SO_4^{2-} at concentrations of 50 mg L^{-1} exerted a minor negative influence on the adsorption activity of SCU-8 toward PFOS (1 mg L^{-1}). All atom molecular dynamics (MD) simulations were carried out to clarify the quick adsorption of PFOS over SCU-8 (see Figure 14.3) and investigate the corresponding adsorption mechanism. The results revealed that the early

adsorption process was driven by strong electrostatic and van der Waals interactions, followed by hydrogen bonding and hydrophobic interactions.

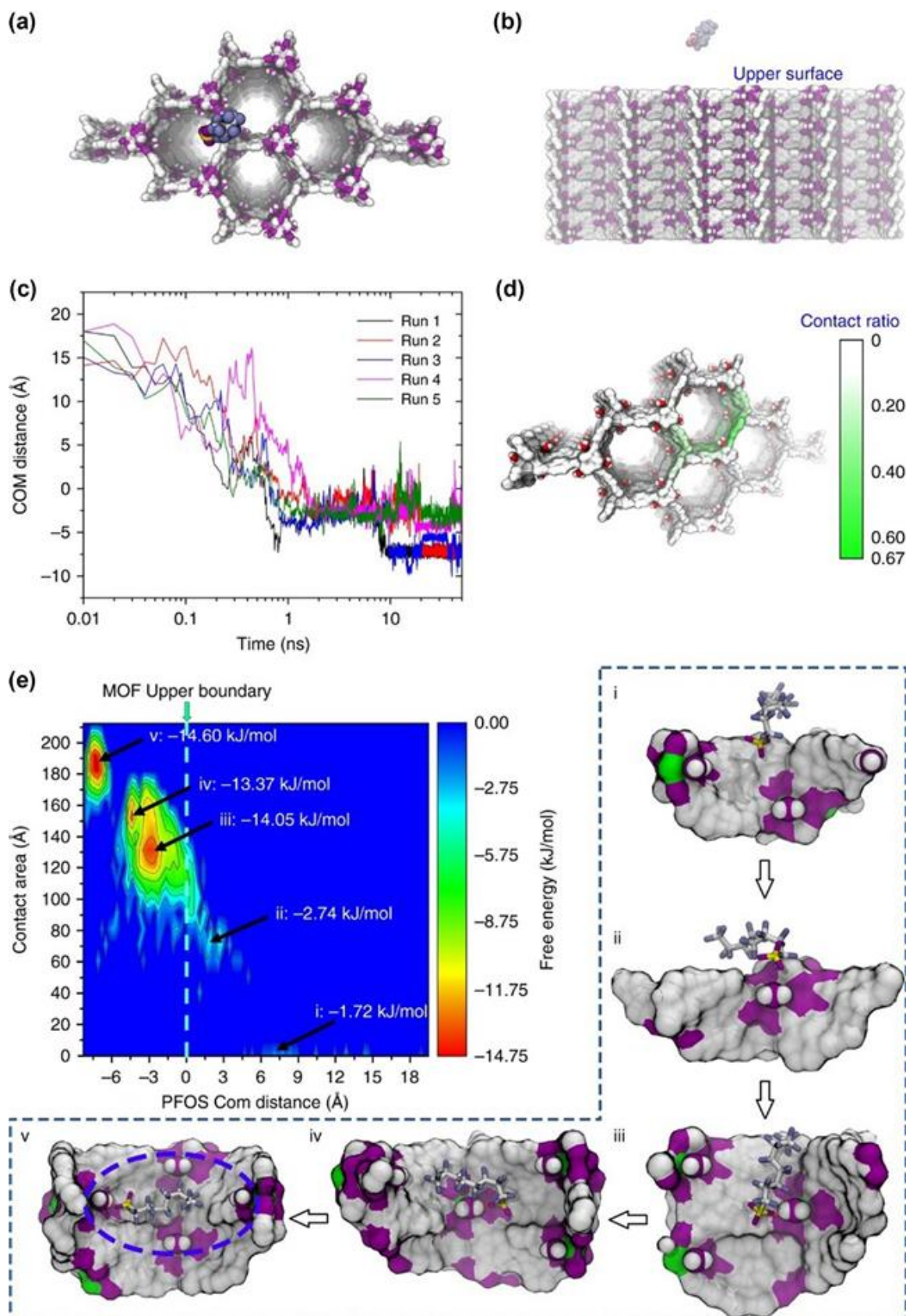


Figure 14.3 MD simulations of the binding pattern and adsorption pathway of PFOS into SCU-8. (a) The top and (b) side view of the simulation system, in which only PFOS and SCU-8 are displayed for clarity. (c) The distance between the center of mass (COM) of PFOS and the upper surface of SCU-8 for all five independent runs. (d) The contact ratio between the PFOS molecule and SCU-8. (e) The PFOS binding free energy surface (in kJ mol^{-1}), in which the snapshots (i)–(v) highlighted using the dashed box represent five specific PFOS–SCU-8 binding modes corresponding to the five free energy basins. Reproduced from ref. ⁶⁴, <https://doi.org/10.1038/s41467-017-01208-w>, under the terms of the CC BY 4.0 license, <http://creativecommons.org/licenses/by/4.0/>.

Lin and co-workers adopted UiO-67, UiO-67(Zr)–NH₂ and UiO-67(Zr)–2NH₂ to remove *p*-ASA. The As–O–Zr coordination, hydrogen bonding interaction as well as π – π stacking interactions contributed to the strong adsorption performance, which was affirmed by X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS) along with density functional theory (DFT) calculations (see Figure 14.4).⁶⁵ Both UiO-67(Zr)–NH₂ and UiO-67(Zr)–2NH₂ could eliminate the *p*-ASA at concentrations as low as 5 mg L^{−1} in both simulated natural wastewater and real wastewater to satisfy the drinking water standards of the World Health Organization (WHO) and the surface water standards of China, respectively. To overcome the difficult recovery and recyclability of powder MOFs adsorbents, Wang and co-workers immobilized MIL-88A(Fe) onto cotton fibers to form MIL-88A/CF composites and adapted the MIL-88A/CF to remove *p*-ASA, roxarsone (ROX), As(iii) and As(v).⁶⁶ A fixed-bed column constructed using MIL-88A/CF continuously cleaned both inorganic and organic arsenic pollutants from the simulated wastewater flow, which provided a new approach to adapt MOFs to achieve large-scale practical application and purify contaminated water.

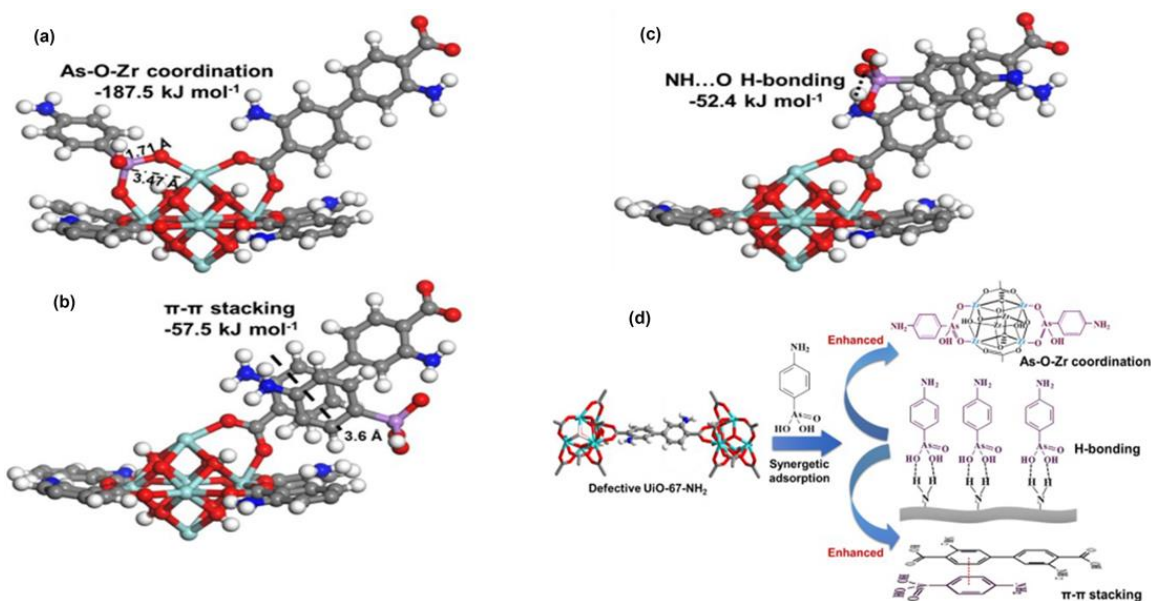


Figure 14.4 The optimal configurations obtained *via* DFT calculations of (a) As–O–Zr coordination, (b) π – π stacking, (c) and H-bonding between UiO-67–NH₂(2) and *p*-ASA. (d) The proposed adsorption mechanism of UiO-67–NH₂ toward *p*-ASA.

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Up to now, various MOFs were used as effective adsorbents to accomplish adsorptive elimination of heavy metals like Pb²⁺, Hg²⁺, Cr(vi)/Cr(iii), Cd²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Mn(vii) and Ba²⁺,^{67–69} noble metal ions like Au³⁺ and Ag⁺ as well as radioactive metal ions.^{70,71} Wang and co-workers designed and synthesized a novel 3D cationic SCU-102 Ni₂(tipm)₃(NO₃)₄ (tipm = tetrakis(4-(1-imidazolyl)phenyl)methane), which exhibited fast adsorption kinetics, a large adsorption capacity of 291 mg g⁻¹, a high distribution coefficient toward TcO₄⁻ *via* anion-exchange.⁷² SCU-102 completely removed TcO₄⁻ at a concentration of 28 mg L⁻¹ within 10 min, even in the presence of excessive SO₄²⁻ and NO₃⁻. Also, SCU-102 was utilized to treat simulated Hanford Site groundwater containing 1 mg L⁻¹ ⁹⁹Tc and co-existing anions like SO₄²⁻, CO₃²⁻, SiO₃²⁻ and Cl⁻. In this work, DFT calculations were carried out to

comprehensively understand the anion-exchange process between the NO_3^- anions in SCU-102 and TcO_4^- .

Generally, desorption can be achieved with the aid of chemicals or energy as conventional sorption is usually spontaneous. As a kind of stimuli to induce desorption, light is highly desired due to some advantages like fine tunability with high spatial and temporal accuracy, non-invasive to the environment, free of transport limitations, no by-product production and abundant sunlight availability. Wang and co-workers fabricated $\text{UIO-66-NH}_2\text{-Ag}_3\text{PO}_4$ (UAP-X) to adsorb sulfamethoxazole (SMX) with a maximum adsorption capacity of 200 mg g^{-1} .⁷³ Upon the irradiation of visible light, the Ag^+ in the light-responsive Ag_3PO_4 nanoparticles of UAP-X was reduced to Ag^0 to induce the desorption of SMX (146 mg g^{-1}). Wang and co-workers also prepared $\text{UiO-66-NH}_2\text{-Ag}_2\text{CO}_3$ (UAC-X) to accomplish sorption and desorption toward SMX, sulfisoxazole and sulfamethazine, in which DFT calculations were conducted to affirm the desorption mechanism.⁷⁴ These works provided the possibility to accomplish light controlled desorption at low cost and free of any further pollution.

Comparing with the counterpart adsorbents, MOFs as adsorbents demonstrated some advantages like large adsorption capacities and quick adsorption kinetics. However, the relatively poor water stability of the MOFs hindered further application. Specifically, the co-existing ions in real water not only influence the adsorption performance, but also destroy the stability of the MOFs. From this point, the investigation of MOFs as adsorbents to accomplish adsorptive removal of pollutants from a matrix should be focused on and investigated in the future.

14.4 Photocatalytic Pollutant Elimination

MOFs, as a class of effective novel photocatalysts, were used in hydrogen/oxygen production from water splitting,⁷⁵ CO_2 reduction,⁷⁶ organic pollutant degradation^{7,77} and $\text{Cr}(\text{vi})$ reduction^{76,78} upon the irradiation of UV-visible/UV-visible light. As photocatalysts, the photocatalysis of MOFs can be ascribed to metal-oxo clusters,

ligands/metalloligands as well as the encapsulated photocatalytic species.⁷⁹ In recent years, MOFs are gaining increasing attention due to the following merits. (i) The MOFs' well-defined and specific crystalline structures facilitate the corresponding characterizations and investigation of the structure–property relationship. (ii) The electronic structure and the active sites can be further tailored and modified for efficient light utilization and fast separation of photo-induced charge carriers. (iii) The intrinsic large porosity, high surface area and regular channels are beneficial to the diffusion of pollutants and discharge of products. (iv) The combination of secondary or even ternary semiconductors or conductors can further enhance light utilization and effective photo-produced electron–hole separation.⁸⁰

For the first time, Garcia and co-workers investigated the semiconductor property of MOF-5 constructed from Zn_4O clusters and terephthalic acid, which opened a new era of MOFs as photocatalysts.⁸¹ MOF-5 displayed a broad absorption band ranging from 500 nm to 840 nm, with band energy of 3.4 eV (CB 0.2 eV and valence band (VB) 3.6 eV). Phenol was selected as a pollutant model to test the photocatalytic activity of MOF-5. The results revealed that the MOF-5 demonstrated superior photocatalytic phenol degradation performance in comparison to commercial P25.

Wang and co-workers found that ZIF-8 (zeolitic imidazolate framework-8) with a band energy of 5.16 eV can be excited by UV light to degrade methylene blue (MB) with the aid the formed $\cdot\text{OH}$ radicals.⁸² The formation of $\cdot\text{OH}$ radicals was detected by the fluorescence approach adopting terephthalic acid as the probe molecule. The photocatalytic MB degradation process over ZIF-8 can be described by a pseudo-first-order kinetics model. It was found that ZIF-8 can exhibit efficient degradation activity in a wide pH range from 4.0 to 12.0. Specifically, the high pH enhances its adsorption and degradation performance toward MB, due to the surface charge of ZIF-8 and the increasing formation of $\cdot\text{OH}$. Also, the MB degradation pathway over ZIF-8 was proposed on the basis of the results of HPLC–Q-TOF–MS equipped with electron spray ionization (ESI).

Wang and co-workers designed and hydrothermally produced a 2D MOF $\text{Zn}(\text{bpy})\text{L}$ (BUC-21, $\text{H}_2\text{L} = \text{cis-1,3-dibenzyl-2-imidazolidone-4,5-}$

dicarboxylic acid, bpy = 4,4'-bipyridine), which displayed outstanding photocatalytic Cr(vi) reduction and organic dye degradation upon the irradiation of UV light.⁸³ Interestingly, BUC-21 demonstrated superior photocatalytic Cr(vi) reduction activity to the commercial P25 under the identical conditions and both the formed photo-induced electrons and O_2^- radicals contributed to the Cr(vi) reduction. To utilize visible light or even real sunlight, Wang and co-workers modified BUC-21 with g-C₃N₄ nanosheets,⁸⁴ Bi₂₄O₃₁Br₁₀ nanosheets,⁸⁵ N-K₂Ti₄O₉⁸⁶ and Cd_{0.5}Zn_{0.5}S nano-particles,⁸⁷ to accomplish Cr(vi) reduction under visible light or solar light. The introduction of semiconductors into BUC-21 inhibited the recombination of photo-induced electrons and holes, which enhanced Cr(vi) reduction. Wang and co-workers also introduced conductive polyaniline (PANI) to modify MIL-100(Fe)⁸⁸ and MIL-88A(Fe)⁸⁹ and boost the separation of photo-induced electrons and holes for the purpose of Cr(vi) reduction and tetracycline degradation. To boost the transformation of Cr(vi) to Cr(iii) and overcome the potential formation of Cr(OH)₃, it was essential to remove the formed Cr(iii) from the reaction system. Wang and co-workers introduced titanate nanotube (TNTs) to modify BUC-21,⁹⁰ which achieved simultaneous photocatalytic Cr(vi) reduction and adsorptive Cr(iii) removal, as well as good reusability and stability. It was believed that the introduction of TNTs as cation trappers adsorbed the formed Cr(iii) from the surface of the BUC-21 photocatalyst to provide more active sites for Cr(vi) reduction.

To overcome the difficult recovery and recyclability of powder MOFs photocatalysts, Wang and co-workers prepared UiO-66-NH₂(Zr/Hf) membranes on α -Al₂O₃ substrates with the aid of a reactive seeding method.⁹¹ The as-prepared UiO-66-NH₂(Zr/Hf) membranes accomplished outstanding Cr(vi) reduction under white light and real solar light (see Figure 14.5), in which the UiO-66-NH₂(Zr) membrane maintained > 94% Cr(vi) (initial concentration 5 mg L⁻¹) reduction efficiency for 20 cycles. The as-prepared UiO-66-NH₂(Zr) membrane was stable in aqueous solution, in which the UiO-66-NH₂(Zr) particles were well remained on the surface of the α -Al₂O₃ substrate. Even when the photocatalytic Cr(vi)

reduction was carried out using water samples simulated from real lake water, the UiO-66-NH₂(Zr) membrane still accomplished a reduction efficiency of 97% in 120 min, implying the potential application for real wastewater treatment.

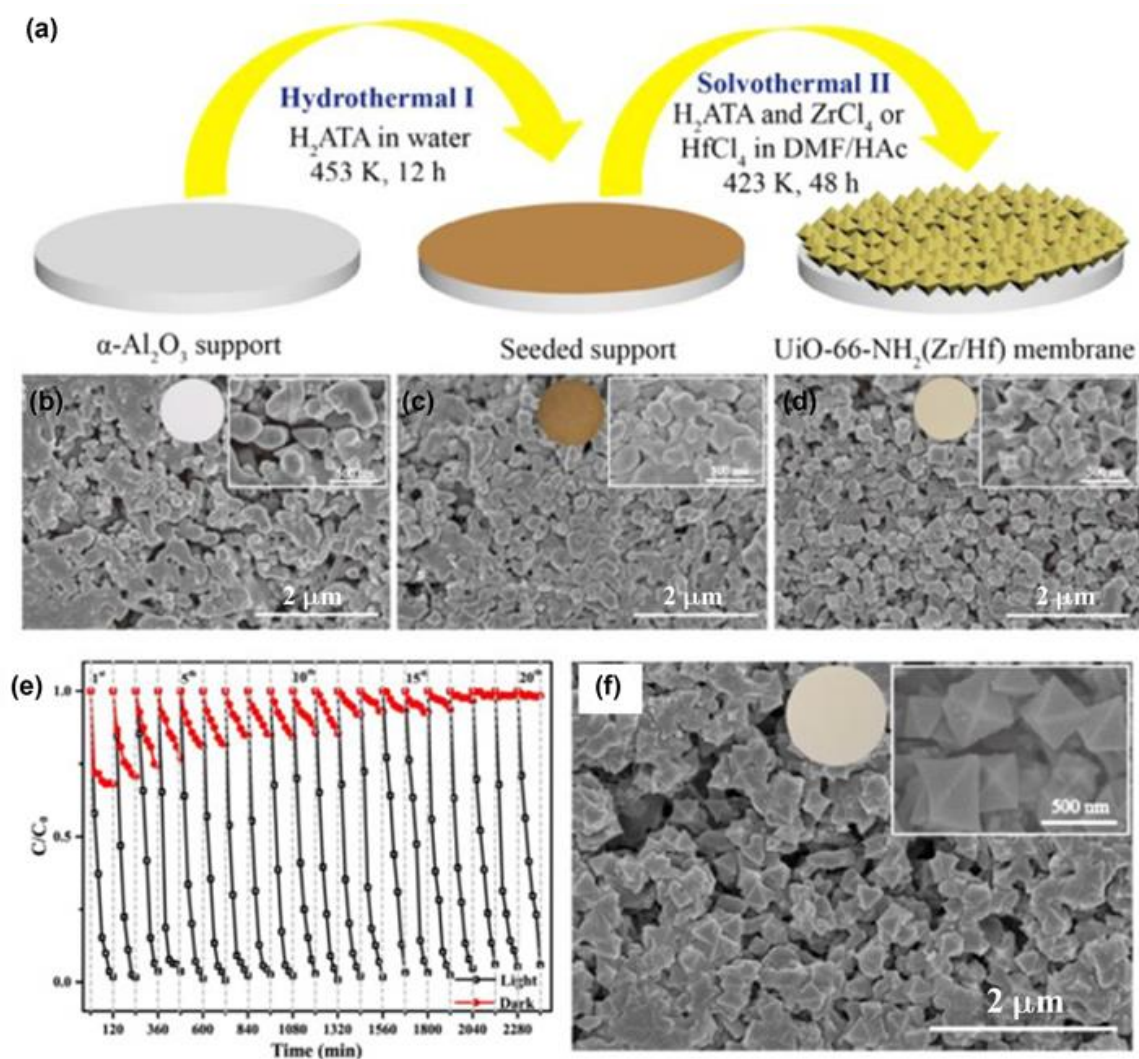


Figure 14.5 (a) Illustration of the preparation of a UiO-66-NH₂(Zr-Hf) membrane. SEM images of (b) the α -Al₂O₃ substrate, (c) the seed layer, (d) UiO-66-NH₂(Zr). (e) Recyclability of the UiO-66-NH₂(Zr) membrane for Cr(vi) reduction under white light irradiation for 20 successive cycles. (f) SEM of the used UiO-66-NH₂(Zr) membrane surface after the 20th photocatalytic Cr(vi) reduction. Reproduced from ref. ⁹¹ with permission from Elsevier, Copyright 2019.

Up to now, the photocatalytic pollutant removal from wastewater over MOFs and MOF composites has attracted increasing attention in the fields of organic pollutants degradation and Cr(vi) reduction.^{92–97} However, some difficulties and concerns should be overcome and addressed to adopt MOFs as photocatalysts for the purpose of purifying real polluted water. For example, the photocatalytic activity of powder MOFs was satisfied, but it was difficult to recover and recycle them. At this point, the immobilization of MOFs on some substrates was an effective approach to solve the dilemma mentioned above. For the utilization of light and even solar light, the influence of turbidity, chroma and the co-existing matters on the photocatalysis should be considered. During operation, notice should be taken of the leached organic linkers and metal ions from the MOFs.

14.5 Fenton-like and Sulfate Radical-based Advanced Oxidation Processes

Upon the irradiation of light, some MOFs can not only produce photo-induced electron–hole pairs, but also catalyze the degradation of H_2O_2 to produce $\cdot\text{OH}$ radicals, in which H_2O_2 can capture the electrons to yield $\cdot\text{OH}$ and enhance the separation of the electron–hole pairs.^{98–100} Also, some MOFs can be adopted as catalyst to activate PDS or PMS and produce $\text{SO}_4^{\cdot-}$ radicals.^{101,102} Just recently, increasing numbers of MOFs have been used as catalysts to accomplish organic pollutant removal *via* Fenton-like AOP and sulfate radical advanced oxidation process (SR-AOP).^{103,104}

Quan and co-workers investigated MIL-88B-Fe as a heterogeneous Fenton-like catalyst to degrade phenol.¹⁰⁵ It was observed that MIL-88B-Fe displayed a superior phenol degradation activity to that of Fe_2O_3 , $\alpha\text{-FeOOH}$, Fe_3O_4 , MIL-53-Fe and MIL-101-Fe, which can be ascribed to an abundance of active sites, boosted Fe(III)/Fe(II) redox cycling, and the flexible structure of MIL-88B-Fe. The hydroxyl radicals produced from the reaction between MIL-88B-Fe and H_2O_2 acted as the primarily reactive oxidative species to complete phenol degradation.

Yu and co-workers tested the degradation performance of a MIL-53(Fe)– H_2O_2 –visible light system toward clofibric acid (CA) and carbamazepine

(CBZ).¹⁰⁶ Both CA and CBZ were adsorbed onto MIL-53(Fe) with adsorption capacities of *ca.* 0.80 mmol g⁻¹ and 0.57 mmol g⁻¹, respectively, due to electrostatic interaction and π - π interactions. CA and CBZ can be effectively degraded in the MIL-53(Fe)-H₂O₂-visible light system, in which the charge carriers are produced in the light-excited MIL-53(Fe) photocatalyst and the synergistic influence of H₂O₂ contributed to the enhanced degradation.

Wang and co-workers produced high throughput MIL-88A(Fe) at room temperature, and used MIL-88A(Fe) as catalyst to carry out Fenton-like AOP for rhodamineB (RhB) and bisphenol A (BPA) degradation with the irradiation of visible light.¹⁰⁷ In this work, the degradation pathway of BPA degradation by $\cdot$ OH radicals was investigated on the basis of LC-MS results (see [Figure 14.6](#)).

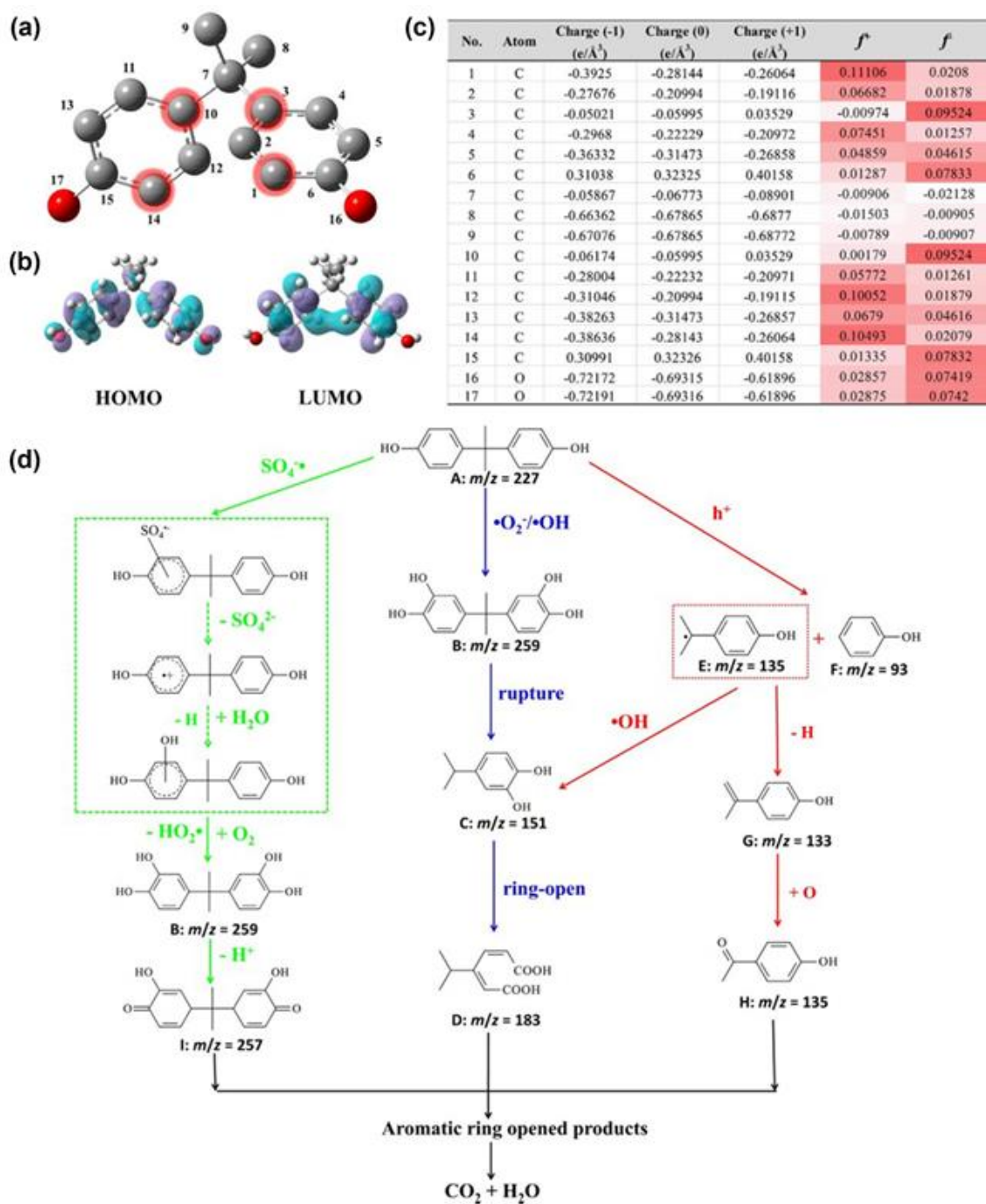


Figure 14.6 (a) Chemical structure, (b) HOMO and LUMO orbitals and (c) NPA charge distribution and Fukui indexes of bisphenol A (BPA). (d) BPA degradation pathway during a BM200–light–PS process proposed on the basis of LC–MS and DFT calculations. Reproduced from ref. ¹¹² with permission from Elsevier, Copyright 2021.

To further enhance the photo-Fenton performance of MOFs, the strategy of constructing compositions with some semi-conductors or conductive organic polymers within the MOFs was used to effectively accelerate the separation of excited electron–hole pairs. Wang and co-workers constructed g-C₃N₄/MIL-100(Fe) as photo-Fenton AOP catalyst to accomplish the effective degradation of diclofenac sodium and BPA under white light.¹⁰⁸ The introduction of the conductive polymer PANI into MIL-88A(Fe) stabilized MIL-88A and enhanced the mobilization of charge carriers, which was used to degrade BPA *via* photo-Fenton AOP under white light.⁸⁹

For the first time, Chang and co-workers adopted ZIF-67 (cobalt 2-methylimidazole) as a heterogeneous catalyst to activate peroxymonosulfate (PMS) for organic dye (RhB) degradation,¹⁰⁹ in which some factors like ZIF-67 dosage, reaction temperature, pH, UV light and ultrasonication toward the activation of PMS over ZIF-67 were explored. The results revealed that higher temperatures, stronger UV irradiation and more vigorous ultrasonication boosted RhB decomposition *via* PMS activation over ZIF-67.

MIL-53(Fe) was once adopted as a photocatalyst to achieve MB decolorization,¹¹⁰ however, the photocatalytic performance of the individual MIL-53(Fe) was not satisfactory because of the quick recombination of photo-induced charge carriers. Zhang and co-workers introduced persulfate (PS) as an external electron acceptor to accelerate the separation of electron–hole pairs,¹¹¹ which demonstrated enhanced degradation activity toward Acid orange 7 (AO7) in a MIL-53(Fe)–PS–LED visible light system. It was believed that the fast separation of photo-induced electron–hole pairs resulting from PS as an electron acceptor along with the further formation of reactive radicals *via* PS activation contributed to the boosted AO7 degradation in the MIL-53(Fe)–PS–vis system. These research results gave insight into the potential applications of versatile MOFs as catalysts to activate PS for the purpose of contaminated water remediation.

Wang and coworkers produced a Bi₁₂O₁₇Cl₂–MIL-100(Fe) composite with the aid of a ball-milling treatment, in which the optimal Bi₁₂O₁₇Cl₂–MIL-100(Fe) composite displayed highly efficient activation of PS (SR-AOP) for BPA degradation upon the irradiation of white light illumination.¹¹² The SR-AOP BPA degradation was accomplished in wide

pH range from 3.0 to 11.0. The excellent PS activation performance was ascribed to both MIL-100(Fe) for PS activation and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ with suitable band positions, in which the fast separation of charge carriers and the accelerated formation of $\text{SO}_4^{\cdot -}$ radicals were accomplished. In this work, the BPA degradation pathway was proposed on the basis of LC-MS and verified using DFT calculations.

Some MOFs constructed from metal templates with multiple oxidation states like iron and cobalt catalyze the degradation of H_2O_2 or activation of PS to produce corresponding active species for organic pollutant degradation. The concerns and challenges of MOFs as catalysts to catalyze Fenton-like process or activate PS process can be found in the section above on MOFs as photocatalyst. Also, the influence of co-existing matter like inorganic ions and dissolved organic matter should be considered during the reaction process. Finally, the toxicity of the intermediates from the degradation of the targeted pollutants should be assessed using both model calculations and experimental analysis.

