Nanotechnology-Enabled Water Treatment: A Vision to Enable Decentralized Water Purification and Reuse

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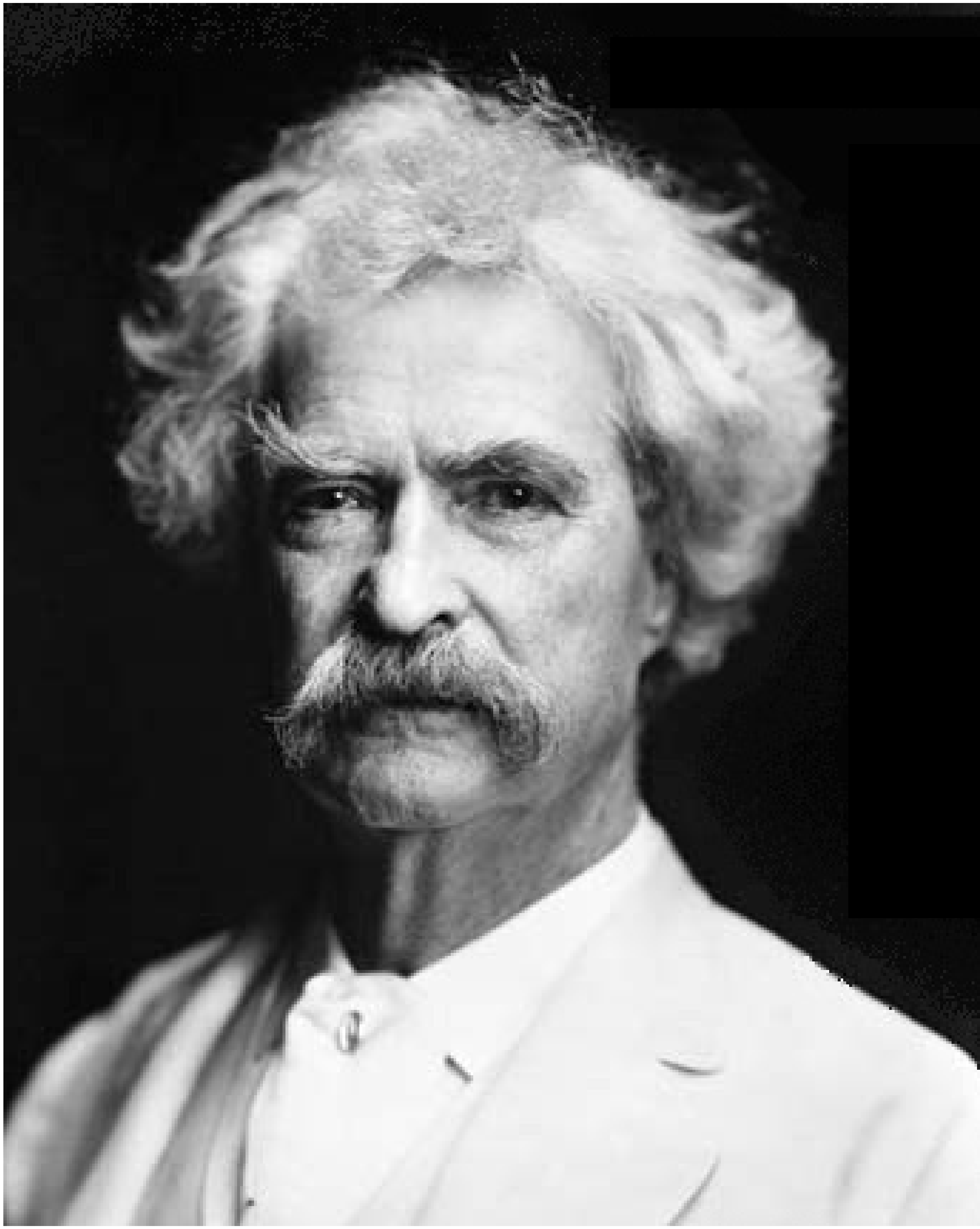
RICE

McGill University
22 September 2015



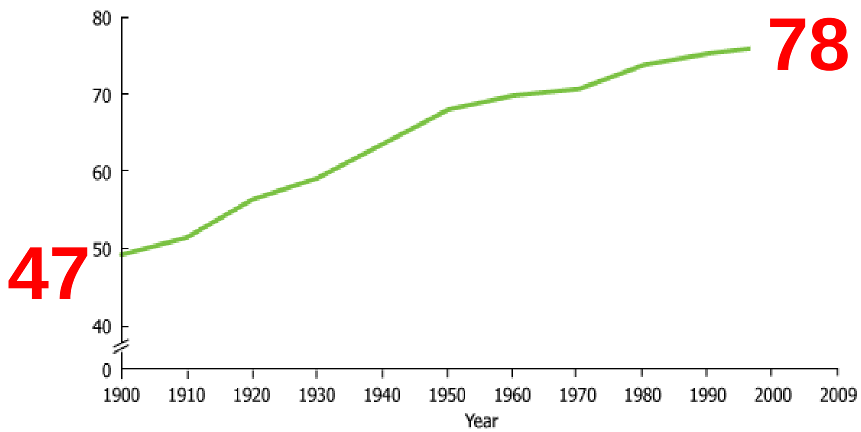
"Whiskey is for Drinking;

Water is for Fighting Over"