14.6 Conclusion and Outlook

As an emerging class of functional materials, increasing numbers of MOFs were adopted to carry out water remediation. However, some barriers like high cost and low water stability should be overcome for potential application in real water treatment. Among all the synthesis strategies, the environmentally friendly mechanochemical method is an ideal way to produce high throughput MOFs with low cost under mild reaction conditions in short times. This approach can be achieved between the metal oxides or metal hydroxide and the corresponding organic linkers with the aid of mechanical power, which is free of the influence of counter ions like sulfates, nitrates, perchlorates and chloride ions. Importantly, the reaction between the reactants strictly follows a stoichiometric ratio with no emission of any hazardous chemicals. As to the water stability of MOFs, it was believed that “hard” metal ions (like Zr^{4+} , Ti^{4+} , and Fe^{3+}) linked by organic carboxylate ligands or soft metal ions (like Zn^{2+}) with imidazolate linkers might produce MOFs (like UiOs, MILs and ZIFs) of high stability in aqueous solutions.

Up to now, the toxicity of MOFs was of concern in the field of drug delivery. There is a big gap that needs to be filled before the real application of MOFs as environment remediation materials. The transfer, transportation, effect and toxicity of MOFs in the real environment should be considered. Also, attention should be paid to how to handle and reuse used MOFs for the purpose of avoiding secondary pollution. It is believed that MOFs, as emerging functional materials, can display their versatile properties in the future of water remediation.

Acknowledgements

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Chapter 15

Engineering Biochars for Environmental Applications

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15.1 Introduction

Water is a critical resource for urban, agricultural, and industrial purposes.¹ However, the rapid development of global industrialization and urbanization makes the safe use of water and the maintenance of ecological stability a great challenge.² Particularly, with the rapid increase in population and fast urbanization nowadays, huge amounts of organic pollutants have been discharged into water bodies, leading to severe environmental pollution and high environmental risks.³ It is, therefore, highly desirable to develop advanced, affordable, and effective strategies in the fight against water contamination.

Recent advances in nanomaterials and nanotechnologies may provide promising countermeasures to the above-mentioned environmental issues. In particular, the intriguing physicochemical attributes of carbonaceous materials can be readily employed as ideal platforms for a variety of environmental applications, such as adsorption of environmental contaminants and catalysis of pollutant decomposition. Moreover, the design of engineered carbonaceous materials will go back to the hand of material-relevant chemists, as the physicochemical properties of carbonaceous materials can be fine-tuned by delicate tailoring of their attributes like morphology, surface chemistry and dimensions. Many types of carbonaceous materials are commercially available, *e.g.*, graphene, carbon nanotube, activated carbon and biochar. However, the relative high cost of mass production of graphene and carbon nanotubes significantly limits their practical engineering applications. Activated carbons are the most widely employed and studied adsorbent for organic compounds, but their wide acceptance is greatly hampered by the difficulties of material regeneration.⁴ Alternatively, considering economic factors and available modification possibilities, biochar has been attracting much research interest by the scientific community as an emerging outstanding nanoreinforcer by virtue of its high specific surface area, ease of fabrication, abundance as well as low cost.⁵ Biochar is a kind of carbon-rich porous material that can be produced by the pyrolysis or hydrothermal carbonization of raw biomass. Thermochemical conversions of biomass (*e.g.*, plant, animal, and microorganism) are illustrated schematically in [Figure 15.1](#).⁶ Biochar has been proposed as a means for mitigating anthropogenic greenhouse gas production because of its capability to store carbon in a stable form, which reduces the release of greenhouse gases into the atmosphere from biomass degradation.⁷ Furthermore, the abundant availability of low-cost waste materials as a feedstock for biochar production makes biochar an alternative sustainable adsorbent or catalyst in relevance to environmental applications. The surface of biochar can be modified either by chemical activation or by making biochar-based composites, thereby the treatment capacity can be further improved.^{8,9} Recently, the synthesis of diverse biochar-based materials from waste biomass as feedstock has been extensively pursued in the field of water remediation and the number of research papers continues to increase. In this context, the topics covered in this chapter are mainly focused on biochar serving as a promising material for environmental applications, hoping to summarize the advance of the subject to those who are interested in acquiring basic and applied knowledge with particular emphasis on applying biochar in water treatment systems.

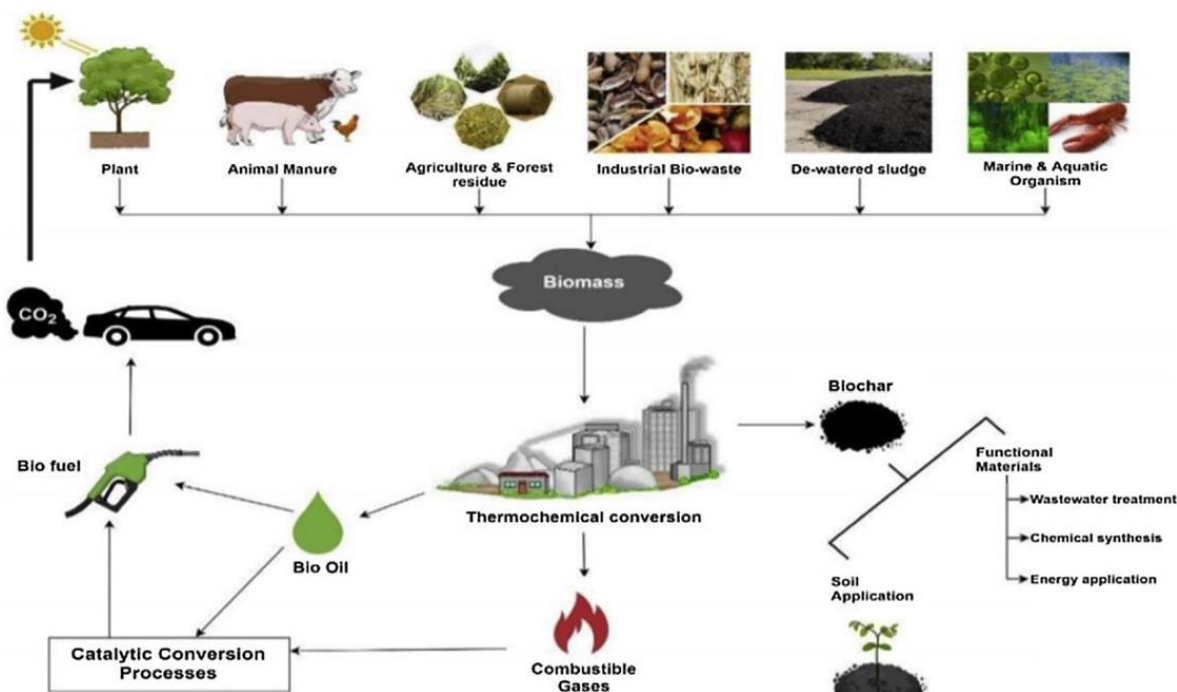


Figure 15.1 Illustration of biomass cycle and biochar production. Reproduced from ref. ⁶ with permission from Elsevier, Copyright 2021.

15.2 Definition of Biochar

Biochar can be defined as a kind of high-carbonization solid residue that is composed of aromatic ring lamellae with close packing and highly twisted structures. Owing to their cost effectiveness, excellent stability and tunable physicochemical properties, biochars have been regarded as economic and sustainable alternatives to other carbon-based materials like activated carbon and carbon nanotubes. Extensive studies suggested that the properties of biochar are strongly dependent on both the nature of biomass and pyrolysis conditions (*i.e.* biomass pre-treatment and handling). Specifically, crack formation and microstructural rearrangement may occur during the pyrolysis processes, thus altering the original structures of biomass to varying degrees.¹⁰ This endows diversities of biochar structure such as 0D spherical, 1D fibrous, 2D lamellar and 3D spatial structures.¹¹ During the pyrolysis process, elevated temperatures drive the volatile substances to be released from the char, which results in the formation of multi-scale porous microstructures and an increased surface area.^{12,13} Micropores have a dominant contribution to the surface area that plays a key role in adsorbing small molecules like solvents and gases, whereas the mesopores are more important in heterogeneous adsorption between liquids and solids. Compared with parent biomass, the biochar demonstrated higher mechanical strength,¹⁴ rich surface chemistry and enhanced stability.¹⁵ Heteroatoms such as S, P, N, O and H are associated with the aromatic rings, which act as ideal platforms for the synthesis of functionalized hybrid materials and have several environmental implications for catalysis and adsorption. For example, Yuan *et al.*¹⁶ defined biochar as a sustainable electron donor/acceptor that involves biogeochemical redox reactions where the biochar has the function of rechargeable reservoirs of bioavailable electrons, giving rise to what is called “geobatteries”. Besides, functional groups can participate in redox reactions on reversible surfaces or interfaces with other ambient species such as electroactive microbial communities. The superficial electroactive functional groups are essential for local electron transfer process. Extended conductive graphitic structures enable long-range electron transfer, facilitating external access to electron acceptors/donors.¹⁷ Based on this fact, the improved electroactive properties make biochar a potential ideal candidate for microbial electrochemical systems.¹⁸ On the other hand, the tunable porosity and surface functionality of biochar-based functional materials may find applications in addressing environmental issues (Table 15.1). This chapter summarizes recent advances on biochar materials and relevant design principles. A detailed summary of techniques available for synthesis and functionalization is elaborated with emphasis on the modification techniques based on physical or chemical

protocols to improve their surface functionalities. Next, we delve into the potential applications of biochar in water treatment, followed by discussion of the constraints and hotspots for future research in relevant fields.

Table 15.1 Recent applications of biochar in wastewater treatment.

Materials	Raw material	Pyrolysis temperature (°C)	Assistive technology	Specific surface area (m ² g ⁻¹)	pH	Pollutants	Removal efficiency
Organic pollutants	Heavy metal						
CO ₂ -biochar	Oak	900	Microwave	432.0	11.2	2,4-Dichlorophenoxy acetic acid	/ 81.6%
KOH-biochar	Corn cob	450	Ultrasound and ball milling	2368.0	6.7	Levofloxacin	/ 99.9%
Cu-biochar	Peanut shells	450	/	/	8.0	Doxycycline hydrochloride	/ 93.2%
Self-functionalized biochar	Corn cob	450	Ultrasound	2368.0	/	Levofloxacin	/ 99.93%
Fe/Zn-biochar	Sawdust	600	/	/	6.0	Tetracycline	/ 96.0%
g-MoS ₂ -biochar	Straw	500	/	176.8	/	Tetracycline hydrochloride	/ 249.5 mg g ⁻¹
Hydrothermal carbon	d-glucose	700	/	31.0	4.2	Alachlor	/ 99.7%
Nanoscale zerovalent iron-biochar	Rice hulls	350	/	/	6.2	Trichloroethylene	/ 99.4%
Co ₃ O ₄ -biochar	Rice straws	450	/	62.7	7.0	Ofloxacin	/ > 90.0%
CoO/Co ₉ S ₈ @N-S-biochar	/	/	/	125.9	3.0	Sulfamethoxazole	/ 100.0%
TiO ₂ /biochar	Reed straws	300	/	102.2	4.0	Sulfamethoxazole	/ 91.3%
Pd-N/biochar	Loofah sponge	800	/	377.9	7.0	Bromate	/ 96.7%
Thiol-modified biochar – biochar	Poplar wood chips	300	/	61.3	/	/	Hg ²⁺ 98.2%
Fe ⁰ -biochar	Corn stalks	700	Ball milling	29.7	/	/	Cr(vi) 97.8%
Phosphorous-biochar	<i>Typha angustifolia</i>	700	Ball milling	357	/	/	U(vi) 128.5 mg g ⁻¹
Fe-Mn/biochar	Walnut shells	600	/	288.8	8.8 ± 0.1	/	Hg ⁰ 4141.0 ng g ⁻¹
NH ₂ -biochar	Rice straws	600	/	170.3	/	/	Cd(ii) 67.6 mg g ⁻¹
N-biochar	Corn straws	600	/	418.7	/	/	Cd(ii) 1.8 mmol g ⁻¹
Nanoscale zerovalent iron –biochar	Corn stalks	700	/	/	10.3	/	As(ii) 148.5 mg g ⁻¹

MnO ₂ -MBCG	Rice husks	500	Ultrasound	31.2	/	/	Cd(ii)	84.8 mg g ⁻¹
Colloids- mycelial- biochar	Rice husks	600	Ultrasound	30.0	/	/	Cd(ii)	102.0 mg g ⁻¹

15.3 Functionalization of Biochar Materials

15.3.1 Physical Modification

To tune the properties of biochar materials suitable for environmental purposes, methods are developed using physical modification and chemical modification.¹⁹ Ball milling, gas or steam activation and microwave are commonly adopted physical strategies to modify biochars. High-energy ball milling, a mechanical activation process, has gained considerable attention recently in the fabrication of engineered nanomaterials or nanocomposites.²⁰ Ball milling can reduce particle size and increase specific surface area, thereby introducing additional active edge sites to improve the adsorption capacity²¹ (Figure 15.2a). Previous studies reported the ball milling to increase the maximum adsorption capacities of biochar from 211 to 1929 mmol kg⁻¹ for Ni²⁺ and 17.2 to 354 mg g⁻¹ for methylene blue.²² In brief, the modified agents and biochar are mixed in the ball milling chamber to prepare nanocomposites using drying or wetting routes. During ball milling, the functional groups of biochar were exposed, which allows the interactions between Fe powder and biochar to form iron carbide phases.²³ The surface area of the micropores was increased by exposure to blocked microporous networks, and the phosphorous moieties of phytic acid were grafted onto the biochar surface.²⁴ In favor of low cost, flexibility and simplicity, this manner has been widely used in large-scale production of modified biochars. Recently, several studies have been carried out to assess the potential applications of ball-milled nanocomposites in a number of fields such as energy, environment, and biomedicine.

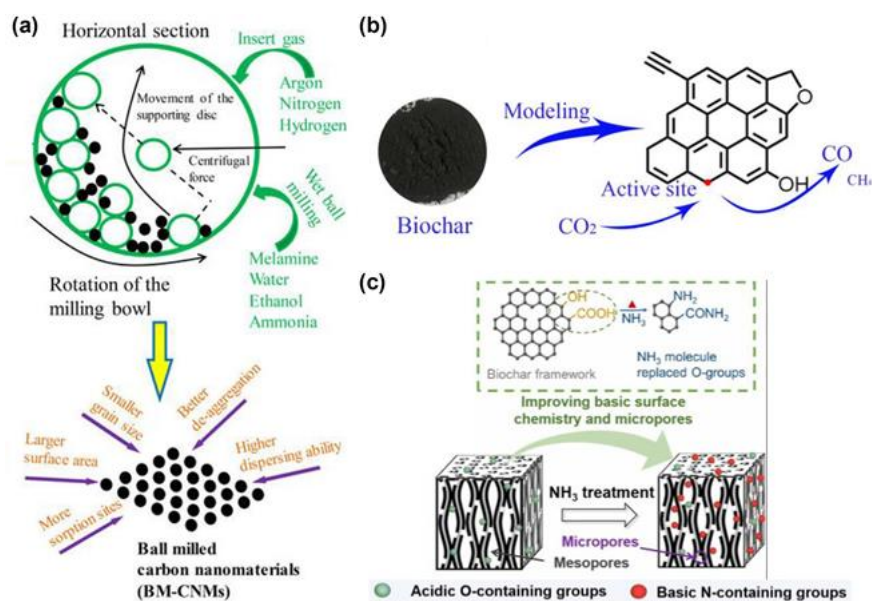


Figure 15.2 Three kinds of physical modification methods of biochar. (a) Adapted from ref. ²¹ with permission from American Chemical Society, Copyright 2017; (b) adapted from ref. ²⁷ with permission from American Chemical Society, Copyright 2020; (c) adapted from ref. ²⁸ with permission from Elsevier, Copyright 2021.

Gas modification is another facile route as partial gasification is available for the formation of crystalline carbon and the partial volatilization of biochar. The oxygen of water molecules is exchanged at the free active centers on the surface of carbon and the hydrogen produced by the loss of oxygen from water molecules reacts with carbon

on the biochar surface to form surface complexes. With gas released, the surface area and pore volume of biochar increased as well.^{24–26} Moreover, CO₂ and NH₃ can also be used for the modification purposes. At elevated temperatures, CO₂ reacts with C in biochar to form CO, which is beneficial for the formation of abundant porous structures²⁷ (Figure 15.2b). While NH₃ can preferentially react with surface acidic O-containing functional groups, allowing organic molecules to diffuse into the pore channels of biochar (*i.e.*, toluene;²⁸Figure 15.2c). Compared with the other mentioned modifications, gas purging does not necessarily require solution treatment after modification, but the use of gas definitely does increase the cost for biochar preparation. In addition, there is also the need for further optimization of preparation conditions to be set between pyrolysis and gas purging, and the selection of modification methods depends on the specific applications of the biochar.

Microwave modification offers a sustainable method to produce bio-energy products such as biochar, bio-oil, and bio-gas. In comparison with conventional manners, microwave technique has several unique advantages in terms of shorter processing times, lower energy input, more effective heat transfer, and better selectivity of heating. Domínguez *et al.*²⁹ took the first initiative to investigate biofuel (syngas, bio-oil, biochar) produced from microwave-assisted pyrolysis of sewage sludge. Microwave pyrolysis of biomass is attractive as it concurrently facilitates biomass recycling and energy recovery without expending as much energy as conventional pyrolysis. The thermal effect of microwave irradiation may produce “hot spots” or micro-plasmas that ionize the surrounding atmosphere,³⁰ which accelerates the organic decomposition and the generation of highly oxidative hydroxyl radicals ($\cdot\text{OH}$). Two kinds of lignocellulosic waste, *e.g.*, oak and apple, were used as the raw materials to fabricate the biochar materials. The results showed the formation of various free radicals such as $\cdot\text{OH}$ and singlet oxygen ($^1\text{O}_2$) on the biochar surface and evident removal of 2,4-dichlorophenoxyacetic acid.³¹

The physical methods provide effective routes to modify the surface properties of biochar, achieving the improvement of multi-scale porous structure and production of functional groups in an economic way without added impurities. The physically modified biochar displayed a high adsorption capacity for a wide range of organic pollutants and heavy metals due to improved specific surface area combined with abundant mesopores and micropores. This modification method is more controllable and safer, and the biochar produced is free of impurities. However, it may not be as excellent as chemical modification in terms of surface properties and adsorption performance, and thus the physical modifications are consequently generally used as an auxiliary strategy in combination with chemical modification.

15.3.2 Chemical Modification

Chemical methods were also investigated extensively for biochar modification. Generally, chemical modification makes use of high-surface area biochar as a scaffold to “host” other materials. The biochar-based nanoparticles fabricated could be classified into three forms: (1) nanoscale metal–metal hydroxide–biochar composites, (2) functional nanoparticle-coated biochar, and (3) clay mineral–biochar composites. It is well known that the surface modification of biochar with nanoscale transition metal particles could further boost their catalytic properties.^{32–34} Common strategies for hybrids of metal nanoparticles with biochar include chemical impregnation and coprecipitation. Glyphosate and ammonium bicarbonate were adsorbed on the attapulgite networks distributed on biochar by mixing and soaking. Then, the obtained complexes were granulated using a pelletizer and wrapped with silicone oil to prepare near-infrared-responsive controlled-release herbicide particles, which provided a promising way to alleviate environmental contamination.³⁵ In order to ensure extremely high localized pressures and temperatures in liquid-phase reactions, a series of new inorganic–organic hybrid materials based on TiO₂ and other biochar-based supports were rationally designed using an ultrasound-assisted wet impregnation method. As the cavitation effect enhances the chemical reactivity,^{36,37} this provides a simple and universal method for the preparation of photocatalysts capable of degrading phenol by 64.1% under UV light and 33.6% under visible light. When TiO₂ was supported on the biochar, it could be recycled at least five times with reproducible photocatalytic performance.

Chemical coprecipitation has been widely accepted as a mature, economical, and efficient method for the preparation of metal or oxide nanoparticles.³⁸ For example, Jia *et al.*³⁹ dissolved Fe³⁺, biochar and HCl in an ammonia solution to form a black precipitate, thereby the modified biochar could be further obtained through pyrolysis treatment. During the addition of the FeCl₃·6H₂O reagent, CuSO₄·5H₂O, Mn(CH₃COO)₂·4H₂O, or KMnO₄ was also added at different loading ratios to investigate the co-doping effect. Spinel structure solid

solutions of MnFe_2O_4 and CuFe_2O_4 were formed in the modified biochar, generating many cation vacancies on the biochar surface. The pore structures and the content of carbonyl, carboxyl, and metal hydroxyl functional groups were significantly increased, which facilitates the uptake of mercury ions from water due to high affinity.

The synthesis of functional nanoparticle-coated biochar could be either conducted through *in situ* or post-modification processes. Various kinds of functional nanoparticles such as graphene, carbon nanotubes, graphitic C_3N_4 and layered double hydroxides (LDHs) could also be coated onto the biochar surface. For example, FeCl_3 is the most commonly used Fe-based catalyst precursor. Iron (Fe^0) sheets *in situ* formed during the reductive carbon thermal conditions at high temperature can act as both template and catalyst.⁴⁰ Top-down fabrication of graphene-like biochar could also be achieved by the post-treatment of biochar using the Hummers method (oxidation and exfoliation using strong acid and KMnO_4).⁴¹ Milled hickory chips and sugarcane bagasse biomass (feedstocks) can be converted to CNT–biochar nanocomposites *via* a dip-coating procedure.⁴² The Mg/Fe–LDH–biochar composites were produced by loading LDH nanoparticles on the surface of pre-activated biochar.⁴³ The rich oxygen-containing functional groups of dissolvable biochar favor interactions with clay minerals *via* various mechanisms including ligand exchange, cation bridges, hydrogen bonding, anion and cation exchange, and van der Waals interactions.⁴⁴ Yang *et al.*⁴⁵ found that the Ca^{2+} , Fe^{3+} and Al^{3+} may act as cation bridges to bind kaolinite and biochar, resulting in the formation of organometallic complexes in the coexistences of kaolinite and metal chlorides.

15.4 Environmental Applications of Biochar

15.4.1 Adsorption of Contaminants from Water

Biomass-derived biochar has been reported to be an efficient absorbent for the elimination of a wide range of pollutants such as emerging contaminants, heavy metals, and other industrial chemicals from synthetic or real wastewaters. The related adsorptive mechanisms and the removal of a few model contaminants are reviewed in this section.

15.4.1.1 Mechanism of Adsorption

In simple terms, the adsorption process on a porous solid such as biochar can be divided into four stages: (1) transport of adsorbate molecules from the solution to biochar; (2) diffusion of the adsorbate through the liquid film surrounding the biochar molecules; (3) diffusion into the pores, *i.e.*, transport of adsorbate molecules from the surface of biochar particles along the solid pore surface to active sites; (4) adsorption as a result of adsorbate–biochar interactions.^{46,47} The adsorption mechanism depends on the adsorbent–adsorbate interactions. Using biochar as an adsorbent, the mechanism of adsorbing organic contaminants can be roughly divided into electrostatic attraction, π – π bond interaction, H-bonding, hydrophobic interactions, ion exchange and pore-filling (see Figure 15.3). Electrostatic attraction is the essence of ionic bonds formation, which includes electrostatic attraction and repulsion.⁴⁸ The magnitude of electrostatic attraction depends on the size of each atomic charge and the distance between two atoms.⁴⁹ π – π bond interactions are a weak interaction that often occurs among aromatic rings. The adsorbent and adsorbate are bound together by electron transfer between electron donor and acceptor.⁵⁰ The carboxylic acid nitro, ketonic groups, and different types of hydroxyl and amine groups on the surface of biochar act as electron acceptors, forming π – π electron donor–acceptor interactions with aromatic molecules, thereby enhancing the adsorption of aromatic molecules.⁵¹ This adsorption mechanism plays a leading role in the adsorption process of many carbonaceous materials on pollutants. When non-polar groups exist in the molecule, there is mutual repulsion between water molecules. Biochars with low surface oxidation general exhibit hydrophobicity. This kind of biochar reacts with hydrophobic organic compounds through hydrophobic interactions to achieve the purpose of removing organic pollutants.⁵²

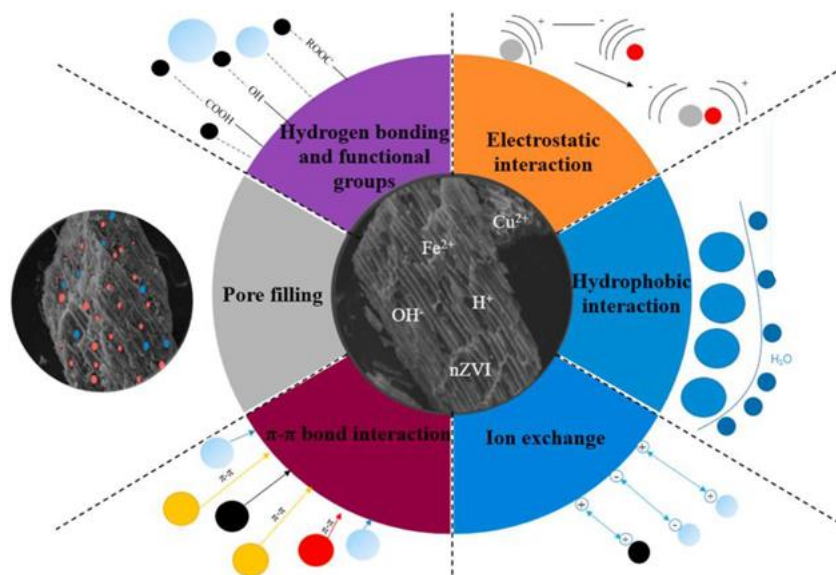


Figure 15.3 Adsorption mechanisms of biochar. Reproduced from ref. ⁵⁰ with permission from Elsevier, Copyright 2021.

15.4.1.2 Biochar-based Adsorbents for Antibiotic Removal

Antibiotics have recently been recognized as an emerging environmental contaminant of concern.⁵³ Researchers adopted modified biochar with peanut shell as the raw material and $\text{Cu}(\text{NO}_3)_2$ added to adsorb doxycycline hydrochloride in water environments. It was shown that the copper nitrate modified the biochar's removal rate for doxycycline hydrochloride twice as much as that of raw biochar.⁵⁴ Li *et al.*⁵⁵ designed a self-functionalized biochar *via* an ultrasonic-assisted pre-modified method with more functional groups, which played important roles in the solid-liquid interactions, posing on the surface of biochar. The removal efficiency of levofloxacin was up to 99.93% in the competitive system. Additionally, a ball milled magnetic biochar was shown to effectively adsorb sulfamethoxazole (83.3%) and sulfapyridine (89.6%).⁵⁶ A systematic study was carried out to remove tetracycline utilizing a mixed iron and zinc sawdust biochar. The results suggest that this type of biochar shows great potential for tetracycline removal from aqueous solutions. Not only was tetracycline separated from water, but the removal rate after three cycles was greater than 89.0%.⁵⁷ In view of tetracycline, Zeng *et al.*⁵⁸ proposed an associative facilitation between biochar and g-MoS₂ nanosheets, discovering that biochar decorated by g-MoS₂ exhibited optimum tetracycline removal with an adsorption capacity up to 249.5 mg g⁻¹. The adsorption behavior of tetracycline molecules on g-MoS₂-biochar can be interpreted using a three-step process, and it is dominated by several mechanisms including pore-filling, electrostatic force, hydrogen bonding and π - π interaction. The g-MoS₂-biochar composite is considered to be a tailor-made adsorbent for tetracycline removal due to the appropriate pore-size distribution, as the increasing mesopores might decrease the steric hindrance effect and enhance adsorption. Moreover, magnetic biochars can be synthesized by oxidative hydrolysis of FeCl_2 with pine sawdust in an alkaline medium. The ultimate aim is to examine the magnetic pine sawdust biochar's potential toward adsorptive removal of sulfamethoxazole from aqueous solutions. They found that pine sawdust biochar has better sorption performance for sulfamethoxazole and faster sorption rate under low pH conditions (pH = 4–9).⁵⁹ Other attempts were carried out using biochar derived from eucalyptus sawdust and used for the removal of nitroimidazole antibiotics. Within two hours of the optimized preparation (activation temperature of 500 °C, activation time of 90 min and an impregnation ratio of 85.0% H_3PO_4 : sawdust of 0.62), the removal efficiency of biochar for metronidazole and dimetridazole at concentrations of 20 mg L⁻¹ and 1000 mg L⁻¹ was 97.1% and 96.4%, respectively.⁶⁰

15.4.1.3 Biochar-based Adsorbents for Heavy Metal Ion Removal

Generally, heavy metal ions can be absorbed on the oppositely charged sites of biochar through electrostatic attraction. The retained heavy metals are considered to be fully hydrated and present in the diffuse double layer as electrostatic outer-sphere complexes.⁶¹ However, the sluggish kinetics of adsorption and limited adsorption capacity obtained in conventional systems restricts the wider application of this technology. Pine biochar was used to remove Cu^{2+} ions from aqueous solutions with an adsorption capacity of 2.73 mg g^{-1} .⁶² Some methods such as surface oxidation and amination endow biochar with abundant surface functional groups (*e.g.*, C–O, COOH, NH_2 , and OH) and greatly improve their adsorption performance. For example, $-\text{NH}_2$ groups were introduced into rice straw-derived biochar surfaces by combining nitrification and amination. The results indicated that the adsorption capacity of the modified biochar was boosted by 72.1%.⁶³

Nanomaterials (such as Fe_3O_4 , MgO, MnO_2 , SiO_2 , and MoS_2) have been applied as adsorbents for heavy metal ion removal due to their high affinity.⁶⁴ Simplified nanoscale zero-valent iron–biochar composites were successfully synthesized and metal ions were separated from solutions *via* electrostatic adsorption, complexation, oxidation, precipitation/co-precipitation, and the formation of type B ternary surface complexes. A rapid adsorption equilibrium of As(III) was achieved within one hour for all cases. The presence of a large mass transfer driving force at the interface between adsorbent and aqueous solutions may account for such fast reaction kinetics.⁶⁵ On the other hand, to solve the difficult separation of biochar, assembling biochar into 3D architectures has been recognized as a more promising method than modifying biochar with magnetic particles as it can be easily removed without any external magnetic field. Wu *et al.* designed a new multifunctional material based on the synthetic properties of MnO_2 -loaded biochar and a 3D polyacrylamide gel to overcome the low sorption capacity and difficulty in solid–liquid separation of biochar with the adsorption equilibrium reaching ten minutes. The rapid adsorption could be ascribed to the loose 3D and porous structure and the excellent water penetration created during the foaming process, which allowed metal ions easy access to the active adsorption sites.⁶⁶ In addition, mycelial pellets show complementary characteristics to biochar with larger particle sizes. With microbial cell growth and physiological metabolism, the biochar unit is induced to assemble into a macroscopic composite material, which effectively addresses the difficulty in recovery and immobilization of biochar. A composite of these two biomass adsorbents would bring further advantages for heavy metal ion removal from industrial wastewater by combining their complementary characters.⁶⁷ In conclusion, using modified biochar to adsorb heavy metals overcomes the limitation of poor adsorption performance and sluggish recovery kinetics in traditional adsorption systems, and provides an economic and feasible solution for the removal of heavy metal ions from water.