~Mark Twain

Clean Water Is Critical for Enhancing Human Capacity

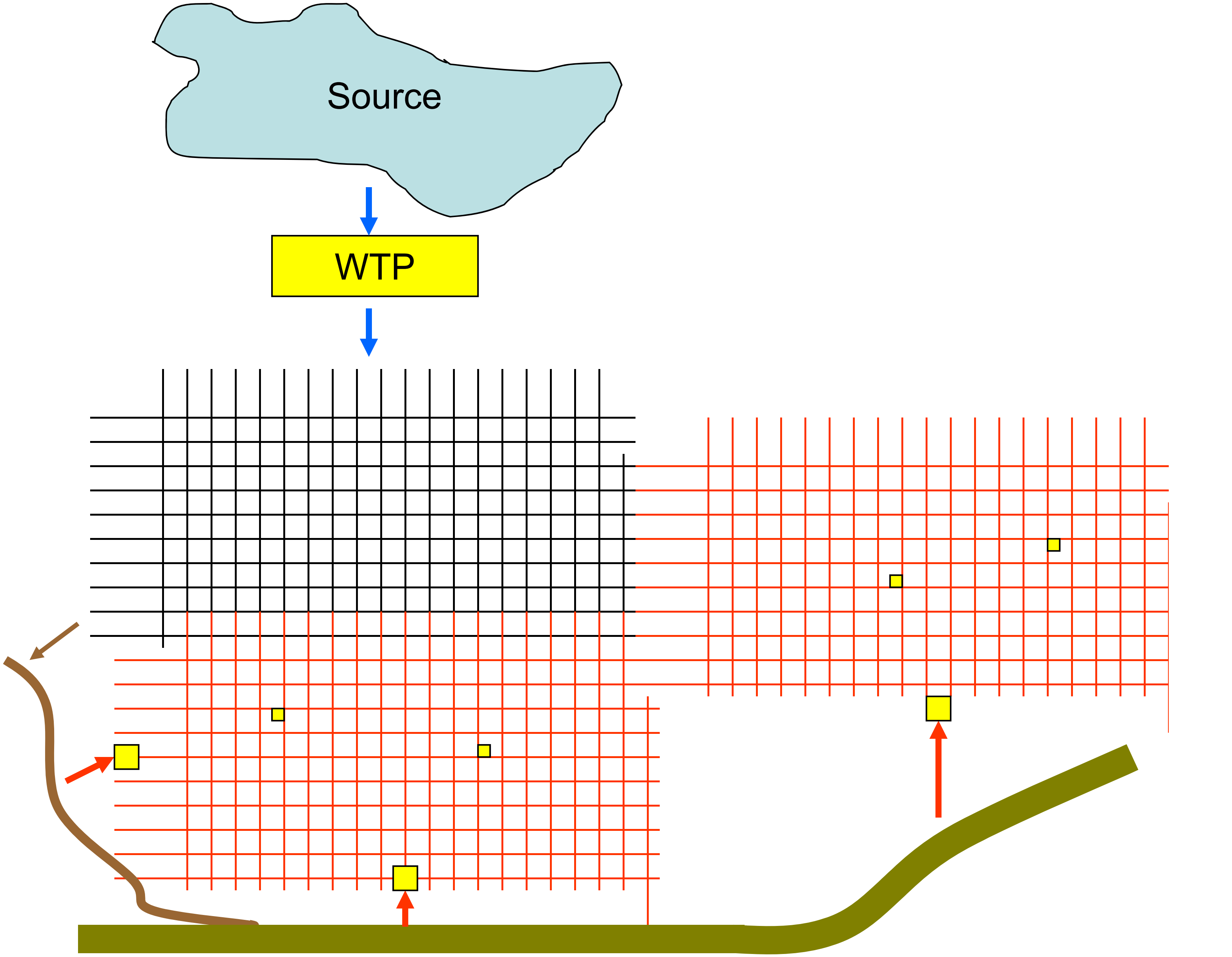
American's life expectancy at birth



http://www.prb.org/Publications/Articles/2011/biodemography.aspx

- Public health
- Energy production
- Food security
- Economic development

- 43 million Americans lack access to municipal water; 800 million worldwide lack access to safe water
- Global market for drinking water ~ $700 billion
- Larger market for industrial wastewater reuse


Source
WTP

Drivers for Decentralized (Distributed) Treatment

- Lack of adequate infrastructure (distribution systems, electricity)
- Match water supply with consumer location (avoid contamination during transport & storage)
- Reduce water losses in large and complex distribution systems.
- Reduce energy requirements