15.4.2 Advanced Oxidation Processes

15.4.2.1 Biochar-activated Fenton-like Processes

Fenton-like systems are deemed to be tradition patterns in advanced oxidation processes (AOPs) and take effect through hydroxyl radicals ($\cdot\text{OH}$), which are produced by the reaction between ferrous ions and hydrogen peroxide. To avoid the adverse side effect of Fenton-like systems (including the production of tremendous amounts of sludge and the exacting requirements of acidic conditions), heterogeneous catalysis was found to be more advantageous. Recently, biochar and its derivatives, which is the economic and environmental one among various heterogeneous catalytic materials, have been consistently used as catalysts in Fenton-like systems to degrade organic contaminants in water, and several different mechanisms have been reported.^{68,69} Yan and co-workers verified the single electron transfer mechanism between biochar and H_2O_2 (see eqn (15.1) and (15.2)).⁷⁰ The $-\text{OH}$ on biochar was the active site in the Fenton-like system, which favored the production of $\cdot\text{OH}$. Besides, the hydroquinone–quinone moieties on biochar could also act as the electron donor to facilitate the generation of reactive oxygen species (such as superoxide radicals, $\text{O}_2^{\cdot-}$). Aside from participating in the reaction directly, $-\text{OH}$ on biochar could assist the degradation of pollutants in Fenton-like systems by competing with the metal elements. Qin *et al.*⁷¹ systematically investigated the effect of hydrothermal carbon on the $\text{Fe(III)}-\text{H}_2\text{O}_2$ Fenton-like reaction and the subsequent degradation of alachlor in water, and the results indicated that an Fe(III) complex with surface hydroxyl groups on carbon was formed to favor the electron transfer and facilitate alachlor degradation (three times higher than $\text{Fe(III)}-\text{H}_2\text{O}_2$). Furthermore, recent reports have validated H_2O_2 activation using environmentally persistent free radicals (EPFRs), generated by biochar and existing in a bound form on the internal and external surfaces of

the biochar. EPFRs exist for minutes and up to several months in contrast to transient radicals and are reactive due to unpaired electrons (see eqn (15.3)).⁷² A growing number of studies have suggested that EPFRs are a major contributor to the catalytic degradation process.^{73,74} Studies to date have used EPFRs as a catalytic oxidant to degrade sulfonamide antibiotics,⁷⁵ endocrine disruptors,⁷⁶ organic pollutants⁷⁷ and composite pollutants.⁷⁸ Additionally, defects have also been reported to work in Fenton-like system. The bond energy in H₂O₂ could be reduced due to the defect structure at the boundary of the carbon materials, resulting in an unstable structure.⁷⁹



As one of the key parts of the traditional Fenton reaction, Fe is a conventional doped element in Fenton-like systems, including Fe(iii), Fe(ii), and Fe(0). Under these circumstances, biochar generally boosts the removal rate by avoiding the aggregation of metal components and enhancing the adsorption capacity of catalysts. Wei *et al.*⁸⁰ prepared iron oxide nanoneedle array-decorated biochar fibers. The vertical growth of iron oxide nanoneedle arrays on the surface of biochar fibers maximizes Fe utilization, thereby increasing As removal kinetics and capacity. Besides, the doping of bimetals further enhanced the degradation efficiency of organics. A study by Li *et al.* constructed a Fenton-like system with MnO_x-Fe₃O₄-biochar composites and reducing agents. The results suggested that hydroxylamine increased the ciprofloxacin degradation efficiency from 38.2% to 92.8% with an economic consumption as low as 4.16 US\$ per m,³ well in agreement with the accelerated Fe(iii/ii) cycle and Mn(iii/ii) cycle.⁸¹ The binary redox cycle could promote the electron transfer process and form the periodic reaction. Thus, the $\bullet\text{OH}$ was generated quickly and consistently.⁸² In summary, biochar offers a new strategy to construct efficient and cost-effective heterogeneous Fenton-like systems, which are fabulous substitutes for several expensive carbon counterparts, such as graphene, activated carbon and carbon fibers.

15.4.2.2 Biochar-activated Persulfate Oxidation Processes

Persulfate (PS) was reported to generate sulfate radicals ($\text{SO}_4^{\bullet-}$), which obtained a redox potential similar to the $\bullet\text{OH}$. PS is convenient for transportation and storage and it can conquer the drawbacks of the traditional Fenton-like systems to some extent. Recently, a multitude of studies applied biochar in PS activation systems to achieve the efficient removal of pollutants. Biochar can activate PS by the following means: (1) various oxygen-containing functional groups like carboxyl, hydroxyl, and carbonyl, *etc.* on the biochar surface can stimulate PS to generate reactive oxygen species;^{33,83} (2) the persistent free radical-like semiquinones and phenoxy that exist on the biochar surface can facilitate PS activation;⁸⁴ (3) the defective structure of biochar materials produced during the pyrolysis process, which contributed to PS activation (see eqn (15.4) and (15.5)).⁷⁴ Ouyang *et al.* found that with the increase of biochar pyrolysis temperatures, sp³ carbon would be modulated and transformed, resulting in the collapse of the carbon skeleton, and generation of more defect structures. The defect structures of biochar, such as edge defects, curvatures and vacancies that can generate dangling σ bonds making their π -electrons non-confined by edge carbons, donate electrons from biochar to peroxymonosulfate to generate $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ that caused a 71.4% removal rate of 1,4-dioxane;^{85,86} (4) biochar can provide electrons from its graphite-like electron donor-transfer complex and transfer them from pollutants to PS *via* electronic shuttles;⁸⁷ (5) the electron holes formed when biochar provides electrons might act as active sites to activate PS^{88,89} (see Figure 15.4).

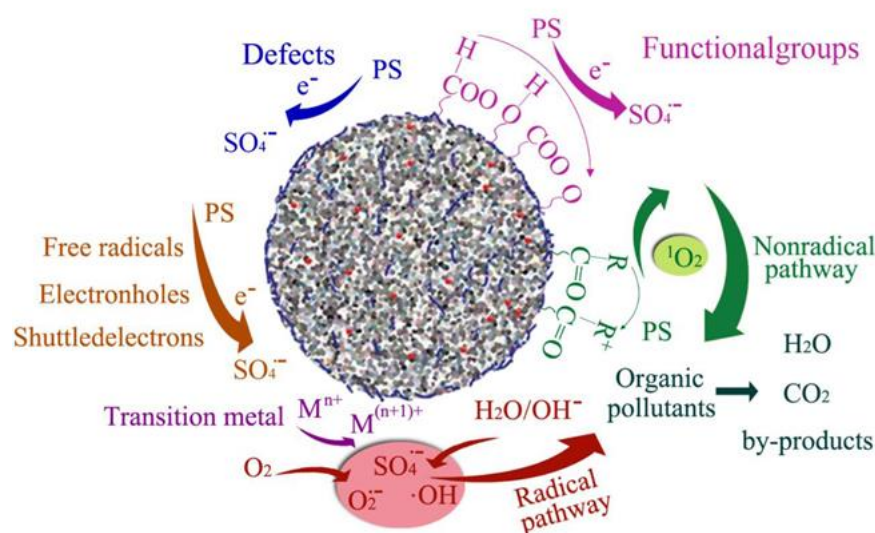


Figure 15.4 The mechanisms involved in the activation of PS by biochar. Adapted from ref. ⁸⁹ with permission from Elsevier, Copyright 2021.

It is intriguing to note that biochar supported catalysts for PS activation have been successfully utilized to eliminate emerging contaminants like pharmaceuticals, estrogens, personal care products as well as dyes and phenolic compounds.⁹⁰ Biochar supported with nano zero-valent iron has been successfully employed in PS activation and more than 80% degradation efficiency was reported in all cases.^{91,92} The study by Chen and co-workers put forward a system of Co_3O_4 and rice straw-derived biochar developed *via* a hydrothermal method that activated PS for the degradation of ofloxacin.⁹³ A recent addition to the cobalt biochar catalytic system is sludge-derived biochar impregnated with CoO and nano Co_9S_8 enclosed by nitrogen and sulfur ($\text{CoO-Co}_9\text{S}_8@\text{N-S}$ -biochar) system.⁶ Co^{2+} activates PS and gets converted to Co^{3+} . Owing to the semiconducting nature of Co_9S_8 , the Co^{3+} can regenerate Co^{2+} by the transfer of electrons from lattice S^{2-} to Co^{3+} . This conversion enhanced the peroxymonosulfate activation and achieved complete degradation of sulfamethoxazole with a rate constant of 0.346 min^{-1} .



15.4.2.3 Biochar-activated Photocatalytic Processes

Photocatalysis is considered as a renewable and sustainable technique to tackle the increasingly serious environmental problems. A myriad of efforts has been made to achieve enhanced photocatalytic efficiency. Narrowing the band gap of photocatalysts and suppressing the recombination rate between electrons and holes are the major routes. As a low-cost carbonaceous material, biochar has been introduced in photocatalytic systems to assist the light irritation process. Different from the role played in PS activation systems and Fenton-like systems, biochar usually plays a subordinate role in the photocatalytic system. Various photocatalysts such as TiO_2 -biochar, ZnO -biochar, CdS -biochar, and Ag -biochar have been applied for the photodegradation of organics.⁹⁴ Biochar is doped with these catalytic nanoparticles due to its porous structure, good conductivity and stability, and optical properties.⁹⁵ These abilities when combined with the catalytic ability of the nanoparticles result in increased efficiency of photodegradation. Zang and Lu synthesized TiO_2 -biochar (coconut shell) for photocatalytic decolorization of reactive brilliant blue KN-R.⁹⁶ The TiO_2 nanoparticles were evenly distributed on the biochar surface, and when incident light energy was equal or greater than their bandgap, electrons and holes will be generated and separated. These holes react with water and OH^- to form $\bullet\text{OH}$ and electrons react with O_2 to form

$O_2^{\cdot -}$. These two radicals oxidize the KN-R molecules and the intermediates. The biochar prevents the recombination of this electron-hole pair, thus increasing the efficiency.⁹⁷ A large number of investigations have confirmed that biochar may serve as a promising and affordable host for photocatalytic and adsorption applications.

15.4.2.4 Other AOP Systems

Aside from the technologies mentioned above, other AOPs have been explored as well. For instance, Yao *et al.*⁹⁸ prepared a novel Pd-N loofah sponge-derived biochar material, and it acted as the cathode in an electrocatalytic system. The results show that N-doped biochar not only provides more tunable adsorption active sites (improving the adsorption capacity), but also disrupts the electronic and spin culture of sp^2 -hybridized carbon to facilitate the electron transfer (enhancing the electrocatalytic reduction activity).⁹⁹ In addition, biochar can also be used as a sonocatalyst to reduce the energy and enhance the degradation efficiency, where $\cdot OH$ dominated these sonocatalytic processes, and removal could be achieved by pre-adsorption and radical oxidation reactions on the surface of biochar.¹⁰⁰ It was noted that biochar produced at high temperature exhibited a hydrophobic nature and possessed an enormous surface area, which turned out to be an advantage because of enhanced cavitation bubble formation in reactions involving ultrasonication using a reducing threshold energy.^{89,101}

15.5 Economic Analysis

Cost is always a determining factor for the practical implementation of a technology. The primary cost of biochar production is the feedstock collection and pyrolysis, while the feedstock transport, biochar transport, and biochar application have small contributions to the total. It has been calculated that the cost of biochar production *via* pyrolysis is estimated as \$21.23–26.81 per ton of dry matter and the total operating cost is \$25.02–31.58 per ton of dry matter.¹⁰² Although the cost of biochar production is relatively high, the environment impacts associated with the production of biochar are significantly lower than other carbonaceous materials of similar properties.¹⁰³ As an example, Roberts *et al.* analyzed the net greenhouse gas emissions of biochar and found that a carbon abatement ranging from 0.07 CO_2eq for cardboard to 1.25 CO_2eq per ton of wood waste, which is in line with the results of Ibarrola *et al.*¹⁰⁴

15.6 Concluding Remarks and Prospects

In this chapter, recent advances in the fundamental understanding, rational design, and applied developments of biochar were systematically summarized. Several functionalization strategies (*e.g.*, physical, and chemical modification) have been applied to improve biochar's performance. In addition, various applications in the water environment were explored including adsorption of antibiotics and heavy metals and degradation of organic pollutants in AOPs.

Biochar may serve as a viable technology for water treatment. To further bring this promising material to industrial engineering applications, advances in nanocomposite and process design will be the primary drivers for biochar technology evolution. This nanocomposite design maximized the advantages of biochar and nanoparticles, which has potential for superior selectivity and precise recognition of target compounds in the complex water matrix. In addition, compared with powder-form biochar, innovative membrane design could be used as a single stand treatment unit without requiring post-treatments to separate and recover nanoparticles from treated water after reaction. To develop scalable production protocols, future research efforts will also aim for large-scale conversion from the laboratory-scale to practical application. Overall, the utilization of biochar is springing up rapidly and it is believed that its studies will be more fully explored in the foreseeable future.

Abbreviations

LHD	Layered double hydroxides
AOPs	Advanced oxidation process
$\cdot OH$	Hydroxyl radical
	Superoxide radical

$O_2^{\cdot-}$	
EPFRs	Persistent free radicals
PS	Persulfate
$SO_4^{\cdot-}$	Sulfate radical
ROS	Reactive oxygen species
$^1O_2$	Singlet oxygen

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Chapter 16

Nanobubble Technology: Generation, Properties and Applications

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16.1 Introduction

16.1.1 Definition of Nanobubbles

Ultra-small gaseous bubbles with diameters of 10–50 μm and $<1 \mu\text{m}$ are often called microbubbles (MBs) and nanobubbles (NBs).^{1–4} In many cases, MBs and NBs are inseparable and they come together in a mixture of micronanobubbles (MNBs) in many generation processes.⁵ Figure 16.1 shows the key differences in aquatic behavior among bulk bubbles or macrobubbles, and small MBs or NBs. For instance, large bubbles such as macrobubbles and MBs rise up quickly due to buoyance. Meanwhile, some bubbles may decrease in size due to dissolution and collapse. By contrast, due to the dominant Brownian motion, NBs remain suspended and stay in liquid for much longer times (a few hours to weeks) and do not burst.^{6–8} NBs have a higher efficiency of mass transfer compared to bulk scale bubbles due to the high specific surface areas.^{9–11} The high specific surface areas also increase physical adsorption and chemical reactions at the gas–liquid interface. The collapse of NBs creates shock waves, localized heating and even sonochemical processes that may generate reactive hydroxyl radicals ($\cdot\text{OH}$).^{9–11} Therefore, NBs have proven useful in many industrial and engineering applications, such as

detergent-free cleaning,^{12–14} water aeration,^{15–18} water purification and wastewater treatment.^{19–21}

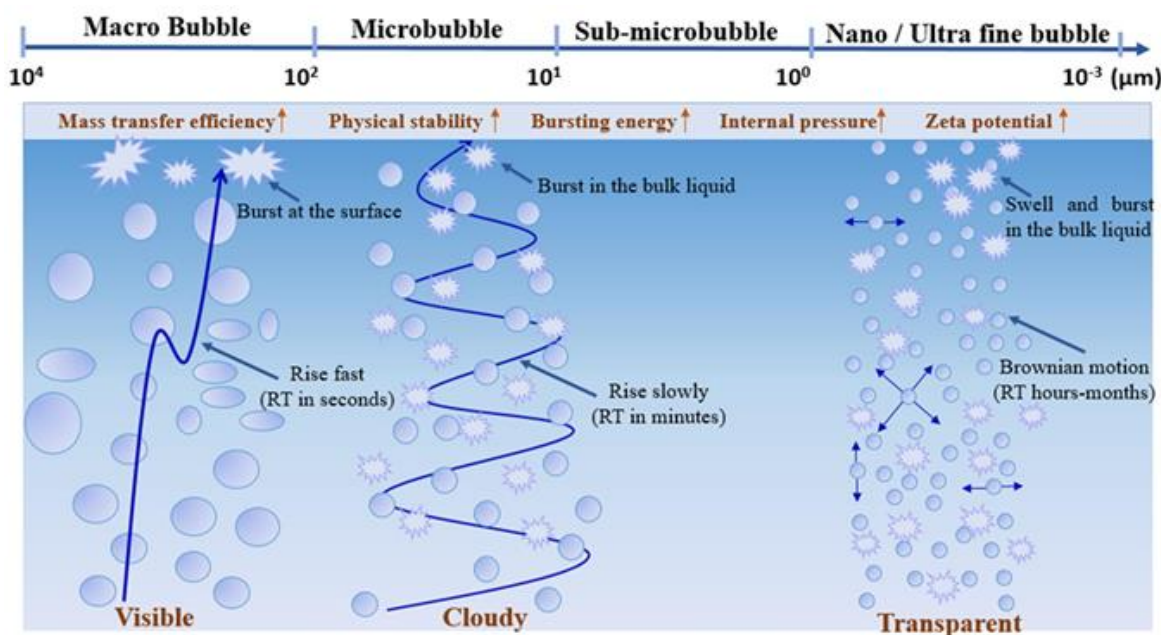


Figure 16.1 Rising behavior of different bubbles and other major aquatic properties. Reproduced from ref. ²¹² with permission from Elsevier, Copyright 2017.

16.1.2 Generation Methods of MBs and NBs

Different generation methods have been reported and investigated for ultrafine bubbles, mainly including membrane bubbling,^{22,23} hydrodynamic cavitation,¹¹ acoustic cavitation or sonication,^{11,24,25} electrochemical cavitation,²⁶ and mechanical agitation.²⁴ For example, injection of pressured gases through hydrophobic membrane pores is reported to produce NBs in liquid.^{22,23} Different from other generation techniques (*e.g.*, hydrodynamic cavitation, electrochemical production, laser ablation or sonication), the membrane bubbling method enables precise control of bubble sizes and internal pressures.¹⁰⁹ The bubble size varies with the surface tension of the membrane, pore size, and internal or injection pressure. The bubble size would decrease on a hydrophobic ceramic membrane compared to a hydrophilic one, because a highly hydrophobic surface may repel and squeeze out bubbles that are hydrophobic by nature.^{27,28}

The transport of NBs across the membrane pores may be affected by many factors such as gas flow and pressure, pore sizes, surface tension of water, fluid viscosity, temperature, and membrane surface energy. In a quasi-static contact

between NBs and membrane pore as illustrated in [Figure 16.2a](#),²⁹ where the relation of solid–vapor interfacial energy (γ_{SV}), the solid–liquid interfacial energy (γ_{SL}), the liquid–vapor interfacial energy (γ_{LV}) and the equilibrium contact angle (θ) at this solid–liquid–vapor interface can be described by the Young equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (16.1)$$

$$2 \cdot r \cdot \sin \theta = D \quad (16.2)$$

where the radius of NBs (r) depends on the pore size (D) and contact angle (θ). The potential effects of gaseous pressures or temperature as well as liquid properties are discussed in detail in Section 16.2.3.

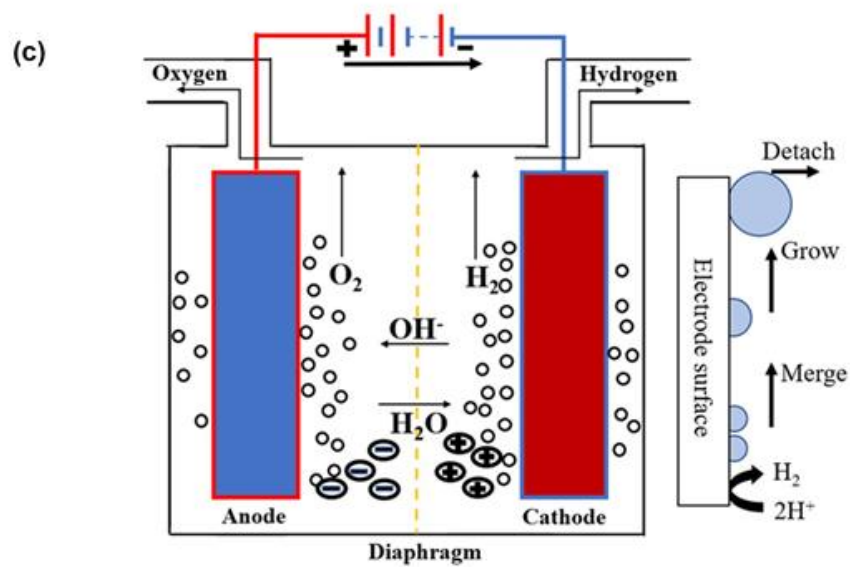
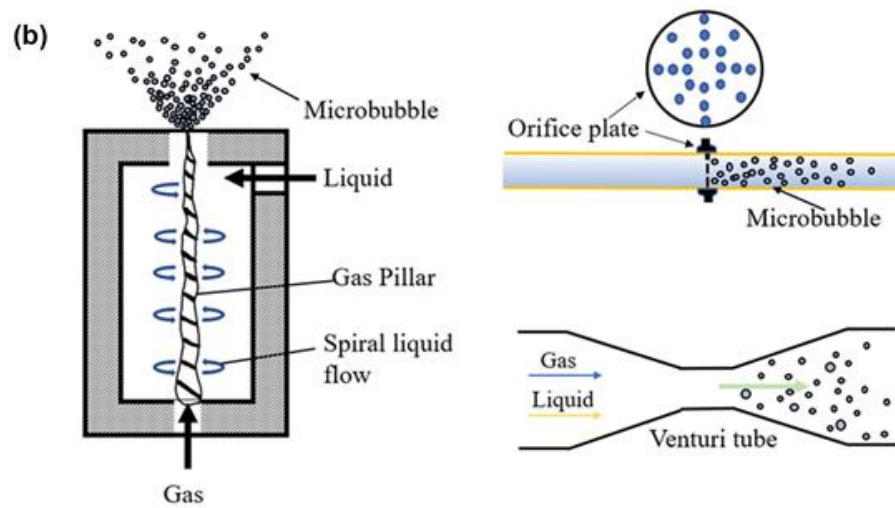
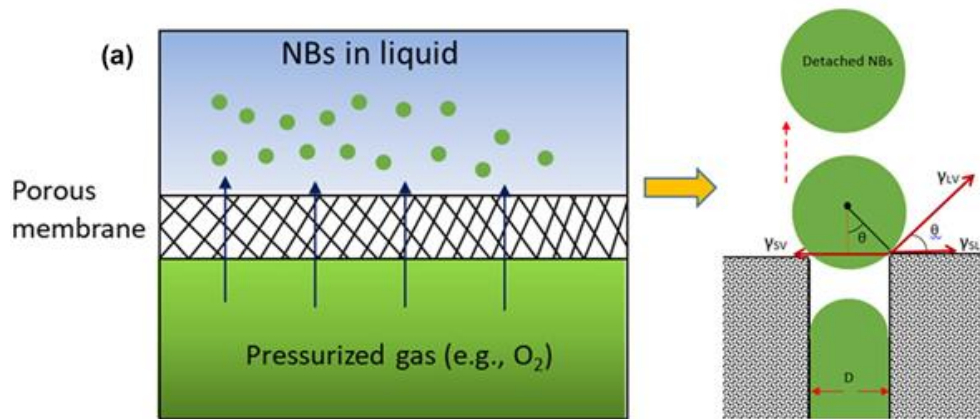


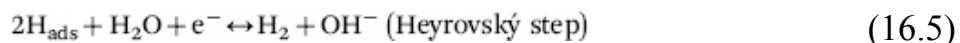
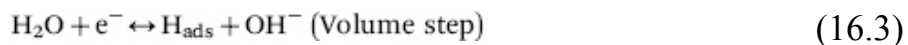
Figure 16.2 (a) Schematics of membrane bubbling and the interfacial process of bubble detachment at one single membrane pore. (b) The spiral liquid flow type, orifice plate and Venturi type. (c) The formation of surface NBs in an electrochemical system.

Cavitation is a rapid process of forming vapor cavities in liquids, because of a sudden pressure drop or depressurization (hydrodynamic cavitation) or due to a passage of ultrasonic waves (acoustic cavitation). Different from boiling, bubble formation in cavitation is caused by a reduction of pressure instead of a temperature change.²⁸ For example, hydrodynamic cavitation achieves the pressure variation due to the flow velocity variation or under the influence of an acoustic field as shown in Figure 16.2b. The spiral liquid-flow type,³⁰ Venturi type³¹ and orifice plate³² follow a hydrodynamic cavitation mechanism.³³ Moreover, hydrodynamic cavitation involves other possible physical or mechanical agitation such as bubble shearing and splitting.^{7,8,25,34–38} However, the major drawback of this cavitation-based generation is the lack of a control of bubble sizes and generation of essentially a mixture of MBs and NBs.

An ultrasonic probe inside the bulk liquid²⁴ or external ultrasonic wave generator²⁵ induces the ultrasonic waves and causes cavitation when there is a high negative pressure exceeding the ambient hydrostatic pressure.³⁹ Two possible mechanisms are proposed to explain the cavitation: (1) homogeneous nucleation, where the liquid molecules rupture when the tensile stress or stretch from the acoustic wave exceeds the intermolecular cohesion forces; (2) heterogeneous nucleation, where nucleation starts from surface cracks as the cracks are filled with gas (“gas pockets”). The gas molecules are agitated to detach and form bubbles.⁴⁰ Similar to acoustic cavitation, optical cavitation is also reported to generate cavitation by passing high intensity particles (*e.g.*, laser, proton and neutrinos) into the liquid.^{11,28,41}

The formation of surface and bulk NBs in an electrochemical system has increasingly been studied.^{42–44} Typically, when an electrical current runs through the electrode surface that is immersed into a given solution,²⁶ surface electrochemical reactions will generate surface nuclei of gaseous molecules and they merge and grow into NBs that eventually detach from the electrode surface. Water electrolysis, for example, splits water into hydrogen and oxygen gases as shown Figure 16.2c. Typically, an electrolyzer consists of an anode and a cathode separated by an ion exchange membrane. A direct current (DC) is applied to run currents through anode, electrolyte and cathode, where anodic reactions involve electron sequestration from electrolyte (*e.g.*, water) and cathodic reactions donate electrons to electrolyte and achieve reductive reactions such as hydrogen evolution as illustrated in Figure 16.2c.

The cathodic hydrogen evolution reaction (HER) follows the Volmer–Tafel and Volmer–Heyrovský mechanisms,^{45–47} which involves the formation of adsorbed hydrogen in eqn (16.3) and either chemical desorption eqn (16.4) or electrochemical desorption eqn (16.5).



Where H_{ads} is an adsorbed hydrogen atom. Hydrogen bubble formation is determined by the bond strength between hydrogen and the electrode surface. Platinum (Pd) has the lowest heat of adsorption of hydrogen ($\Delta H_{\text{ads,Pd,298}}(\text{H}_2) = 83 \text{ kJ mol}^{-1}$), followed by nickel (Ni) with a $\Delta H_{\text{ads,Ni,298}}(\text{H}_2)$ of 105 kJ mol^{-1} .⁴⁸ Electrode properties, electrolyte types and concentrations, and temperature also influence the hydrogen bubble formation. For example, an electrode surface with edges and cavities will favor electron transfer and hydrogen ion adsorption and conversion into gas nuclei and hydrogen NBs.

16.2 Bubble Properties and Behavior in Aquatic Environments

16.2.1 Bubble Sizes, Shapes, and Rising Behavior

In liquid environments, ultrafine bubbles undergo many intriguing and dynamic processes or phenomena such as shape deformation, swelling or shrinkage, rising, coalescence, collapse and dissolution, which may interplay with each other. The typical bubble shapes are spherical, ellipsoidal, and spherical cap depending on the hydrodynamic shear stresses. The surface tension at a gas–liquid interface tends to hold gas molecules together and minimize the bubble surface or surface energy, which corresponds to a spherical shape.⁴⁹ A bubble is considered spherical when the lengths on two principle axes vary by less than 5%,⁵⁰ where the major axis is along the longest distance between two points of the projected bubble area, and the minor axis is the longest line perpendicular to the major axis. The spherical shape may occur when either Reynolds or Bond numbers are low ($\text{Re} < 1$ or $\text{Bo} < 1$). A simulation study by Tripathi, Sahu, and Govindarajan indicated that bubble shapes are a function of the Eötvös number (a ratio of buoyancy and interfacial tension

force) and the Galilei number (a ratio of the inertial and viscous forces) as shown in Figure 16.3.

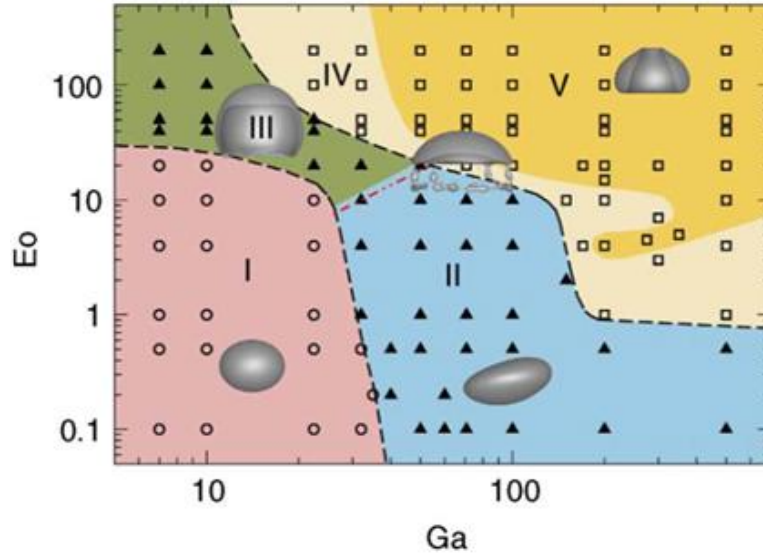


Figure 16.3 Different regimes of bubble shapes under different Eötvös numbers and Galilei numbers. The different regions are axisymmetric (circle) asymmetric (solid triangle), and breakup (square). The two shades within the breakup regime represent the peripheral breakup region (IV) and the central breakup region (V). Reproduced from ref. ⁵¹ with permission from Macmillan Publishers Ltd, Copyright 2015.

According to the report from Bhaga and Weber,⁵² bubble shapes vary with different bubble rising velocities, density differences of liquid/gas phases and liquid viscosity. With a small Reynolds number ($Re = 5$), the bubble shape would still remain spherical for low Bo numbers and flat or slightly dimpled for high $Bond$ numbers. Elliptic/oblate ellipsoid shapes are observed with $5 < Re < 20$ or $0.5 < Bo < 20$. A spherical-cap bubble is observed at $Re > 100$. Skirt bubbles are formed at $50 < Re < 200$ and $100 < Bo < 200$. Toroidal bubbles (ring-shaped bubbles) are observed at $100 < Re < 200$ and $100 < Bo < 200$.⁵³ The non-dimensional Eötvös number (Eo) or the Bond number (Bo), Morton, Reynolds, and Weber numbers are defined as follows:

$$Bo = \frac{g(\rho_L - \rho_G)d^2}{\sigma} \quad (16.6)$$

$$Mo = \frac{g(\rho_L - \rho_G)\mu_L^4}{\rho_L^2\sigma^3} \quad (16.7)$$

$$\text{Re} = \frac{\rho_G U_b d}{\mu_L} \quad (16.8)$$

$$\text{We} = \frac{\text{Drag Force}}{\text{Cohesion Force}} = \text{Re}^2 \sqrt{\frac{\text{Eo}}{\text{Mo}}} \quad (16.9)$$

$$\text{Eo} = \text{Bo} = \frac{\Delta \rho g L^2}{\gamma} \quad (16.10)$$

where g is the gravity acceleration (9.81 m s^{-2}), d is the diameter of a spherical bubble (m), $(\rho_L - \rho_G)$ is the density difference between liquid and gas (g cm^{-3}), σ is the surface tension at the air–water interface ($72.86 \times 10^3 \text{ N m}$), μ_L is the dynamic viscosity of the liquid (e.g., for water, $8.90 \times 10^{-4} \text{ Pa s}$ at 25°C), and U_b is the bubble's rising velocity (m s^{-1}).

Similar to shapes, bubble sizes in liquid are subjected to dynamic changes due to factors such as dissolution. To account for the variations of bubble sizes in liquid, there are two typical measures of the mean bubble sizes, a number/average (mean) size ($\bar{d}$) in polydisperse flows and a Sauter mean/average diameter (d_{32}),⁵⁴ which are defined respectively below:

$$\bar{d} = \frac{\sum_{i=1}^N d_i f_i}{\sum_{i=1}^N f_i} \quad (16.11)$$

$$\bar{d}_{32} = \frac{\sum_{i=1}^N d_i^3 f_i}{\sum_{i=1}^N d_i^2 f_i} \quad (16.12)$$

where f_i is the absolute frequency for the bubbles with a size d_i .

Bubble sizes affect the bubble rising velocity if they rise. Whether or not bubbles may rise depends on the interplay of Brownian motion and buoyancy force on bubbles. The Peclet number (Pe) was calculated:²³

$$\text{Pe} = \frac{\pi(\rho_L - \rho_G)gd^4}{24k_B T} \quad (16.13)$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$) and T is the absolute temperature (e.g., 298 K). Peclet numbers at different diameters of NBs are compared in Figure 16.4. When the diameter of bubbles is smaller than 1020 nm, the Peclet number becomes less than 1, which indicates that the Brownian motion dominates the movement of bubbles and the buoyancy-induced rising or floating could be ignored. This prediction coincides with the definition of NBs with a cutoff size of 1 μm , below which NBs are not experiencing significant rising unlike bulk or large bubbles.

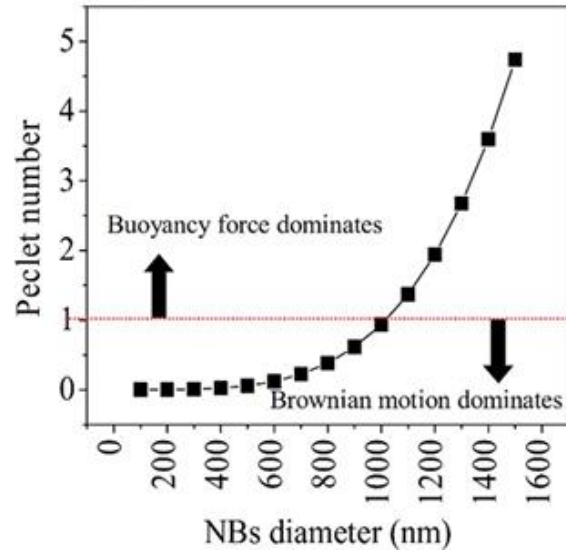


Figure 16.4 Peclet number *versus* the bubble diameters of air NBs. Reproduced from ref. [23](#) with permission from Mary Anne Liebert, Inc.

The rising velocity is usually governed by a balance of gravity F_G , buoyancy (Archimedes) F_f and drag forces F_D . The terminal rising velocity of a spherical bubble is expressed as:

$$U_{b,sp} = \frac{g(\rho_L - \rho_G)d^2}{6\mu_L} \left(\frac{1 + \frac{\mu_G}{\mu_L}}{\frac{2 + 3\frac{\mu_G}{\mu_L}}{\mu_L}} \right) \quad (16.14)$$

For most liquid and gases, which have viscosities and densities of $\mu_G \ll \mu_L$ and $\rho_G \ll \rho_L$, eqn (16.14) is simplified to:

$$U_{b,sp} = \frac{g\rho_L d^2}{12\mu_L} \quad (16.15)$$

The above calculation is applicable only when the bubble size is smaller than 0.1 of the surrounding environment such as a reactor ($d/W < 0.1$, W is the reactor width) such that the bubble velocity is not influenced by the reactor dimension nor the interactions with other bubbles. For ellipsoid shapes,⁵⁵ oblate or prolate spheroidal bubbles⁵⁶ and spherical-cap bubbles,⁵⁷ their terminal rising velocities in a laminar flow are given by:

$$U_{b,el} = 0.14425 g^{\frac{5}{6}} \left(\frac{\rho_L}{\mu_L} \right)^{\frac{2}{3}} d^{\frac{3}{2}} \quad (16.16)$$

$$U_{b,sph} = \sqrt{\frac{2.14\sigma_L}{\rho_L d} + 0.505gd} \quad (16.17)$$

$$U_{b,cap} = 0.721\sqrt{gd} \quad (16.18)$$

Figure 16.5a compares the rising velocities of bubbles of different shapes and sizes. The rising velocity of spherical and ellipsoid bubbles rises steeply with an increase in bubble size due to a power dependency on bubble cross-section area ($\sim d^2$) indicating that small bubbles essentially behave as rigid spheres. The rising velocity of spheroidal and spherical-cap bubbles is proportional to $\sqrt{d}$. The rising velocity of a spherical bubble increases as the bubble size increases because of a higher buoyancy. As the bubble shape changes to spheroidal, the rising velocity begins to decrease as the bubble size increases because the increased friction or drag force becomes greater than the increased buoyancy. When a spheroidal bubble becomes too large, it changes its shape at around 2 mm into a spherical cap, and its rising velocity slightly increases with an increase in bubble size.⁵⁸

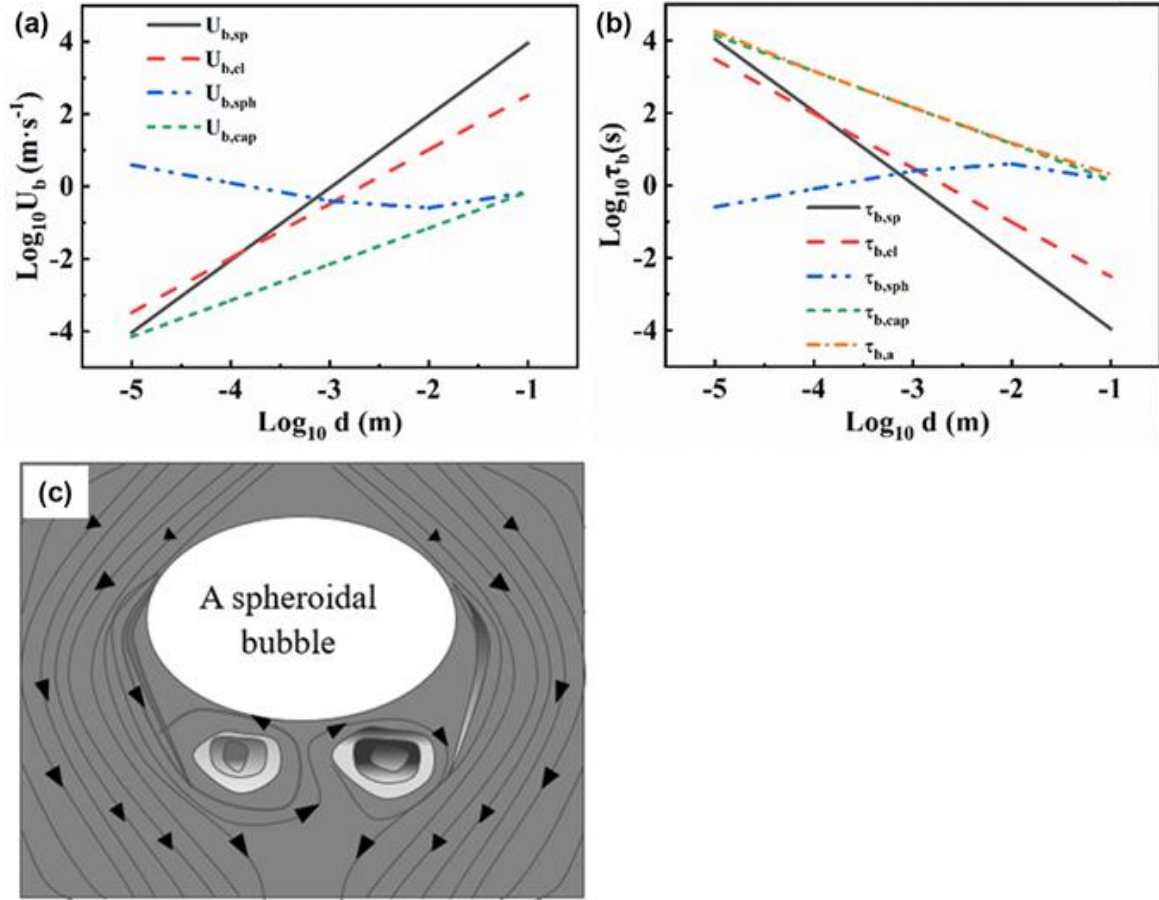


Figure 16.5 (a) Bubble rising velocities of spherical ($U_{b,sp}$), ellipsoid ($U_{b,el}$), spheroidal ($U_{b,sph}$) and spherical-cap ($U_{b,cap}$) bubbles. Calculations are based on eqn (16.15)–(16.18) using water as a liquid and air as a gas, at 25 °C. (b) Bubble residence time of spherical ($\tau_{b,sp}$), ellipsoid ($\tau_{b,el}$), spheroidal ($\tau_{b,sph}$), and spherical-cap ($\tau_{b,cap}$) bubbles. Calculations are based on eqn (16.15)–(16.19) and other parameters such as ρ_L (997 kg m³), μ_L (8.90×10^{-4} Pa s⁻¹), σ_L (71.99×10^{-3} N m⁻¹) and L (1 m). (c) Simulated mean velocity streamlines of the axisymmetric wave or flow that passes around a floating oblate spheroid bubble (the white region) with two swirls formed under the rising bubble.

Figure 16.5b compares the bubble residence time in liquid as a function of size and shape with a distance from a bubble to the gas–liquid interface as L . For small bubble sizes, except spheroidal bubbles, other shapes all have a decreasing residence time with the increase of bubble size. At large bubbles sizes, spherical bubbles have the least residence time in liquid ($\tau_{b,sp}$) compared other shapes. Moreover, spheroidal bubbles have much shorter hydraulic residence or retention time (HRT) than spherical ($\tau_{b,sp}$), ellipsoid ($\tau_{b,el}$), and spherical-cap ($\tau_{b,cap}$) bubbles. Particularly, a new equation in eqn (16.20) is proposed to determine the residence

time without identifying the bubble shape in advance. The predicted results (short dashed line) largely overlaps with the results (dash-dotted line) for ellipsoid ($\tau_{b,el}$).

$$\tau_b = \frac{L}{U_b} \quad (16.19)$$

$$\begin{aligned} \tau_b &= L \sqrt{\frac{1}{U_{b,sp}^2} + \frac{1}{U_{b,el}^2} + \frac{1}{U_{b,sph}^2} + \frac{1}{U_{b,cap}^2}} \\ &= L \sqrt{\frac{144\mu_L^2}{g^2\rho_L^2d^4} + \frac{\mu_L^{\frac{4}{3}}}{0.14425^2g^{\frac{5}{3}}\rho_L^{\frac{4}{3}}d^3} + \frac{1}{\frac{2.14\sigma_L}{\rho_L d} + 0.505gd} + \frac{1.387}{gd}} \end{aligned} \quad (16.20)$$

As a result of the different rising velocities, the HRT or how much time a bubble resides inside the liquid will differ with bubble sizes or shapes, which is critical for eliciting many anticipated performances such as aeration and ozonation for water disinfection. Higher HRT values usually yield better performances of mass transfer or reaction efficiency. Bubbles do not usually rise vertically straight during their rise in water but rather exhibit many complicated trajectories such as spiraling, zigzagging, or rocking motion. Gas bubbles will raise rectilinearly only when they are small and Reynolds number is low. The transition to a non-rectilinear path is caused by an instability of the axisymmetric water flow or wave that passes around the bubble interface and becomes two-threaded. As shown [Figure 16.5c](#), the two threads of flow wave have opposite circulation and thus provide a lift force similar to the trailing vortices of an airplane.⁵⁹

16.2.2 Colloidal Behavior and Interactions of Ultrafine Bubbles

NBs may undergo many dynamic processes, such as dissolution, coalescence and collapse.¹¹ These processes are influenced by the types of NBs (*e.g.*, air, oxygen and nitrogen) and environmental factors such as pH, ionic strength, and organic matters.²³ [Figure 16.6](#) shows that three different types of NBs exhibited different stable bubble size distribution and zeta potentials. Furthermore, membrane pores size, surface energy, and the injected gas pressures were shown to affect the bubble size and zeta potential.²² For example, increasing the injection air pressure reduces the bubble size, which is explained by the Laplace–Young Equation.^{60,61} The bubble size distribution of oxygen NBs in water in sealed containers was measured under different temperatures for 15 hours, which shows that the size of ONBs reduced from 255 ± 30 nm under 6 °C to 147 ± 11 nm under 40 °C. The decreased

NBs’ size under higher temperatures may be due to the decreased surface tension of water at high temperatures and removal of large-sized NBs.^{62,63}

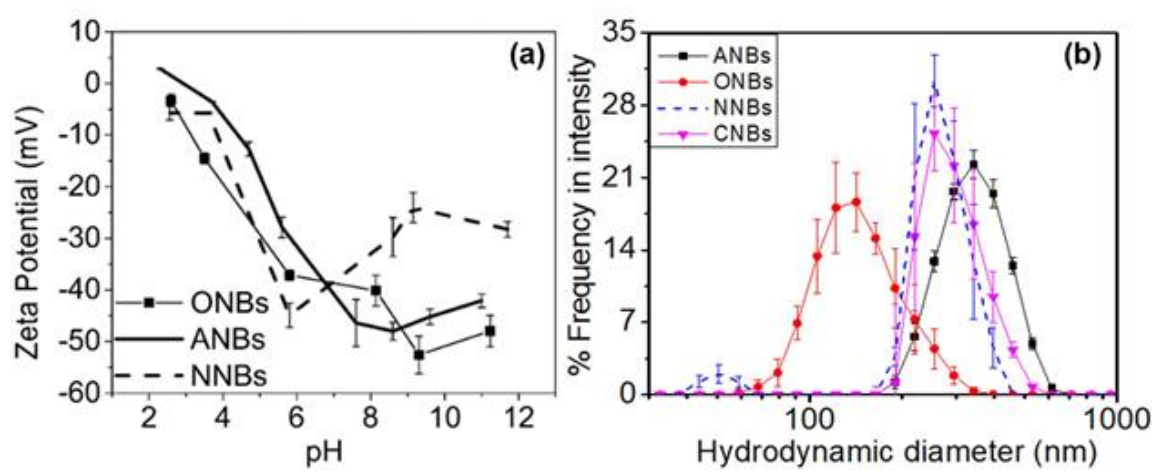


Figure 16.6 (a) Zeta potential for ANBs, ONBs, and NNBs at different pH values; (b) hydrodynamic diameter of air NBs (ANBs), oxygen NBs (ONBs), nitrogen NBs (NNBs), and carbon dioxide NBs (CNBs). Reproduced from ref. ²³ with permission from Mary Anne Liebert, Inc.

Similar to aqueous thin-liquid films,^{64–66} and due to the softness and deformation potential, the bubble–bubble interaction energy may be studied by the soft-particle extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory (Table 16.1).^{64–69} Soft-particle EDLVO calculation is used to simplify the quantification of surface interaction energies of two identical soft particles such as bacterial cells (before attachment, coalescence or deformation occurs). Here the sphere–sphere geometry was adopted in the application of EDLVO equations. This hypothesis is made because NBs, due to the high internal pressure, are believed to have taut inflexible surfaces (like high pressure balloons) that limit distortion.⁷⁰

Table 16.1 Parameters and values used in the EDLVO theory analysis. Reproduced from ref. ²³.

A	a_1 and a_2 are the two interacting particle or bubble radii (nm)
R	Radius of NBs (nm)
A_{131}	The effective Hamaker constant (J) for bubbles (1) interacting with bubbles (1) in the aqueous medium (3), which is approximately equal to 4×10^{-20}
A_{132}	The effective Hamaker constant (J) for bubbles (1) interacting with subject (2) in the aqueous medium (3)
h	The separation distance between the two interacting bubbles (nm)

λ_c	The “characteristic wavelength” of the interaction, often assumed to be 100 nm. ⁸⁴
K	The inverse Debye length (m^{-1})
N_A	Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$
e	Unit charge, $1.602 \times 10^{-19} \text{ C}$
c_i	c_i is the molar concentration of one species ions (i), mol L^{-1}
ε_0	The dielectric permittivity of a vacuum, $8.854 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$
ε	The dielectric constant of water, 78.5 (dimensionless)
η	The viscosity of the liquid media (<i>e.g.</i> , water: $8.90 \times 10^{-4} \text{ Pa s}^{-1}$)
z_i	The valence of the i th ion
k_B	Boltzmann constant, $1.38 \times 10^{-23} \text{ J K}^{-1}$
T	The absolute temperature taken as 298 K
n	The molar concentration of ionic species in the medium (mol m^{-3}) multiplied by Avogadro's number (mol^{-1})
ψ	The surface potential (mV)
ξ	ξ_1 and ξ_2 are zeta potentials of spherical particle (1) and spherical particle (2), respectively (mV)
$\Delta G_{131,D_0}^{AB}$	The standard polar or acid–base free energy of interaction between two identical interacting NBs (1) in water (3) at the distance (D_0)
$\Delta G_{132,D_0}^{AB}$	The standard polar or acid–base free energy of interaction between NBs (1) and subject (2) in water (3) at the distance (D_0)
λ	The correlation length, or decay length, of the molecules of the liquid medium. For pure water, it is approximately 0.6 nm ⁸⁵
h_0	The minimum equilibrium distance due to Born repulsion, 0.157 nm ⁸⁶
Φ	The normalized dimensionless surface potentials of NBs ⁸⁷
θ	The water contact angles of NBs

NBs often carry electric charges when they are dispersed in electrolyte due to the surface sorption of counter ions. The cloud of counter ions surrounding the charged bubbles results in an electrical repulsion or attraction between them depending on the net interaction energy. The zeta potential is the potential difference between the bulk fluid and the layer of counter ions that remain associated with the charged NBs. When zeta potential is high in magnitude (positive or negative), electrical repulsion between colloidal bubbles is strong and would stabilize the bubble suspension. When zeta potential is close to zero, colloidal bubbles may coalesce due to the van der Waals forces or attraction. When that happens, colloidal bubbles will coalesce or aggregate.

In general, a two-step mechanism (adsorption and attachment) could mediate bubble coalescence⁷¹. Both steps are influenced by the chemical properties of interacting surfaces and the electrolytic environment.^{72–74} As the bubbles approach each other they will experience short-range forces such as Lifshitz–van der Waals and electrostatic forces, as usually described by the DLVO theory,^{75,76} which however is preferably used for monovalent salts at relatively low concentrations. Although the dominating factors involved in NBs interactions remain elusive, quantitative information on the nonspecific interaction force between NBs can be directly obtained with the extended DLVO theory assuming that Lifshitz–van der Waals, Lewis acid–base (AB) interaction, and electrostatic forces are the dominant forces. The electrostatic forces obtained for each condition investigated were modeled using the Ohshima's soft particle electrophoresis modeling.⁷⁷

The total interaction energies, $U_{\text{Total}} - \text{EDLVO}$, between the interacting NBs are calculated by:

$$U_{\text{Total-EDLVO}} = U_{\text{vdw}} + U_{\text{EL}} + U_{\text{AB}} \quad (16.21)$$

where U_{vdw} is the van der Waals interaction energy ($k_{\text{B}}T$), U_{EL} is the electrostatic interaction energy ($k_{\text{B}}T$), and U_{AB} is the Lewis acid–base interaction energy ($k_{\text{B}}T$). Besides these three forces, other non-DLVO forces, such as hydration force,^{78,79} hydrophobic force,⁷¹ oscillatory force,⁸⁰ osmotic force,^{81,82} and steric, and Helfrich repulsion force (an entropy effect),⁸³ may play a role under different scenarios of bubble–bubble or bubble–surface interactions.

16.2.2.1 Calculation of Lifshitz–van der Waals Interaction Energy

The retarded Lifshitz–van der Waals interaction energy for a sphere–sphere or particle–particle geometry is calculated when $h < \lambda_{\text{c}}/4\pi$ and $h < a_i$.⁸⁹

$$U_{\text{vdw}} = \frac{-A_{132}a_1a_2}{6h(a_1 + a_2)} \left[\frac{1}{1 + 11.12h/\lambda_{\text{c}}} \right] \quad (16.22)$$

When $a_1 = a_2$, the eqn (16.22) can be simplified to be:

$$U_{\text{vdw}} = \frac{-A_{131}a}{12h} \left[\frac{1}{1 + 11.12h/\lambda_{\text{c}}} \right] \quad (16.23)$$

For a sphere–plate geometry, the following equation is used calculate the non-retarded Lifshitz–van der Waals interaction energy when $h < \lambda_c/4\pi$ and $h < a_i$.⁹⁰

$$U_{\text{vdW}} = -\frac{A_{132}}{6} \left[\frac{a}{h} + \frac{a}{h+2a} + \ln\left(\frac{h}{h+2a}\right) \right] \quad (16.24)$$

16.2.2.2 Estimation of Hamaker's Constant

The Hamaker constant (A_{132}) for interacting subject 1 and subject 2 in the medium 3 is estimated on the basis of Lifshitz theory, which is given by two terms, $A_v = 0$ and $A_v > 0$, respectively, for the dipole–dipole and dipole–induced dipole interactions and for the dispersion forces.⁹¹

$$A_{132} = A_{v=0} + A_{v>0} \approx \frac{3}{4} k_B T \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) \quad (16.25)$$

$$+ \frac{3h_p \nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2} \left[(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2} \right]}$$

where, k_B is the Boltzmann constant, T is the temperature, ε_i and n_i are static dielectric constant and refractive index of phase i , h_p is the Planck constant (6.626×10^{-34} J s), ν_e is the electronic absorption frequency, which is assumed to be constant (3×10^{15} s⁻¹). ε_i is the intrinsic properties of the materials.⁹² ε_i can be detected by instruments such as network analyzers, LCR meters, and impedance analyzers.^{93,94} Capacitance is considered to be one of the simplest measurable dielectric properties in dielectric characterization, which can be converted to dielectric constant.⁹² Usually, $\varepsilon_1 = 1.00$ for air and ε_3 for liquid (e.g., water) depends on the ionic strength (for $c = 0.001$ M, $\varepsilon_3 = 79.98$; for $c = 0.01$ M, $\varepsilon_3 = 79.84$; for $c = 0.1$ M, $\varepsilon_3 = 78.48$). For air and water, $n_1 = 1.00$ and $n_3 = 1.333$. For the “symmetric case” of two identical phases 1 interacting across medium 3, [eqn \(16.25\)](#) reduces to the simple expression:⁹⁵

$$A_{131} = \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h_p \nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (16.26)$$

Another reported method to estimate A_{132} is the use of polar and non-polar interface energy components by the method of van Oss:

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (16.27)$$

$$A_{ii} = 24\pi D_0^2 \times \gamma_i^{\text{LW}} \quad (16.28)$$

where D_0 is the minimum equilibrium distance (0.157 nm). Combining the above two equations yields:

$$A_{132} = 24\pi D_0^2 \left(\sqrt{\gamma_1^{\text{LW}}} - \sqrt{\gamma_3^{\text{LW}}} \right) \left(\sqrt{\gamma_2^{\text{LW}}} - \sqrt{\gamma_3^{\text{LW}}} \right) \quad (16.29)$$

The apolar surface tension component, γ_i^{LW} , could be obtained through contact angle measurements on the flat surfaces of the interacting particles using the thermodynamic-based harmonic mean (HM) model.⁹⁶ This model relates the contact angle (θ) to γ_i^{LW} , the apolar part of surface tension of condensed material (i) caused by dispersion energy between molecules, and to γ_i^+ or γ_i^- , the polar part of surface tension of condensed material (i) caused by dipole interaction included dipole moments and hydrogen bonds according to the extended Young's equation:⁹⁷

$$(1 + \cos \theta) \times \gamma_L = 2 \left(\sqrt{\gamma_i^{\text{LW}} \gamma_L^{\text{LW}}} + \sqrt{\gamma_i^+ \gamma_L^-} + \sqrt{\gamma_i^- \gamma_L^+} \right) \quad (16.30)$$

where γ_L is the probe liquid surface energy (mJ m^{-2}), which is known for the probe liquids (water: 72.8, formamide: 58, glycerol: 64, and 1-bromnaphthalene: 44). This method has been reported for the determination of the surface tension components on surfaces of bacteria, algae, polymer membranes and inorganic oxides.^{69,98,99} However, for gaseous bubbles in liquid and their surface tension determination, it is often not straightforward or easy to conduct the liquid's contact angel measurement. Some works observed that contact angle of the NBs was around 110° on hydrophobized Si(100) substrates detected by tapping-mode atomic force microscopy.^{100–102}

16.2.2.3 Calculation of the Electrostatic Interaction Energy

The electrostatic interaction energy is calculated using the linearized version of the Poisson–Boltzmann expression:⁸⁷

$$U_{EL} = \frac{2\pi a_1 a_2 n k_B T}{(a_1 + a_2) \kappa^2} (\Phi_1^2 + \Phi_2^2) \left[\frac{2\Phi_1 \Phi_2}{\Phi_1^2 + \Phi_2^2} \ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) + \ln(1 - e^{-2\kappa h}) \right] \quad (16.31)$$

When $a_1 = a_2$ and $\Phi_1 = \Phi_2$, eqn (16.31) can be simplified to be:

$$U_{EL} = \frac{2\pi a n k_B T \Phi^2}{\kappa^2} \left[\ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) + \ln(1 - e^{-2\kappa h}) \right] \quad (16.32)$$

where κ^{-1} is the Debye length (nm), indicative of the thickness of the electrical diffuse layer as a function of the ionic strength and electrolyte:

$$\kappa^{-1} = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 N_A I e^2}} \quad (16.33)$$

and Φ is the normalized dimensionless surface potential of the NBs, which is related to the surface potential (ψ) by $\Phi = z \cdot e \cdot \Psi / k_B \cdot T$.⁸⁷ Often, zeta potentials (ζ , mV) are determined by DLS to calculate the surface potential (ψ) using the Debye-Hückel approximation in eqn (16.34).¹⁰³

$$\Psi = \zeta (1 + d/R) \exp(\kappa d) \quad (16.34)$$

here, d is the distance from the bubble's surface to the slipping layer, which is often taken as 0.5 nm,¹⁰³ and R is the Stokes radius and calculated by:¹⁰⁴

$$R = \frac{k_B T}{6\pi\eta D} \quad (16.35)$$

where η is the solution viscosity (Pa s⁻¹), and D is the diffusion coefficient in liquid (cm² s⁻¹).¹⁰⁵

Under the Derjaguin integration approximation, the electrostatic interaction energy between two spherical particles with radii of R_1 and R_2 is also expressed as:^{106,107}

$$U_{EL}(h) = 4\pi\epsilon\epsilon_0 \frac{a_1 a_2}{(a_1 + a_2)} \left[\zeta_1 \zeta_2 \exp(-\kappa h) - \frac{1}{4} (\zeta_1^2 + \zeta_2^2) \exp(-2\kappa h) \right] \quad (16.36)$$

16.2.2.4 Calculation of the Electrostatic Interaction Using the Ohshima's Soft Particle DLVO

In the Ohshima and Kondo's soft particle electrophoresis modeling,^{77,108} the electrostatic interaction energy is still calculated by eqn (16.31) or (16.32). This theory assumes the presence of an ion-penetrable, charged polyelectrolyte layer around a rigid core of soft particles such as biological cells that usually have fixed ionogenic groups in their surface region. For example, “soft” biopolymers on biological cells such as proteins, peptidoglycans, lipopolysaccharides generally render variable charges. The surface potential of soft particles such as large bubbles is related to electrophoretic mobility (μ_E) as follows:

$$\mu_E = \frac{\varepsilon_0 \varepsilon \psi_0 / k_m + \psi_{\text{DON}} / \lambda}{\eta \left(1/k_m + 1/\lambda \right)} + \frac{eZN}{\eta \lambda^2} \quad (16.37)$$

Here, μ_E is the electrophoretic mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$), η is the solvent viscosity ($8.9 \times 10^{-4} \text{Pa s}^{-1}$ for water at room temperature), ZN represents the spatial charge density (M or mol L^{-1}) in the polyelectrolyte region, which describes the effect of the density of the charged groups present within the soft layer on surface potential, λ is a parameter characterizing the degree of resistance to liquid flow in the polyelectrolyte region and $1/\lambda$ indicates the effects of the particle softness on surface potential, k_m is a Debye–Hückel parameter of the surface region, ψ_{DON} is the Donnan potential, which is a measure of surface potential inside the soft layer, ψ_0 is the potential at the boundary between the surface region and the solution and is recognized as the surface potential of soft particles.

$$\psi_{\text{DON}} = \frac{k_B T}{z_i e} \ln \left\{ \frac{ZN}{2z_i c_i} + \left[\left(\frac{ZN}{2z_i c_i} \right)^2 + 1 \right]^{1/2} \right\} \quad (16.38)$$

$$\psi_0 = \frac{k_B T}{z_i e} \left(\ln \left\{ \frac{ZN}{2z_i c_i} + \left[\left(\frac{ZN}{2z_i c_i} \right)^2 + 1 \right]^{1/2} \right\} + \frac{2z_i c_i}{ZN} \left\{ 1 - \left[\left(\frac{ZN}{2z_i c_i} \right)^2 + 1 \right]^{1/2} \right\} \right) \quad (16.39)$$

$$k_m = \kappa \left[1 + \left(\frac{ZN}{2z_i c_i} \right)^2 \right]^{1/4} \quad (16.40)$$

To utilize the above equations, we need to measure the electrophoretic mobility of the dispersed particles or bubbles in a range of electrolyte concentrations (e.g., in

NaCl solutions). From the plot of experimental electrophoretic mobility data against ionic concentrations, curve fitting with eqn (16.37) can determine the two unknown parameters of ZN and $1/\lambda$.

By contrast, for solid or rigid colloidal particles, we apply the Henry's equation to determine their zeta potential from electrophoretic mobility by:

$$\mu_E = \frac{2\varepsilon\zeta \times f(\kappa r)}{3\eta} \quad (16.41)$$

where $f(\kappa r)$ is the Henry's function that depends on the value of κr . κ is the inverse Debye length (m^{-1}) and r is the particle or bubble radius (m). $f(\kappa r)$ is assumed to be 1 (Hückel approximation) or 1.5 (Smoluchowski approximation). The main difference between the two approximations is that the Smoluchowski approximation assumes that the electrical double layer thickness is much thinner than the particles themselves [$\kappa r > 1$], while the Hückel approximation instead assumes the double layer to be much thicker than the radius of the particles [$\kappa r < 1$]. The Ohshima correction is applied when both the Hückel and the Smoluchowski approximation are invalid.

$$f(\kappa r) = 1 + \frac{1}{(1 + \delta)^3} \quad (16.42)$$

$$\delta = \frac{5}{2\kappa r(1 + 2 \exp(-\kappa \cdot r))} \quad (16.43)$$

16.2.2.5 Calculation of the Lewis Acid–Base (AB) Interaction

The Lewis acid–base (AB) interaction is calculated by: ^{109,110}

$$U_{132}^{AB}(h) = \pi \frac{a_1 a_2}{a_1 + a_2} \lambda \Delta G_{132,D_0}^{AB} \exp\left(\frac{h_0 - h}{\lambda}\right) \quad (16.44)$$

When $a_1 = a_2$, eqn (16.44) can be simplified to be:

$$U_{131}^{AB}(h) = \frac{\pi a}{2} \lambda \Delta G_{131,D_0}^{AB} \exp\left(\frac{h_0 - h}{\lambda}\right) \quad (16.45)$$

where $\Delta G_{132,D_0}^{AB}$ and $\Delta G_{131,D_0}^{AB}$ can be estimated by the following equations:

$$\Delta G_{132,D_0}^{AB} = -\frac{K_{132}}{2\pi h_0 \lambda} \quad (16.46)$$

$$\log K_{132} = -7 \left(\frac{\cos \theta_1 + \cos \theta_2}{2} \right) - 18 \quad (16.47)$$

As mentioned above in Section 16.2.2.2, we may also use probe liquids (e.g., water, formamide, and glycerol) to experimentally determine the surface tension properties (γ^{LW} , γ^+ and γ^-). Then, the polar interaction energy $\Delta G_{132,D_0}^{AB}$ could be calculated by the Dupré equation:⁸⁵

$$\begin{aligned} \Delta G_{132,D_0}^{AB} = 2 \left[\left(\sqrt{\gamma_1^+} - \sqrt{\gamma_2^+} \right) \left(\sqrt{\gamma_1^-} - \sqrt{\gamma_2^-} \right) - \left(\sqrt{\gamma_1^+} - \sqrt{\gamma_3^+} \right) \left(\sqrt{\gamma_1^-} - \sqrt{\gamma_3^-} \right) \right. \\ \left. - \left(\sqrt{\gamma_2^+} - \sqrt{\gamma_3^+} \right) \left(\sqrt{\gamma_2^-} - \sqrt{\gamma_3^-} \right) \right] \end{aligned} \quad (16.48)$$

16.2.2.6 Calculation of the Steric Interaction Energy

When there is a coating layer present on the surface of colloidal particles such as polymeric substances, we may estimate the interactions of the surface coating molecules using the steric interaction energy ($k_B T$), U_S , which is expressed as:⁸⁸

$$U_S = \left(\frac{2\pi a_1 a_2}{a_1 + a_2} \right) \left(\frac{\alpha_{Sc} k_B T}{a_m^3} \right) \Phi_{s0}^{\frac{9}{4}} D_{Sc} \left\{ -\frac{16\Gamma D_{Sc}}{\Gamma_0} \times \ln \left(\frac{2\delta}{h} \right) + \frac{4D_{Sc}^{\frac{5}{4}}}{2^{\frac{5}{4}}} \left(\frac{8\Gamma}{\Gamma_0} \right) \left[\frac{1}{h^{\frac{1}{4}}} - \frac{1}{(2\delta)^{\frac{1}{4}}} \right] \right\} \quad (16.49)$$

The first term within the curly brackets in eqn (16.49) accounts for the short-range bridging attraction while the second term represents the excluded volume steric repulsion. The relative magnitudes of these two contributions determine whether polymer adsorption results in bridging attraction or steric repulsion.