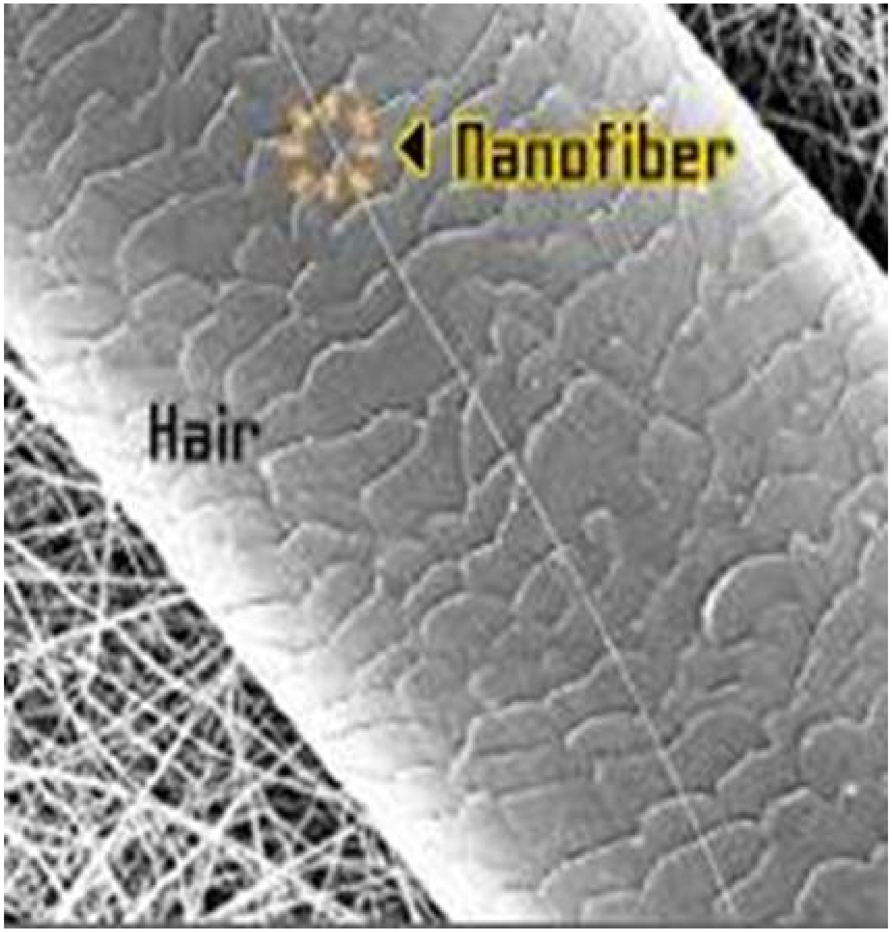
Research Needs and Opportunities

- **Network topology analysis to exploit the interconnectivity of complex water systems** (e.g., integrated drinking water, wastewater & storm water networks to enhance water availability and reuse).
- **Advanced materials and technologies** to obtain drinking water from unconventional sources, and to enable reuse and resource recovery (e.g., drinking water, energy, nutrients) from challenging wastewaters.

Nano = Dwarf (Greek) = 10^{-9}

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications."

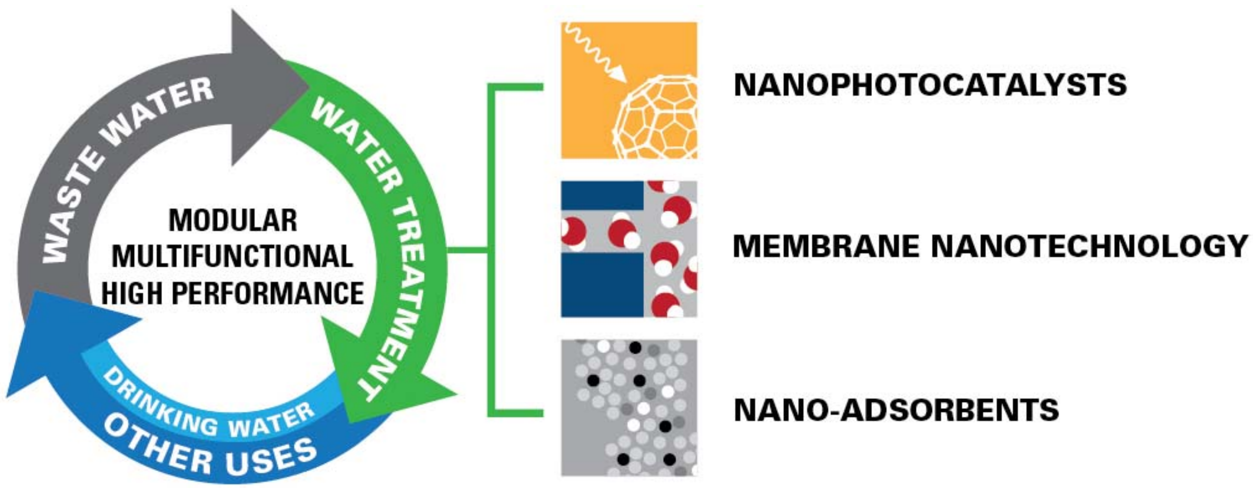
-National Nanotechnology Initiative



Why Nano?

Leap-frogging opportunities to:

- Develop high-performance multifunctional materials and systems that are easy to deploy, can tap unconventional water sources, and reduce the cost of remote water treatment
- Transform predominantly chemical treatment processes into modular and more efficient catalytic and physical processes that exploit the solar spectrum and generate less waste