Case Study: The Use of the EDLVO to Analyze the Coalescence of NBs in the Presence of Salts or Surfactants

The analysis of the inter-NB interaction energies was calculated for ANBs, ONBs, and NNBs in pure water and in the presence of different ionic strengths and surfactants. The total interaction energy profiles in Figure 16.7 indicate that the energy barriers were substantially high ($> 5000 k_B T$) for the three different NBs in

pure water. The energy barrier peaks decreased to 29–287 $k_B T$ when DTAC (a cationic surfactant), NaCl, and CaCl₂ were added. Adsorption of DTAC molecules on the negatively charged surfaces of NBs may add positive charges on the surface of NBs. That leads to an obvious reduction of the electrostatic interaction energy, which in turn decreases the energy barrier peaks.¹¹¹ In the presence of NaCl and CaCl₂, the energy barrier peaks also decreased because of the increase of ionic strength and compression of the electric double layer.^{112,113} For all types of NBs, addition of SDS (an anionic surfactant) significantly increased the energy barrier peaks due to the increase of the electrostatic repulsion for all three types of NBs, whereas the addition of humic acid (HA) slightly decreased the energy barrier to different extent. Nevertheless, the remaining energy barriers were still in the order of 2000 $k_B T$, which is sufficient to stabilize the suspension of NBs against coalescence. Addition of HA induced minor changes to the interaction energy profiles and barriers of NBs, which is probably because HA is hydrophilic and negatively charged and thus had weak surface binding or adsorption on the negative charged NBs.¹¹⁴

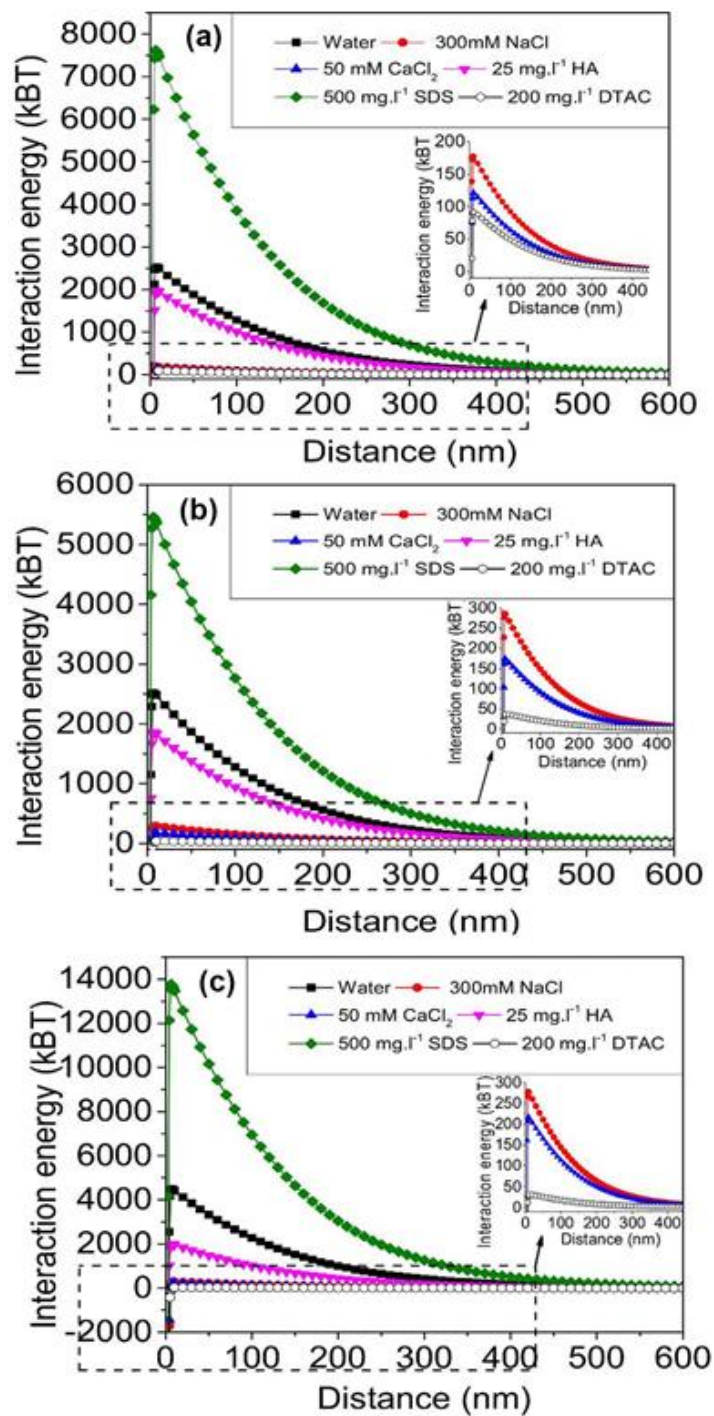


Figure 16.7 Total interaction energy of (a) ANBs, (b) ONBs and (c) NNBs as a function of separation distance in the presence of ionic strengths, surfactants, and NOM. Reproduced from ref. ²³ with permission from Mary Anne Liebert, Inc.

16.2.3 Internal Pressures and Dependence on Bubble Sizes

The stability of NBs against collapse or rapid dissolution may originate from the selective adsorption of anions at their interface, surface zeta potentials and the construction of a hydrogen bonding network at the gas–water interface.^{8,11} The diffusivity of gaseous molecules through the gas–water interface may thus be reduced by these surface charge accumulation and hydrogen bonding network. Recently, NBs have been shown to be kinetically stable against high internal pressures due to the diffusive resistance at the gas–water interface.¹¹⁵ According to a previous study,¹¹⁶ the bulk NBs in water could be stabilized by the outbound and inbound pressures from a number of interfacial forces. **The hypothesis is that** (1) The outbound pressure (P_{out}) is ascribed to surface charge repulsion, and internal gas pressure (P_{int}) as shown in eqn (16.50); particularly, the electric double layer formed at the liquid–gas interface of NBs may also produce repulsion between the surface charges of NBs and thus cause an outbound pressure to the interface of NBs.^{116,117} (2) The inbound pressure (P_{in}) is contributed by the surface tension pressure of NBs (P_r) exerted from the surrounding water molecules, the atmospheric pressure (P_0), and the water head pressure (P_h) as shown in eqn (16.55). For NBs that are at a quasi-steady state (*i.e.*, $P_{\text{in}} = P_{\text{out}}$), we can derive a relationship between the radius of NBs and the internal pressure using eqn (16.50)–(16.56), where σ is the surface charge density (C m^{-2}) and is calculated by the Gouy–Chapman equation in eqn (16.51) or (16.52) when the zeta potential is less than 80 mV.^{118,119}

$$P_{\text{out}} = \frac{\sigma^2}{2D\epsilon_0} + P_{\text{in}} \quad (16.50)$$

$$\sigma = \frac{\epsilon\epsilon_0}{\lambda_D} \zeta \times \left[\left(1 + \frac{z}{r} \right) \right] \exp\left(-\frac{z}{\lambda_D} \right) \quad (16.51)$$

$$\sigma = \epsilon_0 D \frac{k_B T}{z_1 e \lambda_D} \times \left[2 \sinh\left(\frac{z_1 e \psi}{2 k_B T} \right) + \frac{2 \lambda_D}{r} \tanh\left(\frac{z_1 e \psi}{4 k_B T} \right) \right] \quad (16.52)$$

$$\tanh\left(\frac{z_1 e \psi}{k_B T} \right) = \tanh\left(\frac{z_1 e \psi}{4 k_B T} \right) \exp\left(-\frac{x}{\lambda_D} \right), x = 0.3 \text{ nm} \quad (16.53)$$

$$P_{\text{in}} = P_r + P_0 + P_h \quad (16.54)$$

$$P_r = \frac{2\gamma}{r} \quad (16.55)$$

$$P_h = \rho gh \quad (16.56)$$

$$P_{\text{int}} = \frac{2\gamma}{r} + (P_0 + \rho gh) - \frac{\sigma^2}{2D\epsilon_0} \quad (16.57)$$

where D is the relative dielectric constant of the gas bubbles (assumed unity), ϵ is the dielectric constant of water, 78.54 (25 °C), ϵ_0 is the dielectric permittivity of a vacuum, 8.854×10^{-12} (C V⁻¹ m⁻¹), ζ is the zeta potential of NBs (V), and λ_D is the Debye length (m). γ is the water surface tension (71.99 mN m⁻¹ for pure water at 20 °C),¹²⁰ r is the radius of NBs (m), ρ is the density of water (kg m⁻³), g is the gravity acceleration (9.80 m s⁻²), and h is the height of water (m). By measuring the colloidal properties of NBs, such as bubble diameter and zeta potential, the internal pressures of NBs can be estimated or predicted using eqn (16.58), which further permits the assessment of the dependence of bubble radius on internal pressures, if NBs are at a quasi-steady state without significant dissolution or other forms of action that destabilize their sizes or internal pressures. Eqn (16.58) predicts that increasing salinity compresses the electric double layer and reduces the net surface charge of colloidal particles,^{30,121,122} which will reduce the outbound force and potentially reduce bubble size as the inbound force outweighs the outbound force. Moreover, water temperatures affect water surface tension, density and dielectric constant as well as solubility of gases, which may indirectly change the stability of NBs in water.^{62,63}

The experimental bubble size distribution of NBs reduced after the injection gas pressure increased from 60 psi to 80 psi.²² The model prediction using eqn (16.57) and (16.50) supports the above experimental observation as shown in Figure 16.8. Compared to the prediction result from the Laplace–Young model, this new model equation in eqn (16.57) reflects a colloidal force balance that further considers the charge repulsion in the stabilization mechanisms of NBs in liquid. This new model prediction yielded a slightly reduced level of internal pressures, especially for large NBs at a few hundred nm. The reduced internal pressure, as compared to the classic prediction by the Laplace–Young Equation, is largely attributed to the Helmholtz double charge layer that tends to repel the air–water interface out. Some previous studies reported high internal gas pressures of more than 1000 psi (~ 68 atm),^{110,111} whereas the colloidal force balance model predicted lower internal pressures (2–10 atm) so that the gas NBs could still remain in a dense gas phase.¹¹²

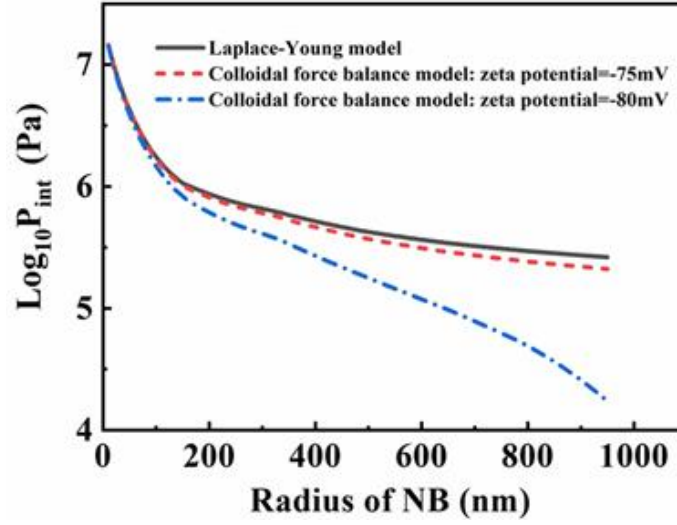


Figure 16.8 Prediction of internal pressures of oxygen NBs of different bubble radius. Calculations are based on eqn (16.50)–(16.58), the concentration of ions species (i) is 0.01 mM and other parameters used in these equations are shown in Table 16.2.

Besides the above colloidal characterization method, prior studies also measured the internal pressures of NBs using an atomic force microscope (AFM) and theories of contact mechanics. There are two major contact mechanics models, JKR or DMT, to assess mechanical properties such as Young's modulus and hardness of soft particles such as bacteria, viruses and bubbles.^{123–127} In this method, a sharp AFM probe is used to compress a local sample surface to induce the indentation or deformation (δ) as illustrated in Figure 16.9.¹²⁸ The internal pressure of the soft sample body can be calculated by eqn (16.58), where the loading force (F_{loading}) is the pressing force that the AFM probe tip exerts on the sample surface; a is the radius of the spherical contact area, which is related to the indentation (δ) and the AFM tip radius (R) in eqn (16.59) according to the contact geometry shown in Figure 16.9b, where F_{loading} can be controlled by AFM and δ is directly read from the force–distance curve in Figure 16.9a. Thus, the internal pressure of NBs can be calculated by applying different F_{loading} values that correspond to different levels of δ . Furthermore, the Young's modulus of NBs could be calculated by the following equations.^{129,130}

$$P = \frac{F_{\text{loading}}}{\pi a^2} \quad (16.58)$$

$$(R - \delta)^2 + a^2 = R^2 \quad (16.59)$$

$$\delta = \frac{a^2}{R} - \frac{2}{3} \sqrt{\frac{6\pi W a}{E^*}} \quad (16.60)$$

$$F_{\text{adh}} = \frac{3\pi R W}{2} \quad (16.61)$$

where W is the adhesion energy per unit area (J m^{-2}) and E^* is the reduced Young's modulus (MPa). W could be calculated by eqn (16.61) with the tip-sample adhesion force (F_{adh}) read directly from Figure 16.9a. Eqn (16.62) shows that E^* is related to the Poisson ratios (ν_s and ν_T) and the Young's moduli (E_s and E_T) of the sample and tip, respectively. The Poisson's ratio of NBs (ν_s) is 0.3 as typically used for soft colloids.¹³⁰ As the AFM probe has an E_T of typically 160–290 GPa, which is significantly greater than that of NBs, the deformation of the tip could be neglected when engaged against the NB's surface. Thus, eqn (16.62) can be simplified to directly determine the samples Young's modulus (E_s) with E^* .¹³⁰

$$E^* = \left[\frac{3}{4} \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_T^2}{E_T} \right) \right]^{-1} \approx \left[\frac{3}{4} \left(\frac{1 - \nu_s^2}{E_s} \right) \right]^{-1} \quad (16.62)$$

$$E^* = \frac{F_{\text{adh}} R \sqrt{2R - \delta}}{9\delta^{3/2} (R - \delta)^2} \quad (16.63)$$

$$E^* = \frac{F_{\text{loading}} + F_{\text{adh}}}{\sqrt{R\delta^3}} \quad (16.64)$$

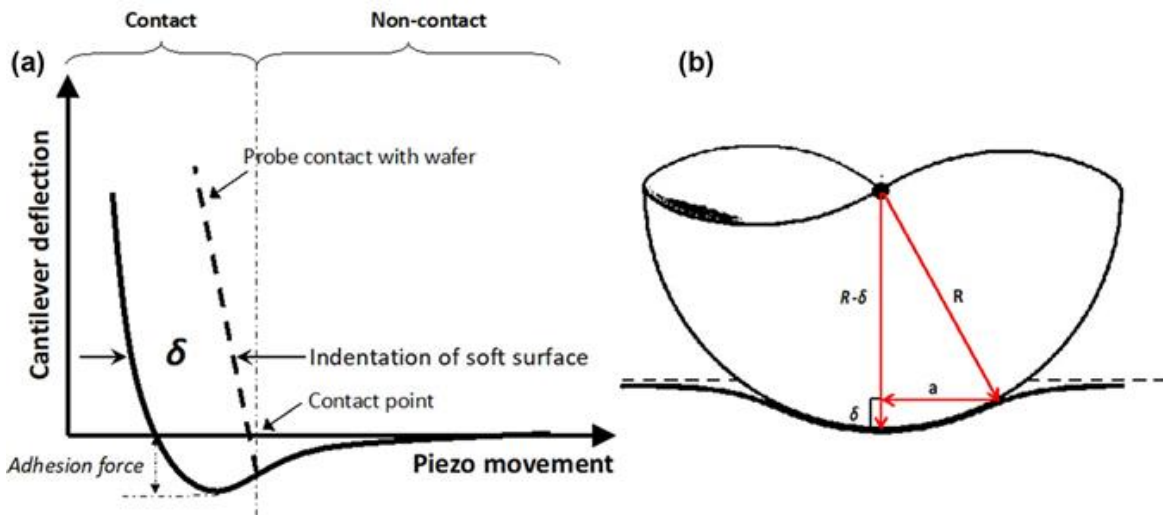


Figure 16.9 (a) Force–distance curve showing the indentation (δ) of the AFM probe in contact with a bubble surface. (b) Illustration of the geometry of the AFM tip on the deformed surface of NBs. Reproduced from ref. ²⁶² with permission from American Chemical Society, Copyright 2021.

Rearranging eqn (16.60)–(16.62) leads to eqn (16.63), which corresponds to the JKR model. Eqn (16.64) is the DMT model equation for the calculation of Young's modulus (without detailed derivation here). **The hypothesis** is that (1) surface NBs may have the same or similar orders of magnitude of internal pressures as suspended or bulk NBs, because although NBs, after deposition onto a solid substrate, may deform, the internal states such as gaseous densities and molecular concentrations remain constant (ignoring dissolution or collapse). (2) During the dissolution or deformation under ambient temperature changes or other stimulating factors, the internal pressure or mechanical properties of surface NBs may change.

This contact mechanics model provides an alternative way to experimentally evaluate the internal pressures of NBs, and, further, the mechanical hardness of NBs, which will be compared with the internal pressures obtained from the colloidal force balance model. Unlike the colloidal modeling method, this contact mechanics model primarily relies on direct AFM measurements of the interfacial force–distance curves with fewer unknown model parameters. Some uncertainties may evolve from the reading of indentation values and adhesion force due to the difficulty in the determination of the tip contact on soft samples that may deform as the tip approaches. The tip–bubble contact is currently defined as the point when the tip experiences a significant attractive force that usually causes a jump-in peak in the force–distance curve.¹³⁰ Additionally, the AFM probe radius may differ slightly from batch to batch. To ensure the reproducibility and accuracy of the experimental results (*e.g.*, the force–distance curves obtained from the tip–NBs contact), morphological mapping of surface NBs should be repeated on each sample. Force measurements should be conducted on the center of one discrete surface NB to produce stable and reproducible values of indentation, adhesion force and Young's modulus and stiffness.

16.2.4 Dissolution Behavior

The existence of NBs is believed to violate the classic Laplace Pressure Bubble Catastrophe theory, which predicts that a bubble with a radius of 200 nm could have an extraordinarily high internal pressure of 5.4 MPa. This high internal pressure should drive bubble dissolution in the liquid instantly ($\sim 1 \mu\text{s}$).¹³¹ According to the Young–Laplace Equation, for bulk NBs in water having a radius of 100 nm, a liquid pressure is 10^5 N m^{-2} and surface tension of water is 72 mN m^{-1} , the internal pressure could be about $15 \times 10^5 \text{ Pa}$ (about 15 atm).

Considering the contribution of surface charge repulsion in the colloidal force balance model as introduced above in Section 16.2.3, the internal pressure could possibly be reduced to 8×10^5 Pa. Such high internal pressures will facilitate rapid dissolution based on Henry's law if the NB suspension is open to the air.^{132,133} Thus, it is challenging to maintain NBs in water that reach thermodynamic stability (unless the water suspension is completely closed to ambient air).⁷ Nevertheless, some studies have demonstrated that NBs may last in liquid for hours,¹³⁴ days,^{7,8,135} and even weeks or months¹³⁶ depending on the water chemistry and storage conditions.¹³⁷ This means that rapid or substantial dissolution of NBs may only be possible when the dissolved gas efficiently escapes the liquid phase. Conversely, if stored in a closed liquid environment, the diffusive dissolution of NBs will significantly slow, thus increasing colloidal stability.^{11,138}

A spherical bubble model in liquid was previously constructed based on the widely-reported Epstein–Plesset (EP) theory in eqn (16.65),¹³⁹ which predicts the dynamics of spherical bubbles with radii as small as 10 μm in the dissolution or unbounded growth.^{140,141} This model could further be modified by adding internal pressure and temperature into the dissolution kinetics of NBs.^{139,142,143}

$$\frac{dr}{dt} = \pm \frac{D' \Delta c}{\rho_g} \left(\frac{1}{r} + \frac{1}{\sqrt{\pi D' t}} \right) \quad (16.65)$$

$$c_s = \frac{P_{\text{int}}}{K_H} \quad (16.66)$$

$$\rho_g = \frac{P_{\text{int}}}{RT} \quad (16.67)$$

where $\Delta c = c_s - c$, which is the difference between the saturation concentration of the dissolved gas (c_s) in the liquid calculated from Henry's law (mol L^{-1}) in eqn (16.66) and the dissolved gas concentration (c) in water at a dissolution time t (mol L^{-1}). This Δc is assumed to be the key driving force for the dissolution of NBs. The gas density of NBs (ρ_g) can be calculated by eqn (16.67). D' is the gaseous diffusion constant in water (*ca.* $2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for O_2 at 25 °C). If NBs are stabilized (*i.e.*, $P_{\text{in}} = P_{\text{out}}$), the radius of NBs can be related to the internal pressure of NBs and other factors. Taking the derivative of eqn (16.58) on both sides leads to:

$$\frac{dP_{\text{int}}}{dt} = -\frac{2\gamma}{r^2} \frac{dr}{dt} \quad (16.68)$$

According to the ideal gas law, the molar concentration of gas within one single NB:

$$\frac{n}{V} = \frac{P_{\text{int}}}{RT} \quad (16.69)$$

Thus, if the increase of the dissolved gas concentration is proportional to the dissolution of the gas molecules from NBs.

$$\begin{aligned} \frac{dc}{dt} &= \frac{N}{V'} \frac{dn}{dt} = \frac{N}{V'} \frac{d(P_{\text{int}}V)}{RTdt} = \frac{1}{RT} \frac{N}{V'} \left(\frac{VdP_{\text{int}}}{dt} + \frac{P_{\text{int}}dV}{dt} \right) \\ &= \frac{1}{RT} \frac{N}{V'} \left(-\frac{8\pi\gamma r}{3} + 4\pi r^2 P_{\text{int}} \right) \frac{dr}{dt} \end{aligned} \quad (16.70)$$

eqn (16.65) can be written in the form:

$$\frac{dr}{dt} = \pm \frac{D'\Delta c}{\rho_g} \left(\frac{1}{r} + \frac{1}{\sqrt{\pi D't}} \right) = \pm \frac{D'(P_{\text{int}}/K_H - c)}{\rho_g} \left(\frac{1}{r} + \frac{1}{\sqrt{\pi D't}} \right) \quad (16.71)$$

where N is the initial number of bulk NBs in the NB water with a volume of V' (m^3). n is the moles of gases molecules within one single NB that dissolve within time t . According to the ideal gas law, n can be expressed by P_{int} , the volume of single NBs (V), the ideal gas constant ($R = 8134.5 \text{ L Pa mol}^{-1} \text{ K}^{-1}$) and the solution temperature (T). As we assume a spherical shape of NBs with a radius of r (thus, $V = 4/3\pi r^3$), eqn (16.70) is further simplified by replacing dV/dt . Similarly, the term dP_{int}/dt can be replaced by eqn (16.68), which is the derivative form of the Young–Laplace equation. Numerical solution of eqn (16.70) and (16.71) will yield the calculated results of the dissolved gaseous concentration (e.g., O_2) and the radius of NBs at different dissolution time t under specific parameters such as P_{int} and N or the initial bubble concentration.

Figure 16.10a indicates that the dissolution of oxygen NBs in water will progressively increase the dissolved oxygen (DO) level that then reaches a plateau. Moreover, the DO concentration increase rate also depends on the initial radius of oxygen NBs as well as many other factors such as the initial number density ($N/V's$) of NBs. For instance, oxygen NBs with a 100 nm radius release DO at a faster rate

than those with a 1000 nm radius. Moreover, the maximum DO level reached over 40 mg L^{-1} for 100 nm oxygen NBs, which is greater than that obtained in a suspension of oxygen NBs with an initial radius of 1000 nm.

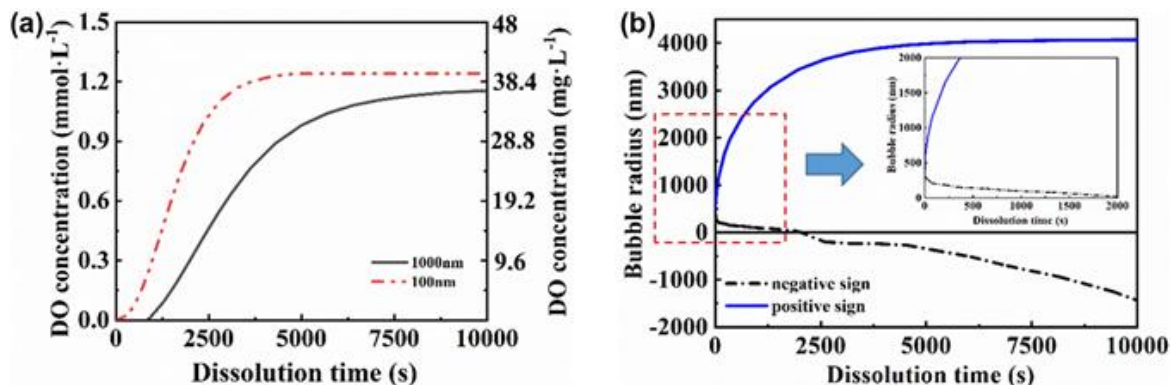


Figure 16.10 (a) The predicted DO concentration and (b) the changes of bubble radius of oxygen NBs at different dissolution time t . Solid and dotted lines are generated by eqn (16.70) and (16.71) with positive or negative signs in eqn (16.65).

The dotted curve in Figure 16.10b indicates that bubble radius will decrease from the initial 500 nm to zero and then negative values if we assume that the bubble radius will shrink during the dissolution and use a negative sign in eqn (16.65). Negative radii are unrealistic so that means NBs will completely dissolve and disappear. Conversely, the solid curve in Figure 16.10b shows that the bubble radius will increase during the dissolution when eqn (16.65) has a positive sign. The radius increase leveled off after around 10 000s. This increased radius is possible as the swelling bubbles may have decreased internal pressures and thus eventually reach a dissolution equilibrium when the driving force (the oxygen concentration difference between the internal NBs and bulk liquid) is zero.

Water chemistries and other environmental conditions as temperature clearly affect the dissolution kinetics of NBs. For instance, water surface tension, density and dielectric constant as well as pH/temperature incorporated in the model eqn (16.70) and (16.71) indicate their influences on dissolution and deformation of NBs in liquid. One intriguing process for NBs in liquid is that they may both grow and shrink when the temperature changes due to Ostwald Ripening.¹⁴⁴ Higher temperatures correspond to lower water surface tension,¹⁴⁵ which reduces the size of NBs according to our model. The dissolution of NBs could increase or decrease at high temperatures because the internal pressures of NBs may increase and thus increase dissolution. But high temperatures also reduce the solubility of DO and thus reduce dissolution of NBs.¹⁴⁴ In addition to temperature, the impact of salinity

on NB dissolution kinetics in water may also be evident. Generally, increasing salinity compresses the electric double layer and reduces the net surface charge of colloidal particles. However, many previous studies found the zeta potential of NBs does not vary sensitively with salinity, and the NBs exhibit superior stability against coalescence.^{30,121,122}

16.2.5 Radical Formation and Plausible Mechanisms of NBs in Liquid

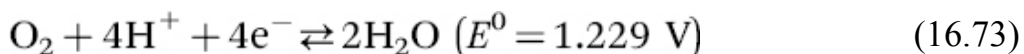
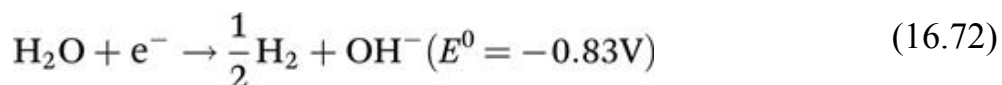
Generation of free radicals such as $\cdot\text{OH}$ through the collapse of MBs or NBs has been widely reported or experimentally observed.^{14,146–148} Highly reactive radical formation may open many valuable opportunities for engineering applications such as water disinfection and cleaning/defouling of solid surface.¹⁴ Radical generation in water suspensions of NBs is usually detected by electron spin resonance spectroscopy¹⁴ and other radical–scavenger indicators.^{149–151} Liu *et al.* experimentally reported that $\cdot\text{OH}$ radicals were detected using a fluorescent reagent APF (3'-*p*-(aminophenyl) fluorescein) from liquid water containing oxygen NBs without dynamic stimuli.¹⁴⁰ They estimated the concentration of $\cdot\text{OH}$ radicals produced from oxygen NBs with a concentration of about 10^8 mL as about $0.25\ \mu\text{M}$ or on the order of 10^{14} per mL. As the typical lifetime of $\cdot\text{OH}$ radicals is in the order of 20 ns,^{152–154} the detected $\cdot\text{OH}$ radicals are considered to be produced from bulk NBs especially under a dynamic stimulus. Takahashi *et al.* detected radicals in a bulk NB solution after ceasing NBs generation to avoid the influence of the external dynamic energy (*i.e.*, hydrodynamic cavitation).¹⁴ It is widely known that during hydrodynamic cavitation many $\cdot\text{OH}$ radicals are produced by cavitation bubbles as temperature and pressure inside the bubbles increases dramatically at their collapse.^{155,156} Similarly, sonochemical production of $\cdot\text{OH}$ radicals in liquid water is attributed to the sonication cavitation effect and energy transfer to break up water molecules and transform them to $\cdot\text{OH}$ radicals.¹⁵⁷

Despite the above research findings, some studies reported negative detection of radicals in similar experimental conditions. For instance, Tada *et al.* and Yasui *et al.* showed the opposite, no $\cdot\text{OH}$ radical generation from air NBs self-collapse in water.¹⁴⁶ The discrepancy could arise from the subtle differences in experimental parameters such as the physical or mechanical stimulus or agitation (*e.g.*, sonication, laser or light irradiation) as well as the type of gases, which could significantly affect the quantity or quality of free radicals generated in water.^{158–162} For example, oxygen MBs favored the formation of $\cdot\text{OH}$ radicals compared to nitrogen MBs.¹⁶¹ Izawa *et al.* reported that reactive oxygen species (ROS) such as

superoxide anion radicals, H_2O_2 and $\cdot\text{OH}$ radicals are generated during the reduction of molecular oxygen to water through acceptance of four electrons.¹⁵⁹ The radical formation inside a bubble is negligible because the probability of nitrogen dissociation is only on the order of 10^{-15} .¹⁶² Furthermore, adding acid to alter the circumstance of the adsorbed ions around the gas–water interface of the microbubble can increase $\cdot\text{OH}$ radicals generation.¹⁴ Some researchers also reported that MBs could accelerate the formation of $\cdot\text{OH}$ radicals during an ozonation process.^{163–167}

16.2.6 Potential Redox Chemistry in Water Suspensions of NBs

In a hydrogen or oxygen NB water, the H_2 – H_2O or O_2 – H_2O redox couples result in a redox potential that is governed by this reaction.



The redox potential can be calculated by the Nernst equation:

$$E_{\text{H}} = E^0 - \frac{1}{2} \frac{1}{16.9} \log(P_{\text{H}_2}) + \frac{1}{16.9} (14 - \text{pH}) \quad (16.74)$$

$$E = E_h^0 + \frac{0.059}{4} \log P_{\text{O}_2} + 0.059 \log(\text{H}^+) \text{ or } E = E_h^0 + \frac{0.059}{4} \log P_{\text{O}_2} - 0.059 \text{ pH} \quad (16.75)$$

Case study: The reductive or oxidative redox potentials of H_2 or O_2 NB water should depend on both pH and the partial pressure of H_2 or O_2 gases. Figure 16.11a indicates that the solution redox potential (E_h) will decline with an increase of the partial pressure of H_2 . A higher pH also lowers the redox potential. Figure 16.11b also reveals that the redox potential curve has a negative slope of 0.059 V per pH unit and an intercept of E^0 (1.229 V) if an arbitrary oxygen pressure is chosen. Similarly, at a fixed pH, E_h proportionally increases with the increase of the partial pressure of oxygen gas. NBs in water create numerous oxygen–water interfaces that will follow this redox potential relation. According to the above analysis in Section 16.2.3, H_2 or O_2 NBs may have a high internal pressure (e.g., 10 atm) and thus elicit different redox potential chemistry compared to the traditional

dissolved hydrogen or oxygen solutions. However, compared to the pH effect, the internal pressure influence on the redox potential is not substantial.

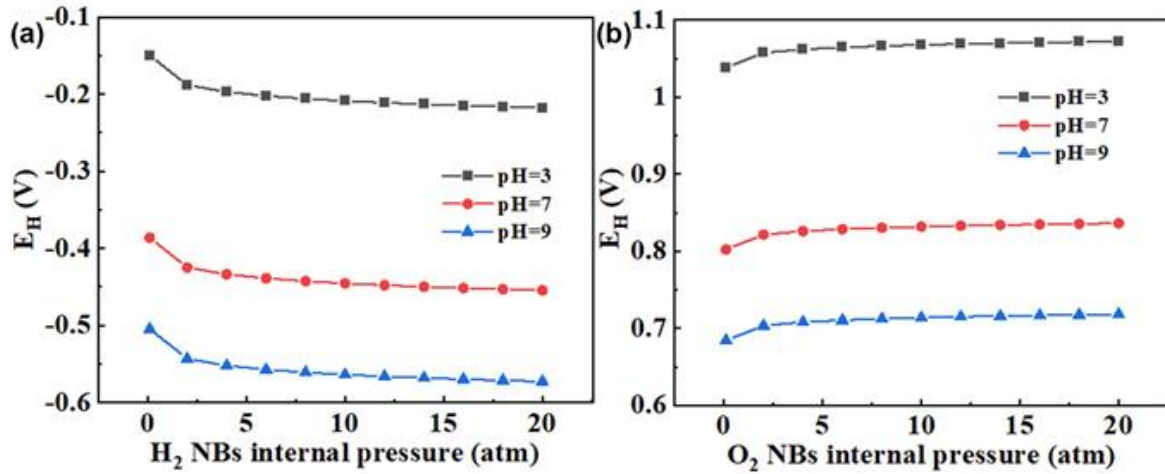


Figure 16.11 The redox potentials of the water solutions with H_2 or O_2 NBs (b) with different internal pressures and solution pHs.

16.3 Reported Engineered Applications of MBs and NBs

Engineering applications of MBs and NBs have widely been demonstrated,²⁵ ranging from aeration, enhanced ozonation, disinfection, surface cleaning, ecological restoration such as harmful algal bloom (HAB) mitigation.^{6,11,15,25,168–171} This section summarizes and discusses the state-of-the-art knowledge with a focus on environmental and agricultural applications.

16.3.1 Aeration with Enhanced Mass Transfer

Aeration is important for water quality and the growth of many aquatic organisms that require proper DO to live.¹⁷² In wastewater treatment aeration is used to support aerobic microorganisms for biodegradation of water pollutants (*e.g.*, organic matter). The bulk transfer coefficient is often assessed to quantify the rate of oxygen across an air–water interface in an aeration process.¹⁷³

$$V \frac{dC}{dt} = KA \left(\frac{P_a}{K_H} - C \right) \quad (16.76)$$

where K is the bulk transfer coefficient (m h^{-1}), C is the oxygen concentration in the water (mol L^{-1}), V is the volume of the solution (m^3), t is the aeration time (h), A is the air–water surface area (m^2), P_a is the partial pressure of oxygen in the air or in the oxygen bubbles dispersed in water (atm), K_H is the Henry's law constant ($770 \text{ L atm mol}^{-1}$), and P_a/K_H is the saturation concentration of oxygen in water (C_s). The bulk transfer coefficient is given as the inverse sum of resistances to transfer on the two sides of the air–water interface.¹⁷⁴

$$\frac{1}{K} = \frac{1}{K_L} + \frac{1}{K_H K_a} \quad (16.77)$$

where K_L is the bulk liquid film coefficient (m h^{-1}) and K_a is the bulk gas film coefficient (m h^{-1}). For many chemicals, including oxygen, mass transfer is water-side controlled because the resistance on the water side is much greater than that on the air side, or $K_L \ll K_H K_a$. Therefore, $K \approx K_L$. However, for those chemicals with low K_H or high solubility in water such as ammonia, the transfer is controlled by the gas layer resistance. Thus, increase of the turbulence in gas phase would decrease the gas layer thickness and increase the overall mass transfer as shown in the following equation for non-coalescing dispersions.

$$K_L a = 0.002 \left(\frac{P}{V'} \right)^{0.7} v_s^{0.2} \quad (16.78)$$

where P/V' is the mixing power density (watts m^{-3}) and v_s is the superficial gas velocity (m s^{-1})

The integration of eqn (16.76) with boundaries of $C = C_0$ and $C = C$ and $t = 0$ and $t = t$ leads to:

$$\int_{C_0}^C \frac{dC}{C_s - C} = (K_L a) \int_0^t dt \quad (16.79)$$

where a (A/V) is the specific surface area of bubbles in liquid ($\text{m}^2 \text{ m}^{-3}$), C_0 and C_t are the DO concentrations in the water at the aeration time 0 and t (mol L^{-1}), and $K_L a$ is the volumetric mass transfer coefficient (h^{-1}).

As NBs undergo drastic random movements or turbulence, they may have a greater mass transfer efficiency than that for the ambient air–water interface. If we

assume that the bulk liquid film coefficient (K_L) remains the same for the ambient air–water interface and the NBs–water interface, the potential differences in aeration efficiencies for NBs and regular air purging lie in the difference of a (the surface area per unit volume) and C_s (the saturated oxygen concentration), which are influenced by bubble sizes and internal bubble pressures. Thus, we can integrate eqn (16.58) and (16.66) into eqn (16.79) to derive the bubble size-dependent aeration in eqn (16.79).

$$C_t = C_s - (C_s - C_0)\exp(-K_L a t) \quad (16.80)$$

where

$$C_s = \frac{P_{\text{int}}}{K_H} = \frac{\frac{2\gamma}{r} + (P_0 + \rho g h) - \frac{\sigma^2}{2D\epsilon_0}}{K_H} \quad (16.81)$$

Moreover, if the bubbles are treated as a spherical shape, the specific surface area is calculated by:

$$a = \frac{N}{V'} 4\pi r^2 \quad (16.82)$$

If we deliver a mass amount of oxygen (m) to the water with a volume of V' at a flow rate of oxygen gas of Q , and consequently, a is also time dependent as the bubble number increases with time, which increases the exposed surface areas for mass transfer.

$$\begin{aligned} a &= \frac{N}{V'} 4\pi r^2 = \frac{m}{\rho_g \frac{4}{3}\pi r^3} \frac{1}{V'} 4\pi r^2 \\ &= \frac{1}{V'} \frac{QtP_{\text{inj}}}{RT} \times M_{O_2} \frac{3}{\rho_g r} = \frac{1}{V'} \times \frac{3}{r} \frac{QtP_{\text{inj}}}{RT} \times M_{O_2} \times \frac{RT}{M_{O_2} P_{\text{inj}}} = \frac{1}{V'} \times \frac{3}{r} \times \frac{QtP_{\text{inj}}}{P_{\text{int}}} \end{aligned} \quad (16.83)$$

Case study: Figure 16.12 shows the comparison of time-resolved concentrations of dissolve oxygen when injecting oxygen NBs with radii of 100 nm and 600 nm into water with an initial DO concentration of 9 mg L⁻¹. This result is predicted with eqn (16.80)–(16.83), which assumes spherical bubbles dispersed to a closed, clean water volume without any DO loss or reduction due to evaporation or bubble exit from liquid to the air. This assumption is certainly unrealistic. However, this model prediction aims to understand the potential differences in aeration when purging different sized NBs within a few microseconds in the initial stage of

aeration, where the DO loss could be ignored. Moreover, to simplify this simulation, the bulk liquid film coefficient (K_L) is treated as a constant but in fact K_L is also bubble size-dependent, which is discussed below. Clearly, small NBs exhibit higher surface areas for mass transfer than large ones, which affects the value of term a in eqn (16.80). Thus, the rate of DO increase for 100 nm NBs is almost 11 times that of 600 nm NBs. Furthermore, the equilibrium level of DO is 539 and 40 mg L⁻¹ for 100 nm and 600 nm NBs, respectively, due to the differences in the internal pressures. In most studies or reports, NBs are usually a few hundred nanometers in diameter in water that is open to the air, which probably results in rapid depressurization and evaporation of DO or other gases species. Thus, it is uncommon to observe such high DO above 100 mg L⁻¹.

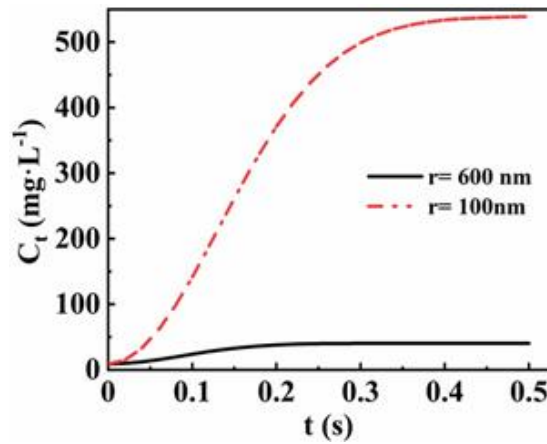


Figure 16.12 The prediction of time-resolved concentrations of dissolve oxygen when purging oxygen NBs of small and large sizes (100 and 600 nm in radius). Other important parameters used in the calculation include: $K_L = 0.0001 \text{ m s}^{-1}$, the oxygen gas flow: $Q = 0.03 \text{ m}^3 \text{ s}^{-1}$ (under 414 kPa (P_{inj}) and 25 °C), $V' = 1 \text{ m}^3$ and other factors/values are taken from Table 16.2.

In realistic aeration processes, the mass transfer rate or efficiency is different (mostly lower than) from that measured in clean water. The alpha and beta factors are considered in the following equations:

$$K_L \cdot a_{(\text{realistic liquid})} = \alpha \cdot K_L \cdot a_{(\text{clean water or test conditions})} \quad (16.84)$$

$$C_{s(\text{realistic liquid})} = \beta \cdot C_{s(\text{clean water or test conditions})} \quad (16.85)$$

The alpha factor is a correction factor accounting for the effects of mixing, aeration device, geometry and liquid properties. Alpha factors for diffused aerators

and mechanical mixers are respectively in the range of 0.4 to 0.8 and 0.6 to 1.2. Also, a beta factor is used to correct the oxygen solubility in liquid media that may contain suspended solids, salts and organic matter.

The temperature correction is often calculated by:

$$K_L a^{Tf} = \alpha (K_L a)^{20} (\theta)^{T-20} \quad (16.86)$$

where $K_L a^{Tf}$ is the volumetric mass transfer coefficient (h^{-1}) at a solution temperature of T , $(K_L a)^{20}$ is the volumetric mass transfer coefficient (h^{-1}) measured at 20 °C, and the correction factor of θ is approximately 1.024.

Finally, in a typical process of aeration, there are numerous dissolving air bubbles, and consequently, the total surface area for the oxygen's mass transfer is not known or incalculable. Thus, K_L could alternatively be estimated by the correlation of mass transfer coefficients using Re, Schmidt Number (Sc), and Sherwood Number (Sh) using [eqn \(16.87\)](#). Re is a ratio of inertial forces to viscous forces, Sc is a ratio of momentum diffusivity to mass diffusivity, and Sh describes the ratio of mass transfer rate to diffusion rate.

$$K_L = \text{Sh} D' / (2r) \quad (16.87)$$

For small bubbles (less than 0.6 mm diameter) under mild agitation, the following correlation may be used in [eqn \(16.88\)](#) to estimate the liquid phase mass transfer coefficient:

$$\text{Sh} = 2 + 0.31 \left[\frac{(\rho - \rho_g) \rho g (2r)^3}{\mu_L^2} \right]^{1/3} \text{Sc}^{1/3} \quad (16.88)$$

For bubbles of 2.5 mm in diameter, the following correlation may be used in [eqn \(16.89\)](#):

$$\text{Sh} = 0.42 \left[\frac{(\rho - \rho_g) \rho g (2r)^3}{\mu_L^2} \right]^{1/3} \text{Sc}^{1/2} \quad (16.89)$$

where

$$\text{Sc} = \frac{\mu_L}{\rho D'} \quad (16.90)$$

Case study: Eqn (16.87), (16.88) and (16.90) are used to estimate the value of K_L when oxygen NBs with different initial radii are dispersed in water that has a dynamic viscosity of water of μ_L of $8.90 \times 10^{-4} \text{ Pa s}^{-1}$ at 25°C . Other parameters used in the calculation are summarized in Table 16.2. Figure 16.13 reveals that the mass transfer coefficient (K_L) is highly bubble size dependent, because as indicated by above equations, the bubble size affects internal pressures and thus gas density (ρ_g) besides the apparent terms of r in those equations.

Table 16.2 Parameters and values used in the dissolution behavior model prediction in eqn (16.70) and (16.71).

Parameters	Values or determination methods	Units
C Concentration of the dissolved gas concentration in water at time t	To be computed	mol L^{-1}
R Radius of NBs at time t	To be computed	m
T Dissolution time	An interesting time range that is manually entered	s
c_S Gas concentration in the liquid adjacent to NBs	Eqn (16.66)	mol L^{-1}
D' Diffusion constant of dissolved gas in water	2×10^{-9}	$\text{m}^2 \text{s}^{-1}$
ρ_g Gas density in NBs	Eqn (16.67)	mol L^{-1}
K_H Henry's constant	7.69×10^7	L Pa mol^{-1}
T Temperature	298	K
P_{int} Internal pressure of NBs	Eqn (16.58)	Pa
V Volume of a single NB	$4/3 \times 3.14 \times r^3$	m^3
R Ideal gas constant	8134.5	$\text{L Pa mol}^{-1} \cdot \text{K}^{-1}$
Σ Surface charge density	Eqn (16.52) or (16.53)	C m^{-2}
ε_0 Dielectric permittivity of a vacuum	8.854×10^{-12}	$\text{C}^2 \text{N}^{-1} \text{m}^{-2}$
E Dielectric constant of water	78.54	Unitless
Ξ Zeta potential of NBs	-0.03	V
λ_D Debye length	$\lambda_D = \left(\frac{\varepsilon_0 \varepsilon k_B T}{N_A e^2 \sum c_i z_i^2} \right)^{0.5}$	m
NA Avogadro's number	6.02×10^{23}	mol^{-1}
E Unit charge	1.602×10^{-19}	C

c_1	The molar concentration of first (dominant) species ions	10^{-2}	mol m^{-3}
z_1	The valence of the first dominate ion (for NaCl or H^+)	1	Unitless
Z	Distance from the particle's surface to the slipping plane	0.335	nm
k_B	Boltzmann constant	1.38×10^{-23}	J K^{-1}
D	Relative dielectric constant of the gas bubble	1.004	Unitless
Γ	Water surface tension	0.07199	N m^{-1}
G	Acceleration of gravity	9.81	N kg^{-1}
P	Water density	998.19	kg m^{-3}
H	Water height or depth	0.1	m
P_h	Water head pressure	$P_h = \rho gh$	Pa
P_0	Atmospheric pressure	10 132	Pa
P_r	Surface tension pressure of NBs	$P_r = \frac{2\gamma}{r}$	Pa
N	Number of NBs in water	$N/V' = 1.4 \times 10^{14} \text{ m}^{-3}$	Unitless
V'	Volume of NB water	m^3	

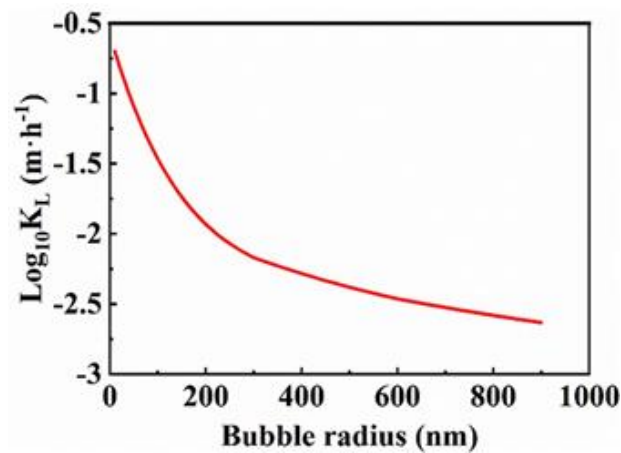


Figure 16.13 The estimated mass transfer coefficient (K_L) for oxygen NBs of different sizes in water.

16.3.2 Surface Cleaning and Biofoulant Prevention and Removal

16.3.2.1 Surface Cleaning Mechanisms of Macro bubble and MBs

Bulk sized or macrobubbles have been used to clean surfaces mainly through three reported mechanisms: (1) physical scrubbing or scouring, (2) mechanical shocking due to bubble bursting, and (3) chemical disruption by radicals. For instance, continuous bubbling near fouled surfaces physically scrubs foulants through bubble–surface interactions that induce drag and lift forces. The hydrodynamic shear forces reduce concentration polarization and foulant deposition.^{175,176} Smaller air bubbles like micrometer-sized bubbles or MBs were shown to reduce surface fouling more efficiently.^{177–180}

Additionally, the presence of NBs reduces water surface tension and loosens the structure of the gel-like materials or the extracellular polymeric substance (EPS) layer of biofilm. Due to their natural shrinking process, MBs may self-burst or trigger-burst, which causes the detachment of biofilms and other contaminants from solid surfaces.^{11,181–183} The internal gas pressure increases sharply due to the shrinking size of the bubbles. As the internal pressure increase is inversely proportional to the bubble diameter, a high-pressure spot is created at the final stage of the collapse. The pressure waves are thus generated and distributed all over the vicinity of a collapsing bubble, which produces turbulent microstreaming or liquid microjet. As illustrated in Figure 16.14a, the collapsing MBs in the vicinity of a biofilm may blow away or break up the EPS matrix or structures of biofilms. However, the transient physical forces generated through uncontrolled self-bursting of individual MBs may not be strong enough and thus require a long bubbling time to achieve substantial detachment of biofilms. Agarwal *et al.* further reported that biofilms were removed through ultrasound-triggered bursting of MBs.¹⁸² Figure 16.14b shows the synchronized bursting of MB by low-intensity and high frequency ultrasound that generated microstreaming along with the generation of liquid micro-jets. Besides pressure waves, the collapse of MBs may generate radical species and degrade the contaminants.^{11,170,184,185}

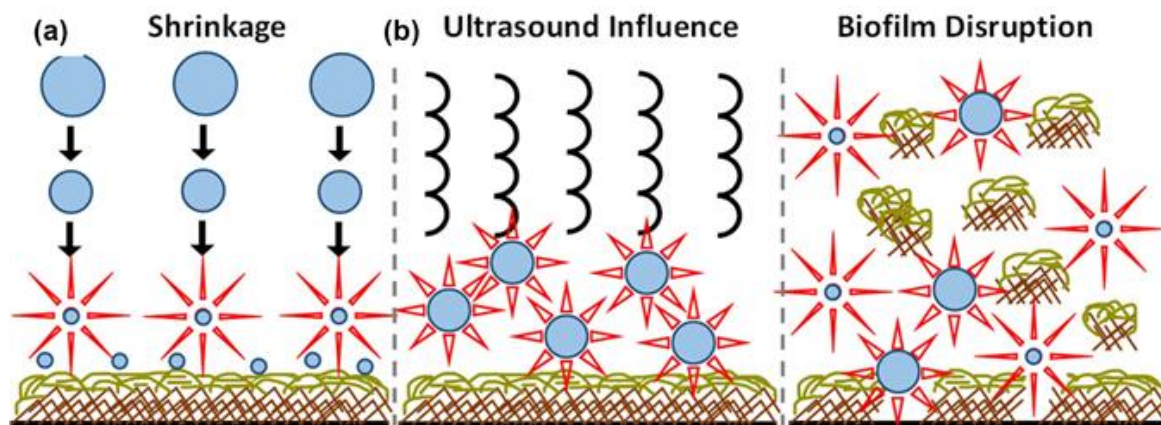


Figure 16.14 Schematic illustration of biofilm detachment by (a) self-bursting of MB; and (b) bursting of MB triggered by ultrasound.

16.3.2.2 *Surface Cleaning Mechanisms of NBs*

NBs are also found to remove organic contaminants from pyrolytic graphite,^{26,186} gold surfaces,¹⁸⁷ and stainless-steel surfaces.¹⁸⁸ Similar to MBs, when NBs collapse they may also produce radicals and wave shocks that contributes to surface foulant removal.^{7,15,147,148,186,189–192} Unlike bulk bubbles, NBs behave like colloids and have much less mechanical impacts (*e.g.*, physical scouring) than MBs do. Therefore, besides mechanical shocks and radicals, there are two additional mechanisms that could lead to efficient surface cleaning^{17,26,187} (1) **Foulant repulsion or surface masking**. As NBs form under microwave irradiation or electrochemical reactions at the interface of a solid surface and surface foulants (*e.g.*, BSA proteins as illustrated in [Figure 16.15a](#)), NBs could mechanically lift and remove the foulants from the solid surface.^{26,193} The coating layer of negatively charged NBs may also establish a physical barrier or surface mask that prevents the adsorption or deposition of contaminants on the surface.^{26,192,194} (2) **Hydrophobic interactions**. NBs are hydrophobic in nature and thus, due to the strong hydrophobic or electrostatic interactions, NBs are able to sequester hydrophobic contaminants or foulants *via* adsorption or partitioning as shown in [Figure 16.15b](#).^{18,192} Some studies employed NBs or MBs or a mixture of them for filtration membrane fouling mitigation.^{26,193} Thus, incorporating MBs for membrane defouling may reduce chemical cleaning that involves the use of detergents, surfactants and chelants.

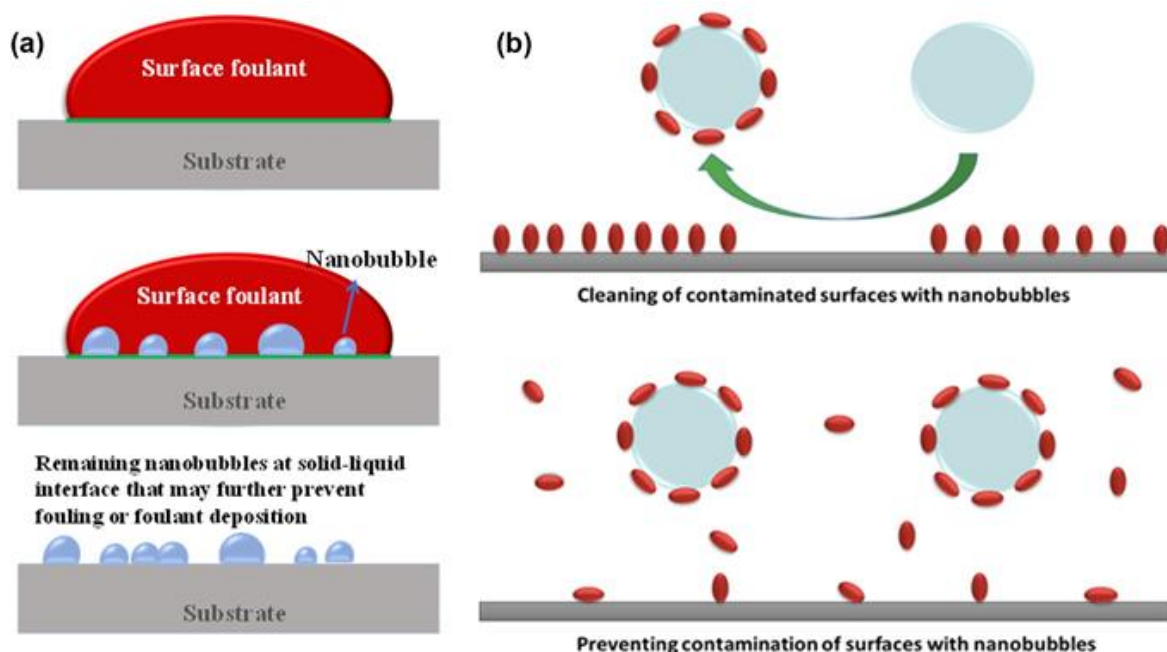


Figure 16.15 (a) Proposed mechanisms of defouling and fouling prevention due to the formation of surface NBs under electrochemical reactions, where the fouling materials may be repelled by the surface NBs, which may further prevent foulant deposition due to electrostatic repulsion or steric repulsion. (b) The modes of surface foulant removal by hydrophobic interactions of NBs with surface foulants (elliptical particles).

16.3.3 Antimicrobial Activity of NBs and Biofilm Mitigation

Microbial contamination in drinking water distribution systems (DWDS) negatively affects public health as well as pertinent infrastructure integrity *via* biocorrosion. Particularly, biofilm formation reduces the drinking water quality and harms human health. Biofilms may act as vectors and habitats or reservoirs for many microorganisms (bacteria, fungi, protozoa, and/or viruses) to survive disinfection, antibiotics and biocides.^{195,196} Biofilms foul many surfaces including food processing systems, interior pipe works, storage tanks, and cooling towers, causing material corrosion and failure. Pathogenic bacteria in biofilms negatively affect water quality and human health,¹⁹⁷ causing disease such as typhoid fever, salmonellosis, bacillary dysentery, cholera, and gastroenteritis.¹⁹⁸

Despite regulated use of residual disinfectants in the United States and other countries to limit the biofilm growth in DWDS, there are well-known drawbacks in traditional disinfection such as disinfection by product (DBP) formation. Chemical disinfectants such as chlorine, chloramines and ozone and germicidal UV irradiation are widely used to inactivate or destroy pathogenic and other microbes in drinking water. Chlorine, for example, effectively inactivates a wide spectrum of

waterborne pathogens,¹⁹⁹ through oxidation or denaturation of enzymes and nucleic acids and damages polysaccharide macromolecular polymers (e.g., depolymerization of carbon–nitrogen bonds of proteins) and thus the metabolic and reproductive capabilities of bacteria are reduced.^{200,201} During disinfection or water storage/delivery, toxic chlorite (ClO_2^-) and chlorate (ClO_3^-) are potentially produced. Moreover, chlorination renders the rise of more than 600 different potentially carcinogenic DBPs (e.g., trichloromethane, bromine dichloromethane, dibromomethane and tribromomethane)^{202–206} and NDMA (*N*-nitrosodimethylamine) during the chlorine disinfection of water containing dimethylamine.²⁰⁷

As opposed to chlorine, ozone has high oxidation potential and is more reactive at comparable doses.²⁰⁸ Moreover, ozone leaves far less chemical residuals during ozonation and disinfection treatment.²⁰⁹ However, ozone has limited water solubility and is unstable and decays rapidly in water, which often reduces the effective exposure dose and disinfection efficacy. Moreover, ozone disinfection suffers from high capital, operation and maintenance costs, corrosive nature of ozone, safety consideration of ozone utilization, high ozone consumption (due to decay and relatively low water solubility)²⁰⁸ and potential formation of bromate from naturally-occurring bromide during ozonation and NDMA found in indirect potable reuse plants.²¹⁰

High efficient *E. coli* deactivation was reported with NBs produced by hydrodynamic cavitation¹⁷¹ and acoustic cavitation (e.g., ultrasonication).¹⁶⁸ A feasibility study investigated the use of ozone MNBs as a disinfectant to prevent airborne disease.²¹¹ The results showed that ozone MNBs achieved a (5.2 to 3.3) and (5.0 to 3.7) log reduction in *Alternaria solani sorauer conidia*, a fungal pathogen and *Cladosporium fulvum conidia*, a genus of fungi. Ozone MBs also achieved 99.99% inactivation of *E. coli* cells with a lower ozone dose and a smaller volume of water disinfection systems.¹⁷⁰ Another study showed that ozone MBs achieved 75% reduction of *E. coli* through three minutes of continuous injection of MBs. In addition, ozone MBs are effective against other types of bacteria such as *Bacillus subtilis* spores and *Cryptosporidium parvum*. Bacteria inactivation and removal by ozone NBs is largely attributed to the formation of hydroxyl radicals or other reactive species especially during collapse or burst.²¹² Bacterial removal can be improved by the burst of high intensity number and smaller size of bubbles.¹⁸⁸ Thus, combinations of NBs with UV irradiation or ultrasonication usually boost up radical formation and improve the disinfection power of NBs.^{11,213,214}

Dr. Zhang's team at New Jersey Institute of Technology characterized the potential prevention of bacterial attachment and biofilm formation using air NBs.

The effectiveness on biofilm control was evaluated in a microfluidic cell, where bacteria was spiked in the buffer solution to flow through as shown in [Figure 16.16a](#). The bacterial strain, *E. coli* purchased from the American Type Culture Collection was used as the bacterial inoculum to simulate the biofilm formation on a substrate surface (a stainless-steel plate). Biofilm growth on the substrate surfaces induces a change in the electrical characteristics in both the surround medium and the interface of the solid substrate surface.²¹⁵ To characterize these changes, EIS measurements were conducted using a CHI electrochemical workstation in the frequency range of 0.316–10⁶ Hz with a gold-coated electrode (18–22AWG CRIMP GOLD) and a stainless-steel plate (exposure area: 1.2 cm × 1.0 cm) as the counter electrode (CE) and the working electrode (WE), respectively, as illustrated in the microfluidic device in [Figure 16.16a](#). The impedance of the fluidic environment between WE and CE in the microfluidic channel was monitored *versus* time with injection of different fluid mixtures. Specifically, to evaluate the influence of NBs on the biofilm growth or deposition on the stainless-steel surface, the following comparative experiments were conducted: (1) the microfluidic cell was separately fed with the bacterial suspension ($4 \times 10^7 \pm 1 \times 10^7$ CFU per mL) in a 1 × PBS (NaCl: 137 mM, KCl: 2.7 mM, Na₂HPO₄: 10 mM, KH₂PO₄: 1.8 mM; pH = 7.4 ± 0.2), the bacteria-free PBS liquid, and the NBs-containing PBS water at a rate of 1 mL min⁻¹ into the device from the inlet A or B; (2) to compare the biofilm growth with or without the presence of NBs in the fluid, the bacterial suspension was injected from the inlet B before and after switching the continuous fluid at the inlet A from the PBS to the NBs PBS water. Before and after this switch, the impedance was recorded to reveal the interfacial electrical resistance increase kinetics as a measure of biofilm deposition rates. (3) The bacterial suspension was pre-mixed with the NBs water and injected from the inlet B, while the PBS was continuously supplied from the inlet A.

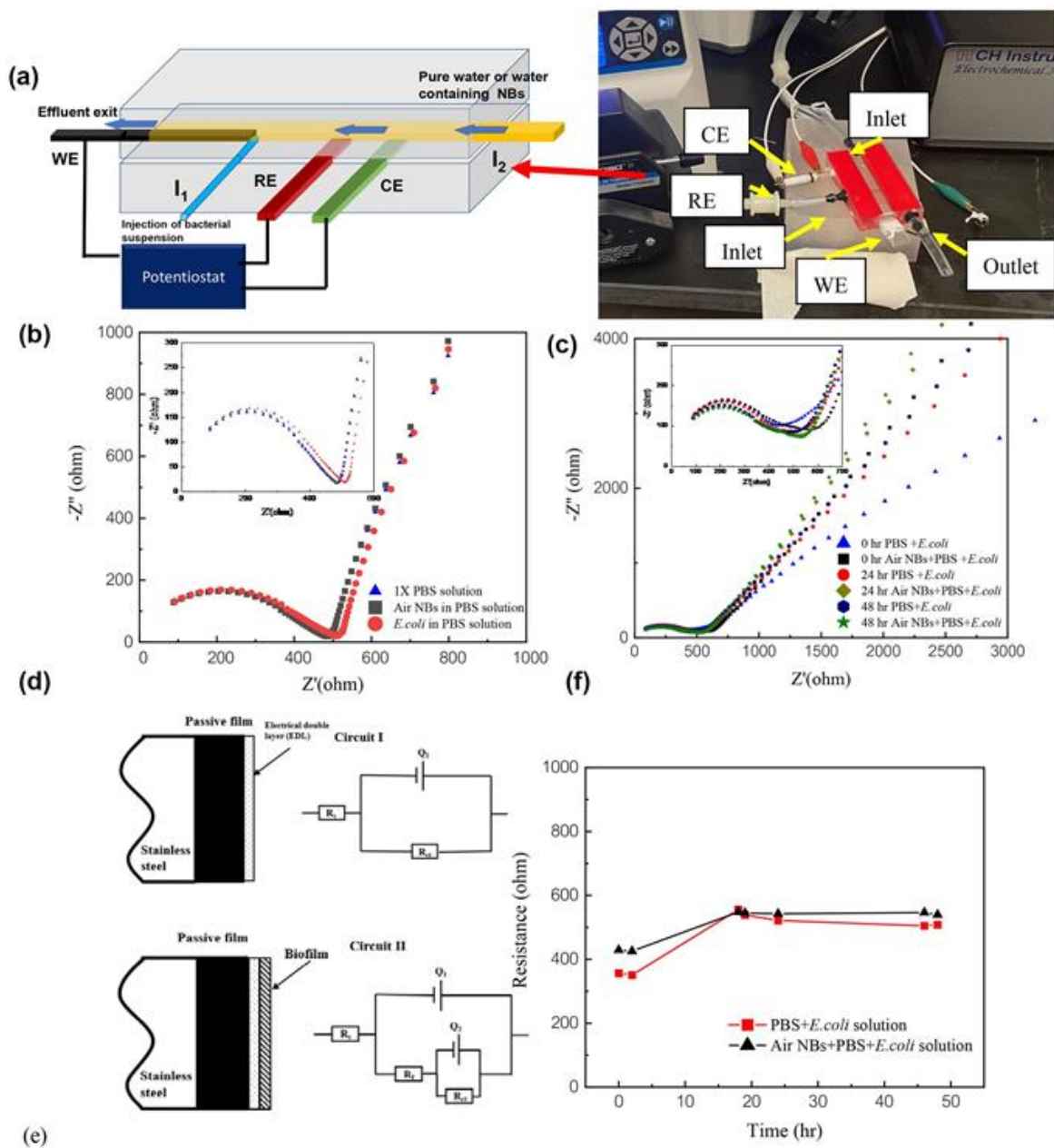


Figure 16.16 (a) Schematics of a microfluidic device that measures the EIS on the biofilm growing surface (working electrode). The photo shows the microfluidic device developed in Dr. Wen Zhang's laboratory at NJIT. (b) Nyquist plots of EIS data obtained with the microfluidic device when only PBS solution, the NBs-containing PBS solution and the bacterial suspension were respectively injected at a flow of 1 mL min^{-1} ; (c) Nyquist plots when the *E. coli* suspension was run through the device for different times to allow the biofilm formation on the surface of the stainless-steel with/without the presence of NBs. (d) and (e) are the hypothetical equivalent circuit models of $R(C(R))$ and $R(Q(R(QR)))$ before and after the formation of the biofilm on the surface of the stainless-steel. (f) The change of resistance of WE with time for the *E. coli* solution with/without the presence of NBs.

Figure 16.16b shows the Nyquist plots of the EIS data when injecting three different solutions through the microfluidic device for four hours. The interfacial charge transfer resistance as indicated by the arc radius in the Nyquist plots were similar for this electrochemical system when varying the flowing liquid. Table 16.3 summarizes the model fitting results for the EIS spectra using an equivalent circuit of $R(QR(QR))$ presented in Figure 16.16e, where R_f (Ω) is the resistance of biofilm formed on the stainless-steel surface, R_s (Ω) is the solution resistance, R_{ct} (Ω) is the charge transfer resistance, Q_1 (μF) and Q_2 (μF) are the capacitance of the electrical double layer (EDL) and the constant phase element parameter, respectively.²¹⁶ The deposition of NBs or bacteria on the stainless-steel surface slightly increased the R_f value from 473 Ω to 489–497 Ω , respectively.

Table 16.3 EIS fitting results on the surface of stainless-steel fed with the PBS solution, the NB solution and the *E. coli* solution.

	Feed time	Module	Chi-squared	Resistance (R_f , Ω)
PBS	4 hour	$R(Q(R(QR)))$	0.0017	473.1
Air NBs	4 hour	$R(Q(R(QR)))$	0.0018	486
<i>E. coli</i> suspension	4 hour	$R(Q(R(QR)))$	0.0019	497

Figure 16.16b compares the Nyquist plots when the biofilm developed under the flows of different mixtures for 48 hours with or without the presence of NBs. The EIS spectra, again, do not reveal significant changes or differences. Table 16.4 compares the fitting parameters using the equivalent electric circuit in Figure 16.16d or 16.16e. The EIS data without NBs for the initial two hours fits the circuit I model better as there was no significant biofilm formation. With the formation of biofilm, the spectra start to fit to the circuit II model. The biofilm formation after 18 hours led to an obvious increase in the resistance (R_f) of the WE. However, Figure 16.16f shows that the coexistence of NBs and bacteria yielded a greater resistance on the surface of the WE than that without NBs, suggesting that the NBs may quickly block or cover the stainless-steel surface, which interfere with and reduce bacterial adhesion.

Table 16.4 EIS fitting results of biofilm formation on the surface of stainless-steel with/without NBs.

PBS + <i>E. coli</i>				NBs + <i>E. coli</i>		
Feed time	Model	Chi-squared	Resistance (R_f , Ω)	Model	Chi-squared	Resistance (R_f , Ω)
0 min	$R(C(R))$	0.004718	356.6	$R(Q(R(QR)))$	0.003013	429.3

2 h	R(C(R))	0.008447	350.8	R(Q(R(QR)))	0.002921	425.5
18 h	R(Q(R(QR)))	0.002187	555.7	R(Q(R(QR)))	0.002187	548.0
19 h	R(Q(R(QR)))	0.002128	539.0	R(Q(R(QR)))	0.002128	545.1
24 h	R(Q(R(QR)))	0.002087	521.45	R(Q(R(QR)))	0.002087	542.6
46 h	R(Q(R(QR)))	0.002352	505.0	R(Q(R(QR)))	0.002352	546.7
48 h	R(Q(R(QR)))	0.002432	508.4	R(Q(R(QR)))	0.002432	539.9

16.3.4 Harmful Algal Bloom Mitigation and Ecological Restoration and Remediation

Excess nutrients can cause eutrophication and HABs in natural waters, which may negatively affect water quality, landscape esthetics, human health and economic development.²¹⁷ HABs have caused direct economic losses of several million pounds in the UK²¹⁸ and >\$2 billion in the USA²¹⁹ in the fishing industry. Owing to rapid population growth and economic development, various human activities, industrial, agricultural and transportation have intensified eutrophication.^{220,221} Despite of the control of external nutrient loading from anthropogenic discharges, the existing N and P loads from contaminated sediment are expected to prolong eutrophication episodes.²²² The main cause of internal nutrient loading would be hypoxia/anoxia ($\text{DO} < 2 \text{ mg L}^{-1}$)-induced biochemical reactions at the sediment–water interface. Therefore, measures for the reduction of nutrient internal loadings and for mediating hypoxia/anoxia have attracted increasing attention for eutrophication control.

Many recent ecological engineering practices and technologies (*e.g.*, aeration, nutrient fixation and algicide use) have been developed and tested for water quality restoration. Various approaches have been developed or explored to reduce nutrient loadings from the sediment, including dredging and *in situ* capping of contaminated sediment, and by artificially aerating the bottom water. For example, capping of the sediment is potentially the most cost effective.²²³ Treatment by spraying of natural materials, such as sand, clay, gravel, and synthetic materials (*e.g.* P adsorbents), in lakes could form a physical barrier that effectively prevents nutrients from entering into the water column.²²⁴ However, this approach can hardly remediate sediment hypoxia/anoxia owing to the absence of extra oxygen delivery. Moreover, traditional bottom water oxygenation methods, such as deep-water aeration, have been reported to be hindered due to excessive costs, high energy consumption and hydrologic disturbance of the benthos.²²⁵

Recently, nanobubble technologies have demonstrated promising potential in sustainable control and abatement of eutrophication and HABs. NBs have been directly introduced into eutrophic/polluted waters to remove aerobically-degradable

pollutants, such as biochemical oxygen demand (BOD) and ammonium.^{226,227} Previous studies have also shown that NBs can improve the lysis of harmful algal cells and the detoxification of cyanotoxins, and companies in Asia, the US and Europe have become increasingly involved in projects that use NB technology for mitigation of HABs.^{228–230} Alongside the use of the bulk NBs, a novel refinement of the technology, which involves interfacial NBs, was developed in 2018, using natural minerals loaded with oxygen to deliver oxygenated NBs onto sediment surfaces.^{231,232} This approach successfully reversed sediment hypoxia and reduced N and P fluxes from the sediment for over four months. Nevertheless, the underlying mechanisms of NB stability and aquatic behavior such as gas diffusion dynamics still remain elusive. Currently, the emerging NB technology for water restoration has been mainly tested in freshwaters or inland lakes. However, HABs and hypoxia problems also occur in coastal areas,²³³ where high salinity and high dissolved organic matter (DOM) may inevitably reduce the longevity of NBs.²³⁴ More importantly, temperature increases and acidification of water bodies may also affect the stability and gas dissolution properties of NBs. Thus, a fundamental understanding of the physicochemical properties and behavior of NBs are worthy of further elucidation to support the engineering applications of NBs.

A modified local soil (MLS) technology was developed and demonstrated in mitigating eutrophication and accelerating ecological restoration.²²⁴ The MLS technology uses natural soil and clay particles modified by natural polymers to remove HABs and remediate polluted sediment. Field trials in several lakes (Figure 16.17) showed that MLS treatment removed HABs within hours and resulted in improved water quality and biodiversity over up to three years. The approach involves the addition of MLS to flocculate the HABs from the water so they settle onto the sediment.^{235,236} An additional layer of MLS material is then used to cap the algal cells, embedding them in the sediment so that diffusion of nutrients into the overlying water is blocked but can be taken up by submerged macrophytes. The MLS method can switch the aquatic environment from an algae-dominated state to one where macrophytes dominate, which is essential for the restoration of an aquatic ecosystem.²³⁷ An MLS that is blended and oxygenated with oxygen NBs achieves controlled release of DO and retains the efficacy of combating sediment hypoxia/anoxia. Several lab-scale column experiments were conducted and successfully demonstrated its superior ability to extend the DO release and hypoxia reversal,²³¹ mitigation of greenhouse gas emissions,²³⁸ and reduction of toxic metals.^{239,240}

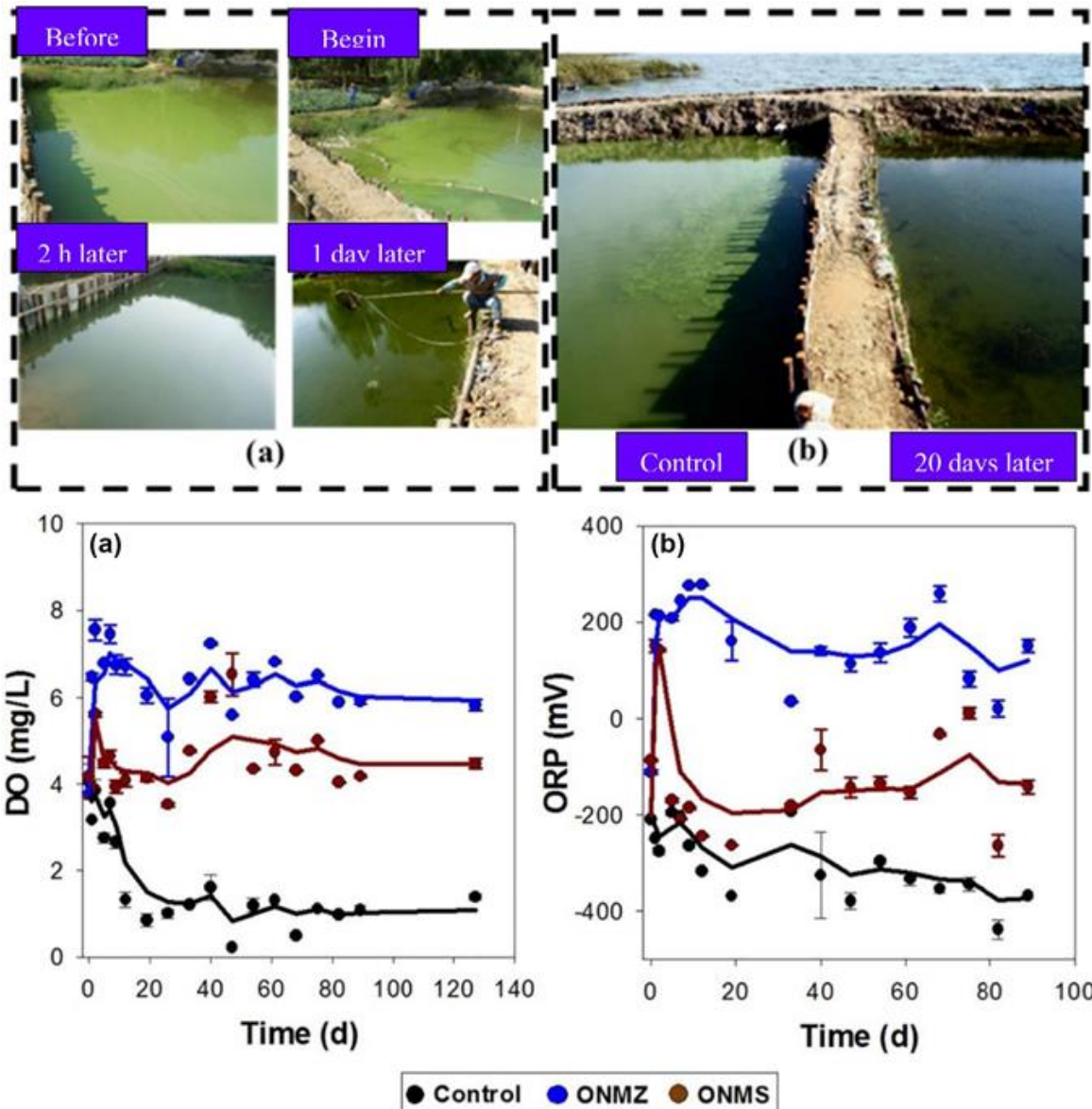


Figure 16.17 Eutrophication control and sediment remediation by spraying oxygen NBs-modified local soil into the impaired lake water.²²⁴ The two graphs compare the DO and ORP levels at the sediment–water interfaces in control, oxygen nanobubble-modified zeolite (ONMZ) and oxygen nanobubble-modified soil (ONMS) treatment systems.²³¹ Reproduced from ref. ²²⁴, <https://doi.org/10.3390/w11061123>, under the terms of the CC BY 4.0 license, <https://creativecommons.org/licenses/by/4.0/>, and reproduced from ref. ²³¹ with permission from Elsevier, Copyright 2018.

16.3.5 Agricultural Applications

Agricultural irrigation consumes about 70%–80% of the global fresh water supply^{241,242} and releases substantial pollutants to coastal and marine surface water.^{243–248} Agriculture therefore has the greatest contribution to water scarcity.²⁴⁹ besides many other factors such as global climate change and a greater variation in annual precipitation.²⁵⁰ Moreover, many other non-renewable resources (e.g. rock phosphate and fossil fuels) are depleted. The limit of natural resources (production land, water, soil, and fertilizers) and the growth of the world population require agricultural systems to be more efficient and smarter than before.

Irrigation methods have considerable impacts on land erosion, pollution and water resource depletion. Conventional irrigation practice involves applying water uniformly with limited considerations of the spatial variability in soil and crop water needs, which causes over-irrigation or underirrigation.²⁵¹ Over half of the total freshwater is estimated to actually reach the targeted crops.²⁴² Precision agriculture (PA) utilizes the latest technologies to increase the efficiency of water or nutrient delivery to reduce detrimental farming effects on resources and the environment.^{252,253}

MNBs and NBs have rapidly transformed many practices in agriculture, aquaculture, food engineering, and sterilization.^{5,254,255} The application of oxygen NBs enhanced the oxygen concentration from 8 mg L⁻¹ in normal distilled water to over 30 mg L⁻¹ after 30 minutes.³⁶ Ozone MBs could effectively remove and degrade fenitrothion and pathogens in food and vegetables in such as lettuce, cherry tomatoes, and strawberries.²⁵⁶

Many studies recently demonstrated proper irrigation with NB water could promote germination and plant growth with improved productivity.^{36,189,190,257} For instance, seed germination rates increased in mixed nitrogen and air NB water compared to that in distilled water, because of the generation of exogenous ROS and increased the mobility of the water molecules.^{147,258} MNBs improved the growth of plants such as lettuce^{259,260} and rice.²⁶¹ Moreover, the influences of air, oxygen, nitrogen, and carbon dioxide NBs may be different as the soil chemistry (e.g., pH or DO) will be changed upon exposure to different NB waters. Figure 16.18a and b compares the hypocotyl growth process of lettuce and fava beans (*Vicia faba*) that differed with the type of NB water. The tap water-treated ones had no leaf sprout during the same initial growth period. Figure 16.18c reveals nitrogen NBs promoted most plants (especially tomato) in terms of leaf numbers. Figure 16.18d illustrates the generation of exogenous ROS by NBs that could activate the cell wall loosening and cell elongation.^{190,258} The positive impacts on germination or plant growth may also be attributed to the effective delivery of nitrogen or CO₂ and other possible factors such as release of soil nutrients.^{9,10}

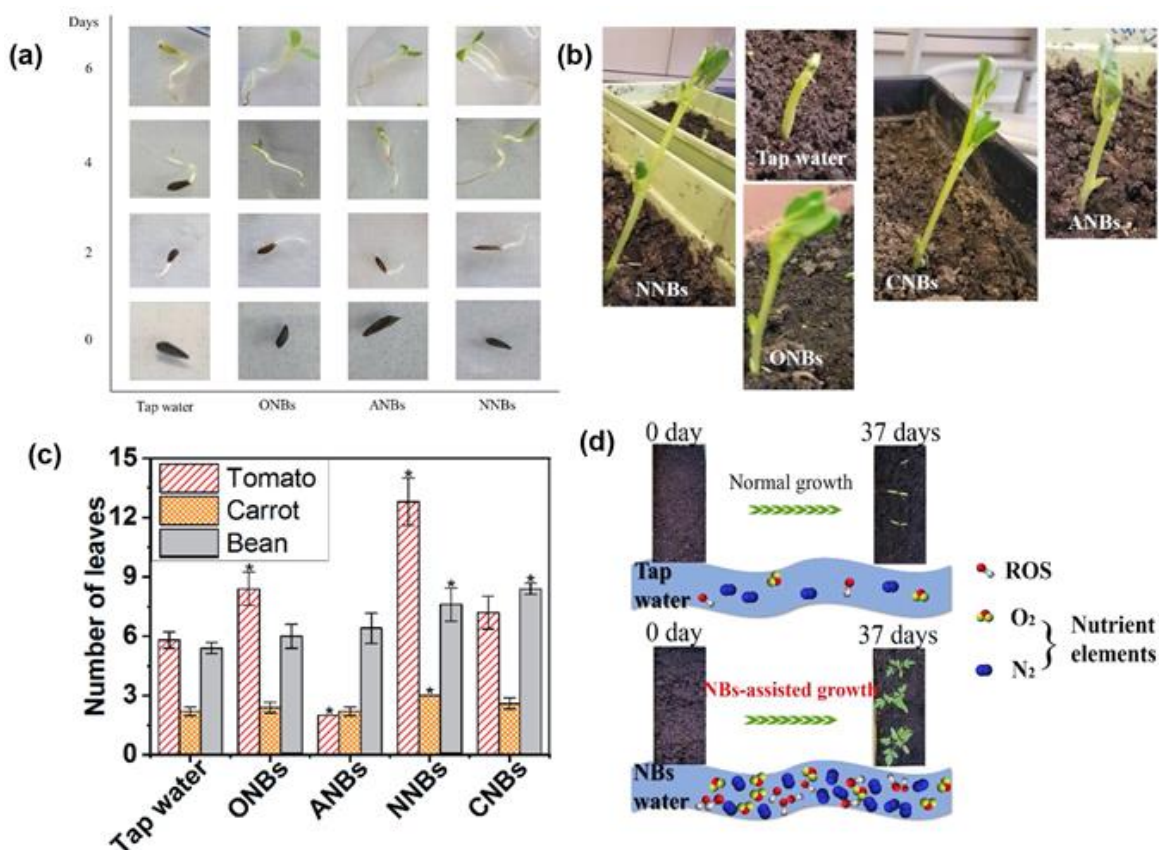


Figure 16.18 (a) Photos of hypocotyl growth process of lettuce seeds at different durations of submersion. (b) Growth of fava bean (*Vicia faba*) taken after the first week of incubation. (c) Influence of water type on number of leaves of tomato, carrot, and bean plants after 37 days. (d) Summary of the promoting effect by NBs and potential mechanisms of promotion. Reproduced from ref. ¹⁸⁹ with permission from American Chemical Society, Copyright 2018.

Moreover, different plants including lettuce, carrot, fava bean, and tomato may have different responses to NBs not only because they have physiological differences but as they also have different rhizosphere bacteria or other microorganisms that grow near the plant roots and play critical roles in the plant's nutrient absorption and growth.

Acknowledgements

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Chapter 17

The Different Toxicity and Mechanism of Titanium Dioxide (TiO₂) and Titanate Nanotubes (TNTs) on Escherichia coli

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17.1 Introduction

Nanomaterials have been extensively used in many fields including chemical, energy, construction, agriculture, wastewater treatment, daily consumption, *etc.*^{1,2} Although the development of nanotechnology has brought a lot of convenience to human life, many recent studies prove the

potential environmental and public health risks of nanomaterials.^{3,4} Generally, nanomaterials are produced through natural biogeochemical process, by-products of combustion reactions, or engineered production for a specialized function. It is estimated that approximately 318 100 metric tons of engineered nanomaterials are produced in the environment all over the world every year, and over 40% of them are expected to release into soil, water, and air environments.⁵ Surprisingly, the amount of engineered nano-TiO₂, carbon nanotubes, nano-Ag, *etc.*, as the most common manmade nanomaterials released into the environment, is around five to six orders of magnitude less than that of naturally-occurring nanomaterials.⁶

TiO₂ nanomaterials are the most commonly engineered nanomaterials utilized in many commercial products, such as food additives, sunscreens, paint, *etc.*⁷ Due to excretion and runoff, nano-TiO₂ has been found to be dominant amongst various engineered nanomaterials released into water bodies and wastewater treatment plant effluents,^{5,7,8} which will cause a series of negative environmental effects.⁹ The physical and chemical properties of these nanoscale materials are different from their bulk-form counterparts, and their environmental toxicity mechanisms are related to their characteristics. TiO₂ is a kind of spherical nanoparticle with acid- and basic-stability, and it commonly consists of a combination of 80% anatase and 20% rutile.¹⁰ In addition to commercial products, TiO₂ is the most widely used efficient photocatalyst material, and it possesses wide-ranging activity towards a variety of organic pollutants because the water molecules adsorbed on the surface of TiO₂ are oxidized to produce active free radicals.¹¹ Except for small amounts of H₂O₂ and superoxide radicals (O₂^{·-}), the hydroxyl radical (·OH) is the main oxidative species in the photocatalytic processes of TiO₂.¹² According to previous reports, the ·OH radical is active in the reaction of oxidizing organic substances and is especially toxic for microorganisms.¹⁰

Titanate nanotubes (TNTs) are a kind of one-dimensional and multi-walled nanotube synthesized by hydrothermal methods from TiO₂ precursors¹³ and have attracted increasing attention as it has a special morphology and unique physicochemical properties. There is a high density

of hydroxyl groups located on the surface of TNTs,¹⁴ and they can provide sites for the formation of surface metal–OH complexes that can greatly facilitate the activation of some compounds.¹⁵ Moreover, TNTs show high capture capacity for metal ions with the mechanism of ion-exchange between metal ions and H^+/Na^+ located in the interlayers of TNTs,¹⁴ and many kinds of metal ions (*e.g.*, Pb^{2+} , Cd^{2+} , Cr^{4+} and Mn^{4+}) can be captured on TNTs. Many studies have proved their specific characteristics: large specific surface area, good ion-exchangeable ability and high chemical stability.^{16–19} This peculiar microstructure means TNTs have great potential applications in adsorption and photocatalytic reactions.

The environmental and health toxicity of nanomaterials have been extensively studied, and the different physicochemical characteristics of nanomaterials govern the cytotoxicity properties.^{20,21} For TiO_2 , it has been revealed that nano- TiO_2 can effect some microbial processes,⁸ and cause cell death under solar light^{11,22} and even potential risks for human health.²³ Some studies have suggested that its toxicity is closely related to its photocatalytic properties.^{10,22,24} However, it is not enough to only investigate the toxicity of nano- TiO_2 in the natural environment under solar light, because the duration of darkness in the natural environment is almost the same as the duration of sunlight. In addition, the emerging TNT nanomaterials have been widely used, but almost no studies have reported the toxicity of TNTs and little is known about their toxicity mechanism.

In this study, we investigated the inactivation capability of nano- TiO_2 and TNTs on model *Escherichia coli* under simulated solar light and a dark chamber, to evaluate the toxicity of these two nanomaterials in the natural environment. The toxic mechanism of nano- TiO_2 and TNT nanomaterials was explored on a subcellular level.

17.2 Methods and Materials

17.2.1 Chemicals

TiO_2 nanoparticles (P25, 80% anatase and 20% rutile) were purchased from Degussa (Evonik) of Germany. TNTs were synthesized through a one-step

hydrothermal method based on our previous studies.⁴³ Specifically, 1.2 g TiO_2 were dispersed into a 10 M NaOH solution (66.7 mL). After continuous stirring for 12 h at room temperature, the mixture was transferred into a Teflon reactor and then heated at 130 °C for 72 h. The precipitate was fully washed with deionized water until the eluent was neutral, and the final products (TNTs) were obtained after drying at 105 °C for 4 h. All the other chemicals including sodium hydroxide and ethanol were of analytical reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure (deionized, DI) water used in all the experiments was obtained from a laboratory purification system (Milli-Q, Millipore, Billerica, MA, USA).

17.2.2 Characterization of TiO_2 and TNTs

The structure of TNTs was analyzed using a D/Max 2400 X-ray diffractometer (XRD, Rigaku, Japan) at 100 kV and 40 mA with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$), and a scanning rate of 4° per min was set. The morphologies of the TNTs were observed on a Tecnai 30 FEG transmission electron microscope (TEM, FEI, USA) operated at 300 kV. The Brunauer–Emmett–Teller (BET) surface area was obtained on an ASAP 2010 surface area analyzer (Micromeritics, USA) in the relative pressure (P/P_0) range 0.06–0.20, while the pore size distribution was obtained following the Barrett–Joyner–Halenda method. The nitrogen adsorption at the relative pressure of 0.99 was used to determine the pore volumes and the average pore diameters. The Zeta potential of the materials was measured using a Nano-ZS90 Zetasizer (Malvern Instruments, UK).

17.2.3 Preparation of *E. coli* Strain

The *E. coli* strain was purchased from American Type Culture Collection (ATCC 15597) and cultured in Luria–Bertani (LB) medium at 37 °C for 16 h at 200 rpm until the early stationary phase was reached. The *E. coli* strain was harvested by centrifugation at 6000 rpm for 6 min at 4 °C in each culture cycle. The pellets were fully washed with sterilized physiological saline (0.9% of NaCl solution) three times to remove the LB medium residue. Finally, the strain cells were resuspended in 10 mL of sterilized

physiological saline to obtain the bacterial stock suspension with a cell concentration of approximately 5×10^9 colony forming units (CFU) per milliliter.

17.2.4 Nanomaterial Inactivation Experiment

The inactivation performance of the nanomaterials was examined by the bacteria inactivation rate of *E. coli* as a model strain. The reaction system contains sterilized physiological saline of 100 mL, a nanomaterial dosage of 0.05 g L^{-1} , an initial *E. coli* density of 10^7 CFU per mL and a solution pH of 7, with a circulating cooling water bath to make the system temperature stable at about 25 °C. The inactivation performance of the TiO_2 and TNTs nanomaterials were analyzed in the above system under simulated solar light and a dark environment, respectively. The simulated solar light was produced by a Microsolar 300A Xenon arc lamp (PerfectLight, China) with a 300 W AM1.5 mode. The incident light intensity in the reactor center was detected to be 100 mW cm^{-2} .²⁵

At predetermined times, *i.e.*, 0, 10, 20, 30, 40, 50, 60, 70 min, the cell suspension samples (0.5 mL) were collected and serially diluted with sterilized DI water. Then, 0.1 mL of the diluted sample was immediately coated on LB agar plates (in triplicate) and cultured at 37 °C for 24 h. The colonies on the plates were then counted to determine the number of viable cells of each sample with a limit of quantification of 100–300 CFU per mL. All experiments were performed in triplicate.

17.2.5 Inactivation Mechanism Exploration

The mechanism of cell inactivation by TiO_2 and TNTs nanomaterials was explored on a subcellular level, including cell morphology, total protein degradation, potassium ion (K^+) leakage, cell membrane permeability, lipid peroxidation and cellular ATP level, according to previous studies.^{26,27} For the morphology analysis of *E. coli* cells, the cell suspension samples (2 mL) were collected from the reaction system and then filtered using $0.22 \text{ }\mu\text{m}$ membranes (Millipore, USA) to capture the *E. coli* cells. The obtained *E. coli* cells were resuspended in sterilized DI water and then fixed on copper

grids. Finally, the prepared samples were observed on a Tecnai 30 FEG transmission electron microscope (TEM, FEI, USA).

At the above given time intervals, the samples were collected to conduct the remaining analysis of mechanism exploration. The total protein content of the collected samples was determined using a Lowry Protein Assay Kit (Sangon Biotech, Shanghai, China) after sonicating using ultrasonic cell disruption (200 W, 10 min) in an ice bath. For K^+ leakage, the samples were filtered using 0.22 μm membranes (Millipore, USA) and the K^+ concentration in the filtrate was determined using a flame atomic absorption spectrophotometer (Analytik Jena, Germany). The degree of damage to the cell membrane permeability was evaluated by the extent of the penetration of extracellular substrate into the cytoplasm with detection of the hydrolysis rate of *o*-nitrophenyl- β -D-galactopyranoside (ONPG).¹² The oxidation of the cell membranes was evaluated by the extent of the peroxidation of polyunsaturated phospholipids in membranes. The malondialdehyde (MDA) is one of the most abundant individual aldehyde formed during lipid peroxidation and is usually detected as the target product.²⁶

As the most important energy molecule, ATP plays an important role in various cell processes. The change of cellular ATP level during the inactivation reaction was measured using a Synergy H1 microplate reader (BioTek, Winooski, USA) and the luciferin–luciferase method using a bioluminescence assay kit (Beyotime Biotech, Shanghai, China).

17.3 Results

17.3.1 Material Characterization

Figure 17.1 shows the different TEM morphologies of the TiO_2 (P25) and TNTs. TiO_2 (P25) is a kind of spherical nanoparticle with diameters of about 20–30 nm (Figure 17.1a), which was consistent with previous reports.²⁸ The TNTs were multi-walled, hollow and open-ended nanotubes (Figure 17.1b). The uniform inner (*ca.* 4.5 nm), outer diameters (*ca.* 9 nm) and interlayer distance (*ca.* 0.75 nm) was also measured and was consistent with previous studies.²⁹ The XRD patterns of TiO_2 (P25) exhibited strong diffraction peaks at 25° , 27° , 36° , 37° , 38° , 39° and 48° , which were

ascribed to the crystal planes of A(101), R(110), R(101), A(103), A(004), A(112), A(200) in the typical anatase and rutile phases (JCPDS No. 21-1272 and 21-1276) (Figure 17.1c). For TNTs, the peaks at 10°, 24°, 28° and 48° were consistent with the crystal planes of T(200), T(201), T(111) and T(020) of titanate (JCPDS No. 31-1329) (Figure 17.1d). The strongest characteristic peak at 10° of T(200) indicated an interlayer distance of 0.75 nm,³⁰ highly consistent with the TEM result. Besides, the physicochemical parameters of these two nanomaterials are quite different.³¹ The specific surface area of TNTs (272 m² g⁻¹) is approximately six times larger than that of TiO₂ (47 m² g⁻¹), and the single point total pore volume of TNTs (1.26 cm³ g⁻¹) is seven times larger than that of TiO₂ (0.18 cm³ g⁻¹). The pH_{PZC} values of TiO₂ and TNTs are 6.67 and 2.56, respectively.

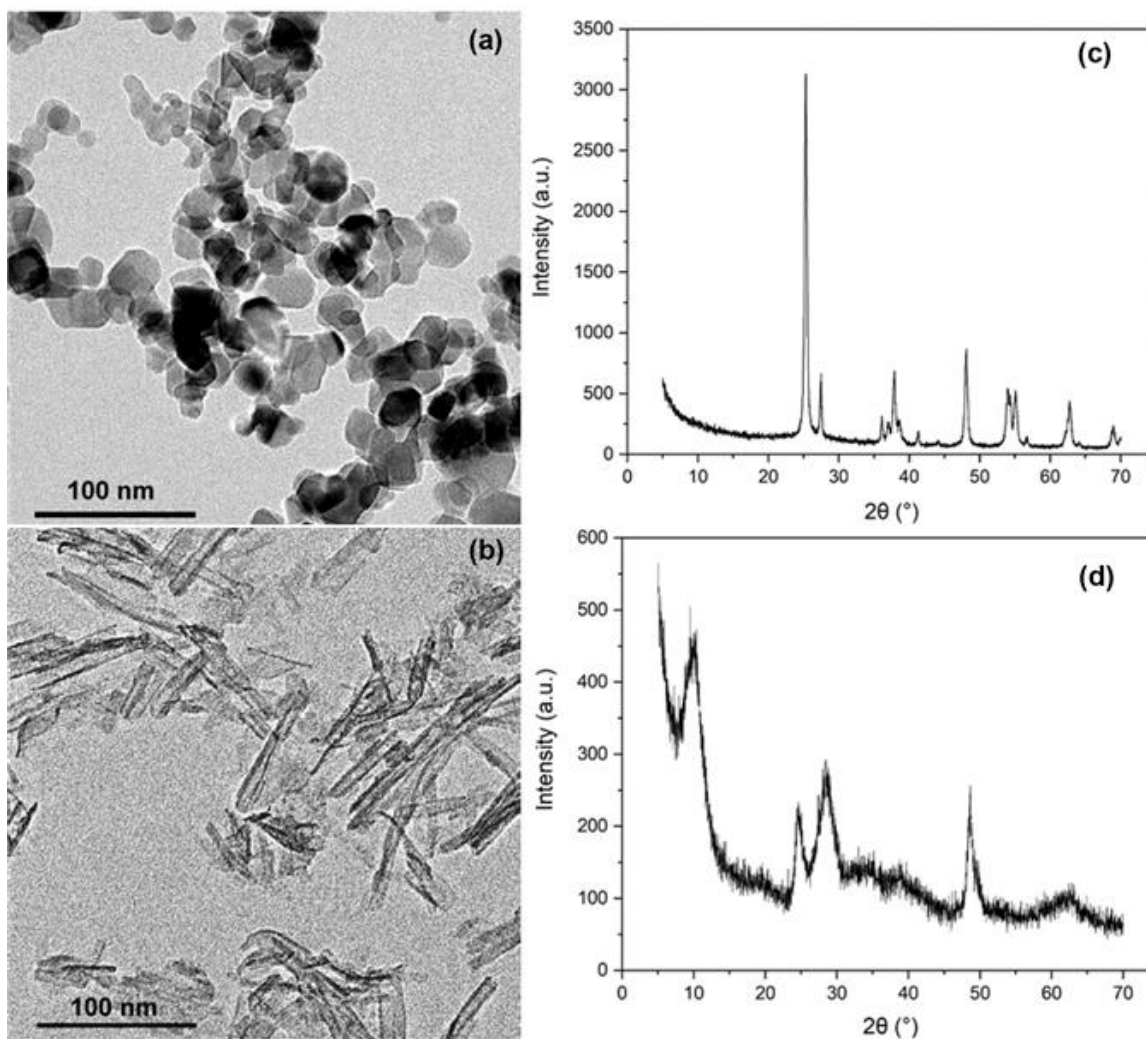


Figure 17.1 TEM images and XRD patterns of TiO_2 and TNT nanomaterials: (a) TiO_2 TEM; (b) TNTs TEM; (c) TiO_2 XRD; (d) TNTs XRD.

17.3.2 Inactivation Performance of TiO_2 and TNT Nanomaterials

The default inactivation reaction system was placed under simulated solar light and a dark chamber to evaluate the inactivation capability of TiO_2 and TNTs nanomaterials in the natural environment on *E. coli* during the day and night, respectively. As shown in [Figure 17.2](#), the *E. coli* was gradually completely inactivated by TiO_2 only under simulated solar light, while the activity of the cells in the dark environment was hardly affected by TiO_2

over a period of 70 minutes. However, for TNTs, the difference in the inactivation effect on *E. coli* was not very obvious between the solar light and dark environments. The inactivation rate under solar light was about 62.7%, and the rate in a dark environment was about 36.6% after a period of 70 minutes. Overall, the order of inactivation performance on *E. coli* was: TiO₂ under solar light > TNTs under solar light > TNTs in the dark > TiO₂ in the dark. These results suggested that solar light can make TiO₂ nanomaterials toxic to *E. coli* cells.

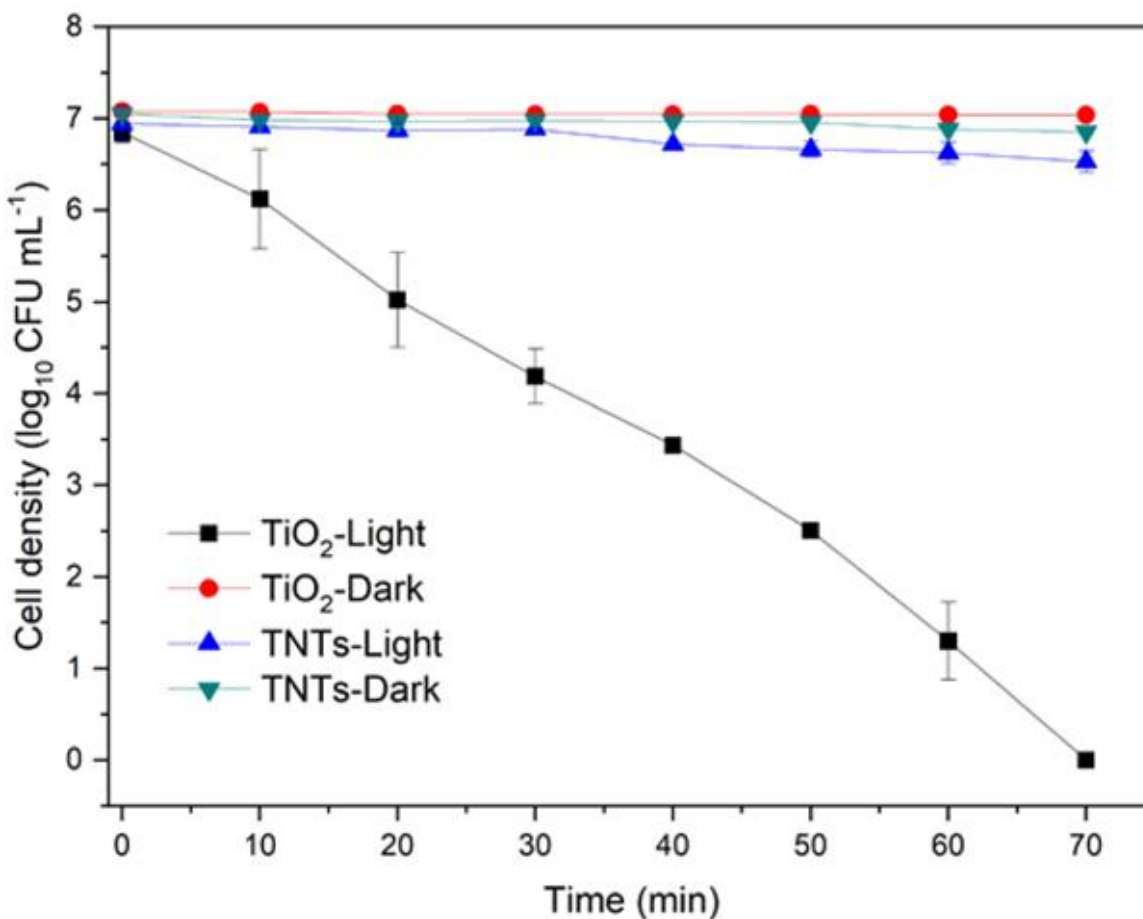


Figure 17.2 The inactivation performance of TiO₂ and TNT nanomaterials under solar light and in a dark environment.

17.3.3 Protein Degradation and K⁺ Leakage

The total protein content of *E. coli* in the inactivation system of TiO_2 under solar light was severely degraded with a degradation percentage of 23%, but the total protein content in the dark reaction system only slightly decreased by 8% (Figure 17.3a). For the TNTs system, although the degradation rate of the total protein content in the dark and solar light environments was different at the beginning of the reaction, the final degradation degree of the total protein content was almost the same, with a percentage of about 10% (Figure 17.3a). Compared with TNTs, TiO_2 seems to possess a greater potential to damage proteins. In total, the degradation of the total protein content was the most pronounced in TiO_2 under solar light, followed by that in the TNTs system (both in the dark and under solar light), and the TiO_2 in a dark environment system.

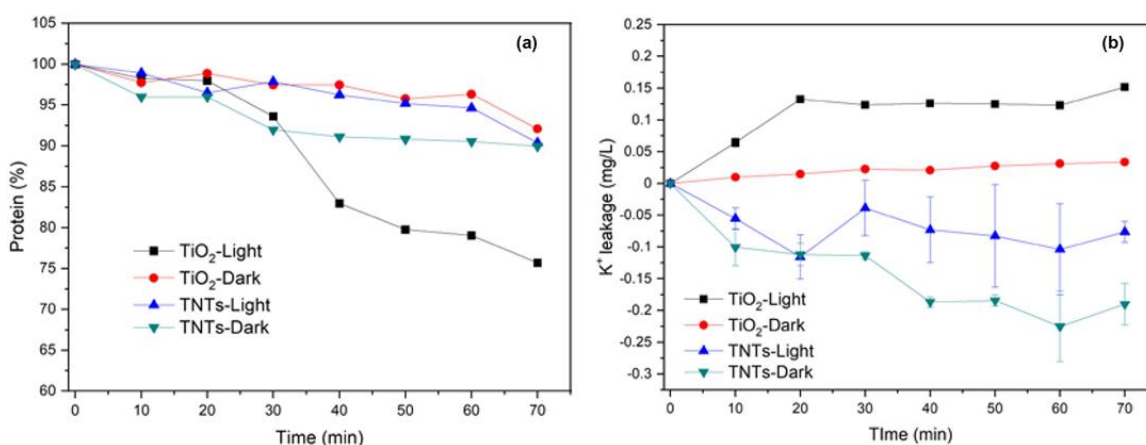


Figure 17.3 (a) Total protein and (b) K^+ leakage of *E. coli* in the inactivation system of TiO_2 and TNT nanomaterials under solar light and in a dark environment.

The leakage of K^+ from *E. coli* cells during the inactivation reaction was detected and the results are shown in Figure 17.3b. In the TiO_2 system, K^+ obviously leaked from the cells both in the dark and solar light environments. A substantial amount of K^+ immediately leaked from the *E. coli* cells when the reaction started under solar light, and then the K^+ concentration leveled off after 20 minutes. However, the K^+ concentration slowly increased until the end of the reaction in a dark environment, and the

degree of K^+ leakage was negligible, which was much lower than that in solar light environment. Unlike the TiO_2 system, no K^+ leakage from cells was observed in the TNTs system, and the K^+ concentration in the system decreased both in the dark and solar light environments. In addition, the degree of K^+ decrease in a dark environment was much higher than that under solar light.

17.3.4 Cell Membrane Permeability

The damage to the cell membrane permeability during the inactivation reaction was evaluated by detecting the hydrolysis rate of extracellular ONPG. [Figure 17.4a](#) shows that the hydrolysis rate of ONPG first increased and then decreased in the inactivation system of TiO_2 under solar light, suggesting the membrane permeability of *E. coli* cells was severely damaged, such as large holes or cracks, during the inactivation process. However, no obvious ONPG hydrolysis rate was observed in the inactivation system of TiO_2 in the dark over the 70 minutes ([Figure 17.4a](#)), which indicated the cell membrane permeability was almost unchanged. Compared with TiO_2 , the ONPG hydrolysis rates in the TNTs systems were negligible during the inactivation process. Nevertheless, for the TNTs systems, the ONPG hydrolysis rate in the dark and solar light environments was to some extent different, and the ONPG hydrolysis rate in the solar light reaction was higher than that in the dark at 70 minutes, indicating the cell membrane damage was more serious under solar light. These results collectively suggested that solar light was an important factor in the damage to the cell membrane permeability caused by the Ti nanomaterials.

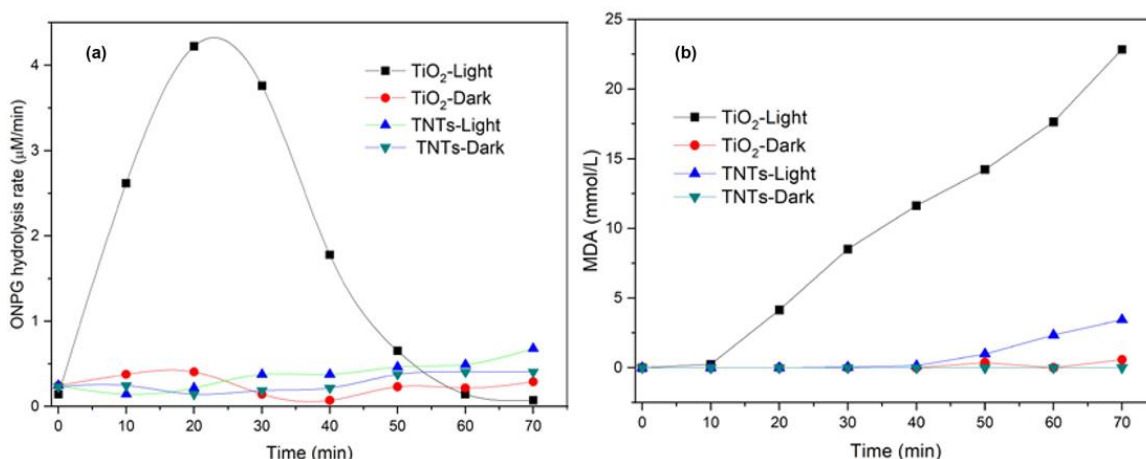


Figure 17.4 (a) The cell permeability evaluated using the ONPG hydrolysis rate and (b) the lipid peroxidation based on MDA accumulation in the inactivation system of TiO₂ and TNT nanomaterials under solar light and in a dark environment.

17.3.5 Lipid Peroxidation

The MDA concentration was detected during the inactivation process to indicate the lipid peroxidation extent. The concentration of MDA gradually increased as the reaction progress in the inactivation system of TiO₂ under solar light (Figure 17.4b), suggesting the unsaturated lipids on the cell membrane were peroxidated during the inactivation process. Similarly, the concentration of MDA also increased in the system of TNTs under solar light, although it occurred after 40 minutes of the reaction and the concentration increase was less than that in the TiO₂ system at 70 minutes (Figure 17.4b). However, there was almost no change in the concentration of MDA in the dark environment both in the TiO₂ and TNTs inactivation systems. These results are consistent with the results in the previous section that indicate that solar light played a key role in the peroxidation process of lipid of cell membrane.

17.3.6 Cellular ATP Level

The ATP level was detected during the inactivation process to reflect the cell metabolism activities. Figure 17.5 shows that the cellular ATP level decreased sharply as the reaction begins in the inactivation system of TiO₂

under solar light. It dropped to 70% of the initial ATP level over 10 minutes and reached the lowest level (10%) at 20 minutes until the end of the reaction. Likewise, the cellular ATP level also decreased to about 55% at 70 minutes in the system of TNTs under solar light. The decrease of cellular ATP in the dark environment was insignificant after 70 minutes of reaction time. The final cellular ATP levels in the TiO_2 and TNTs inactivation systems were about 65% and 75%, respectively.

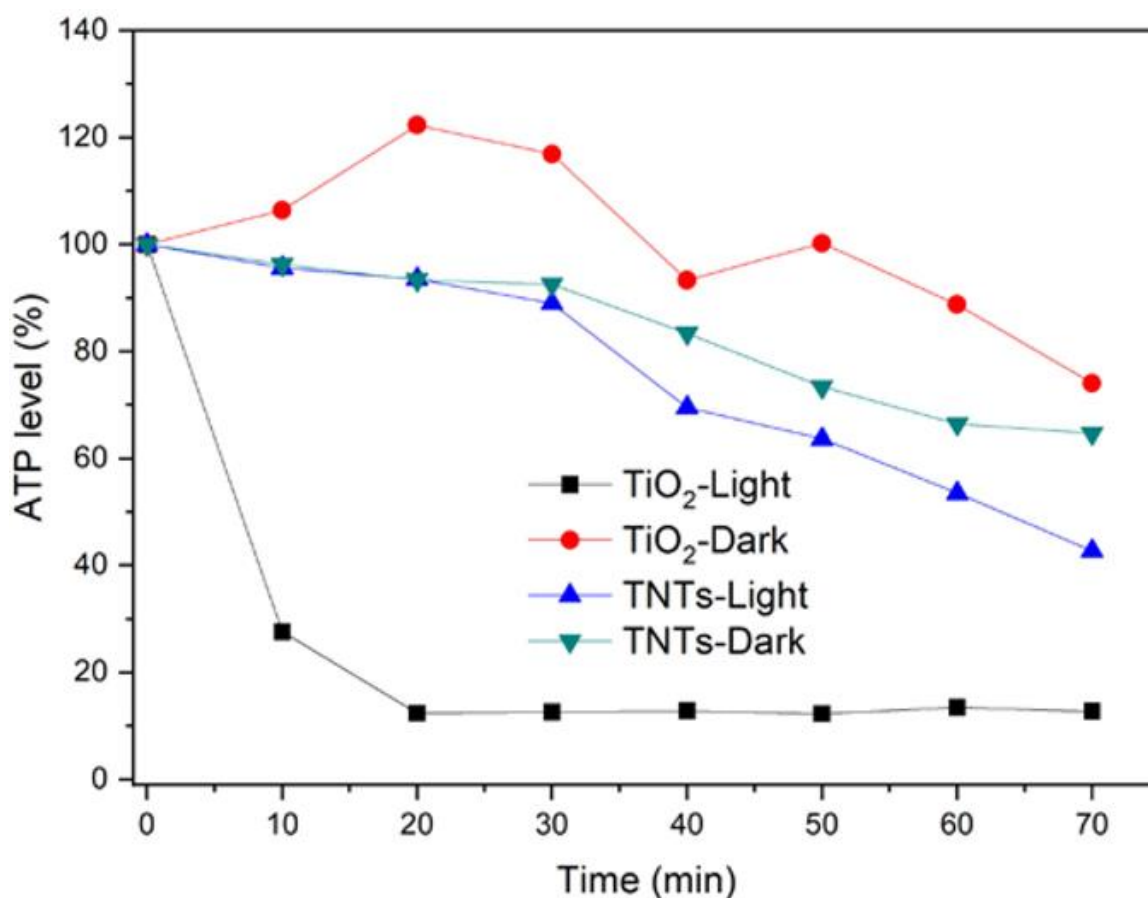


Figure 17.5 The cellular ATP level of *E. coli* in the inactivation system of TiO_2 and TNT nanomaterials under solar light and in a dark environment.

17.4 Discussion

The extensive use of nanomaterials results in massive emissions into the environment. As classical Ti nanomaterials, the toxicity of TiO_2 and TNT

nanomaterials have been investigated under various conditions. However, due to the different properties of the nanomaterials, the differences in material toxicity that are supposed to be caused by the two most important conditions (solar light and dark exposure) in natural environment are not so clear. Judging from our results, the toxicity of TiO₂ and TNT nanomaterials is quite different in solar light and dark environments based on the inactivation performance of *E. coli* cells, and solar light seems to be an indispensable factor for the nanomaterial inactivation of cells.

On the whole, the TiO₂ under solar light possesses the most efficient inactivation performance of *E. coli* cells and kills all the cells (approximately 10⁷ CFU per mL) in 70 minutes, but TiO₂ hardly affects the *E. coli* cell activity in the dark environment. For the TNTs, although the TNTs in the dark environment inactivate 36.6% of *E. coli* cells, the solar light improves the performance to 62.7%. The different inactivation mechanisms of these two nanomaterials can be figured out through a series of subcellular analyses.^{26,27}

Firstly, protein is an essential component of living organisms and participates in every process of cell life activity. Proteases are the most common type of protein, and they catalyze biochemical reactions, especially for the metabolism of organisms.³² The degradation of total protein in our inactivation system means that the organic components of *E. coli* cells have been severely destroyed during the reaction (Figure 17.3a). The distribution pattern of the total protein degradation curve was consistent with the pattern of the *E. coli* inactivation curve, indicating the degradation of total protein is caused by the inactivation of *E. coli* cells. For the TiO₂ system under solar light, significant degradation of total protein was observed and is likely to be mineralization of cells rather than physical lethality.

The K⁺ ion plays a key role in the life activities of *E. coli* cells, such as maintaining a cellular osmotic pressure as an osmotic solute, regulating cell pH, activating intracellular enzymes and stimulating the accumulation of compatible solutes.³³ According to previous studies, some reasons include physical damage of the cell membrane, breakdown of K⁺ transport systems and cell death that causes changes in cell permeability and ultimately leads

to the intracellular K^+ leakage.³⁴ In our results, the leakage of K^+ from the *E. coli* cells indicates the physiological function of the cells was affected to some extent by the nanomaterials. For the TiO_2 system, a significant leakage of K^+ was observed during the inactivation reaction, and the K^+ leakage is obviously greater in solar light. The result was consistent with the inactivation performance of TiO_2 (Figure 17.2), indicating the membrane damage (cracks or holes) or cell death occurred during the inactivation process. For the TNTs system, the final concentration of K^+ in the solution was lower than the initial concentration (Figure 17.3b), suggesting K^+ adsorption occurred during the reaction. This was mainly because TNTs are a good adsorbent for heavy metals and effectively adsorb K^+ cations from the solution.¹⁴ Considering the same adsorption ability in solar light and dark environments, K^+ leaked from the cells more in the solar light system (Figure 17.3b), which was consistent with the inactivation performance, suggesting the membrane damage or cell death also occurred during the inactivation reaction of TNTs.

Usually, the cell membrane provides a strong barrier for the inner essential cytoplasm and organelles cell to resist damage from outside environments. The intact cell membrane prevents ONPG from entering the cytoplasm to undergo hydrolysis;²⁶ however, ONPG could easily penetrate the cytoplasm and hydrolyze when the cell membrane was physically damaged. Our results show that obvious ONPG hydrolysis was observed in the TiO_2 system under solar light (Figure 17.4a), indicating the cell membrane was physically damaged and cannot act as an effective barrier. Notably, the hydrolysis rate of ONPG first increased and decreased with the reaction process. This is mainly because the damage to the cell membrane became more and more serious as the reaction progressed and ONPG hydrolase in the cytoplasm was inactivated leading to termination of the hydrolysis, which can be proved by the results of total protein degradation (Figure 17.3a) and massive leakage of K^+ (Figure 17.3b) in the TiO_2 system under solar light. However, in other inactivation systems including TiO_2 in the dark, TNTs in solar light and the dark, no significant ONPG hydrolysis was observed (Figure 17.4a), but obvious K^+ leakage was observed during these reactions. This seems to indicate that these inactivation systems

cannot cause serious physical destruction to the cell membrane to allow macromolecules (ONPG) to enter the cell, but only damage the K^+ related functions, such as K^+ transport systems and ion channels,³³ causing K^+ leakage.

Based on the above results, we found that the degree of cell membrane damage is different in these four inactivation systems, and even the damage mechanism may be different. To figure out whether the damage to the cell membrane is caused by peroxidation of membrane lipids attacked by active free radicals, we used the MDA concentration to evaluate the lipid peroxidation extent. In our results, the MDA is generated only in the inactivation systems under solar light, and the MDA was first generated in the TiO_2 inactivation system at 10 minutes, and then MDA was generated in the TNTs system at approximately 50 minutes. This observation suggested that the amount of active free radicals generated in the TiO_2 inactivation system was more than that in the TNTs system, and it could effectively destroy the lipids on the cell membrane and wall. Previous researchers also revealed that the cell membrane is the main site of the active free radical attack.²⁴ The severely damaged cell membrane would not protect the extracellular substrate from the cytoplasm, and this was the reason that ONPG hydrolysis occurred in the solar TiO_2 inactivation system. According to the lipid peroxidation assay, we can conclude that the destruction of the cell membrane in the inactivation systems under solar light was not only physical damage but also active free radical attack. In contrast, the damage to the cell membrane in the dark environment was not due to the oxidation of active free radicals. This is likely to be related to the properties of the nanomaterials, because the morphology and photocatalytic performance of TNTs and TiO_2 are quite different.³¹ The reactive oxygen species (ROS) ($\cdot OH$) generated by TiO_2 under solar light was approximately three times higher than the TNTs,³⁵ indicating a strong photo-generated oxidation process from TiO_2 . Similarly, many studies also have demonstrated that TiO_2 possesses better photocatalytic properties than TNTs,^{36,37} and the adsorption ability of TNTs is greater than that of TiO_2 .^{30,38}

As a universal energy-carrying molecule, ATP can be found in all living cells, and its concentration reflects cell metabolism activities.³⁹ From our

results, a significant decrease in ATP level was observed in inactivation systems under solar light (Figure 17.5). The reason has been proven above that the cell inactivation under solar light was caused by the active free radical attack. However, although no lipid peroxidation reaction on the cell membrane was observed in the dark environment (Figure 17.4), the ATP level still decreased in this system (Figure 17.5), which shows that cell inactivation in the dark system was possibly caused by physical damage.

To explore the physical changes in cell morphology, we captured TEM images of the *E. coli* cells during the inactivation process. These images showed an obvious interaction between nanomaterials and *E. coli* cells (Figure 17.6). The TiO₂ nanomaterials were attached to the cell wall (Figure 17.6a), which is a good indication that the ROS generated by the TiO₂ nanomaterials severely damaged the cell membrane. Other studies have also revealed the morphology of cells destroyed by active free radicals.^{27,40} Whereas, Figure 17.6b revealed that the slender and sharp TNT nanotubes pierced the cell, suggesting physical damage of the cell by TNTs. Some other nanomaterials with similar morphology have the same capability, such as carbon nanotubes with sufficiently small radii that can directly pierce the cell membrane.^{41,42}

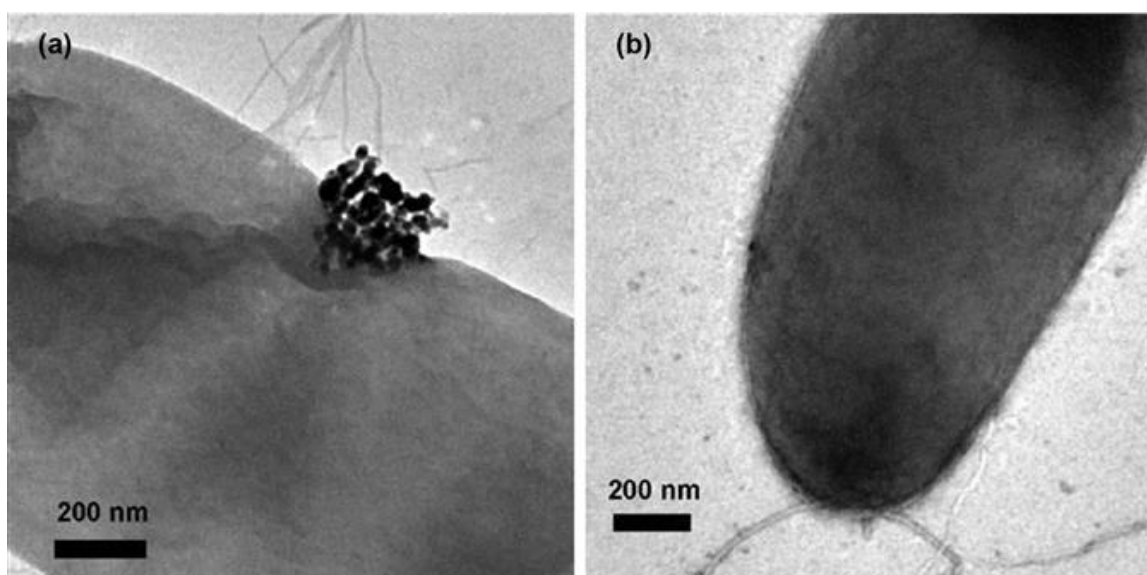


Figure 17.6 TEM images of the interaction between *E. coli* and the nanomaterials: (a) TiO₂ and (b) TNTs.

17.5 Conclusion

In this study, the toxicity of TiO₂ and TNT nanomaterials was tested in the two most important natural conditions (solar light and dark exposure) based on the inactivation performance of *E. coli* cells. The *E. coli* inactivation rate after 70 minutes was: TiO₂ under solar light (100%) > TNTs under solar light (62.7%) > TNTs in the dark (36.6%) > TiO₂ in the dark (0.5%). The inactivation mechanisms of TiO₂ and TNTs were quite different. The strong inactivation performance of TiO₂ under solar light is due to its strong photocatalytic properties and attack of the cell organelles by the generated ROS until peroxidation and death. The inactivation ability of TNTs under solar light is a combination of its weak photocatalytic performance and morphological effects. However, TNTs in the dark environment can only attack cells by physically piercing them, but the TiO₂ showed neither photocatalytic properties nor physical damage in the dark environment. Our findings reveal the potential toxicity of TiO₂ and TNT nanomaterials in the natural environment.

Acknowledgements

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