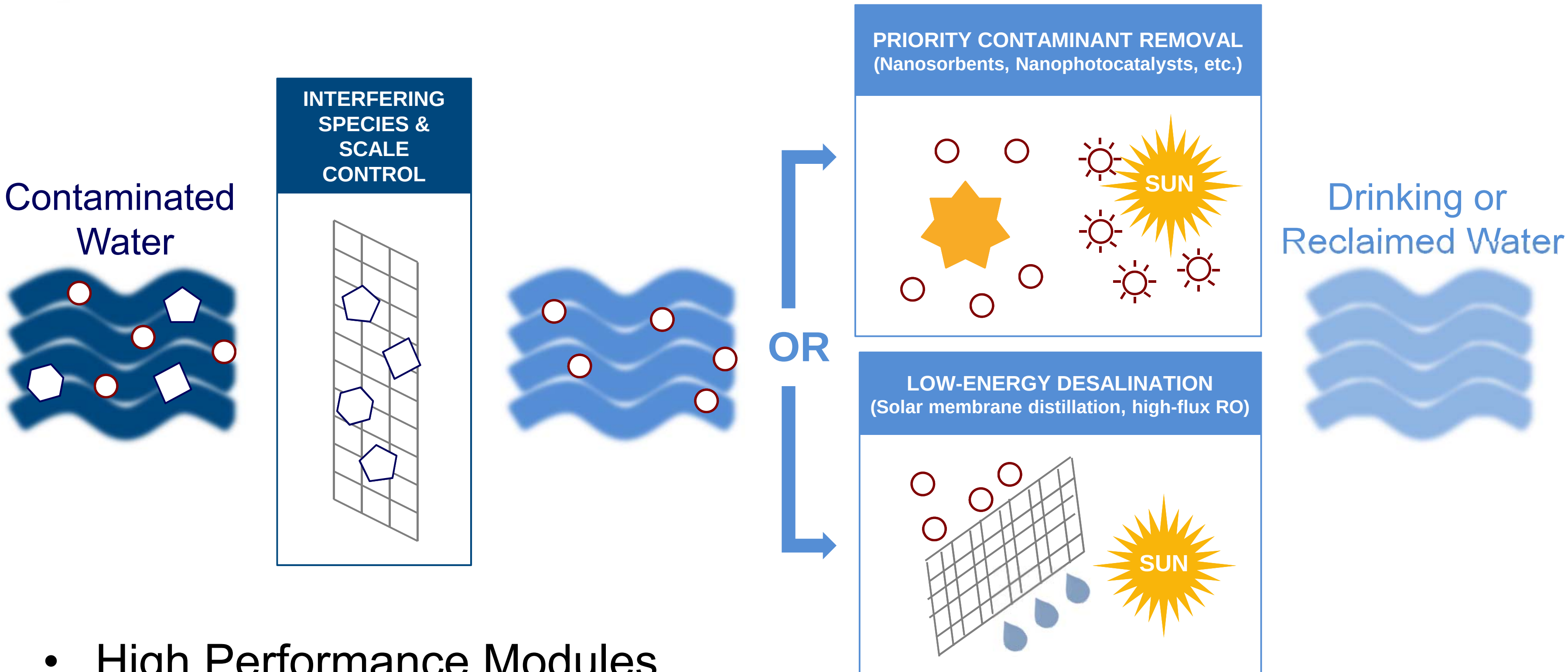


Opportunities for Engineered Nanomaterials (ENMs) in Water Treatment and Reuse

Desirable ENM Properties	***Examples of Enabled Technologies***
Large surface area to volume ratio	Superior sorbents (e.g., nanomagnetite or graphene oxides to remove heavy metals and radionuclides)
Enhanced catalytic properties	Hypercatalysts for advanced oxidation (TiO_2 & fullerene-based photocatalysts) & reduction processes (Pd/Au)
Antimicrobial properties	Disinfection and biofouling control without harmful byproducts
Multi-functionality (antibiotic, catalytic)	Fouling-resistant (self-cleaning and self-repairing) filtration membranes that operate with less energy
Self-assembly on surfaces	Surface structures and nanopatterns that decrease bacterial adhesion, biofouling, and corrosion
High conductivity	Novel electrodes for capacitive deionization (electro-sorption) and energy-efficient desalination
Fluorescence	Sensitive sensors to detect pathogens, priority pollutants

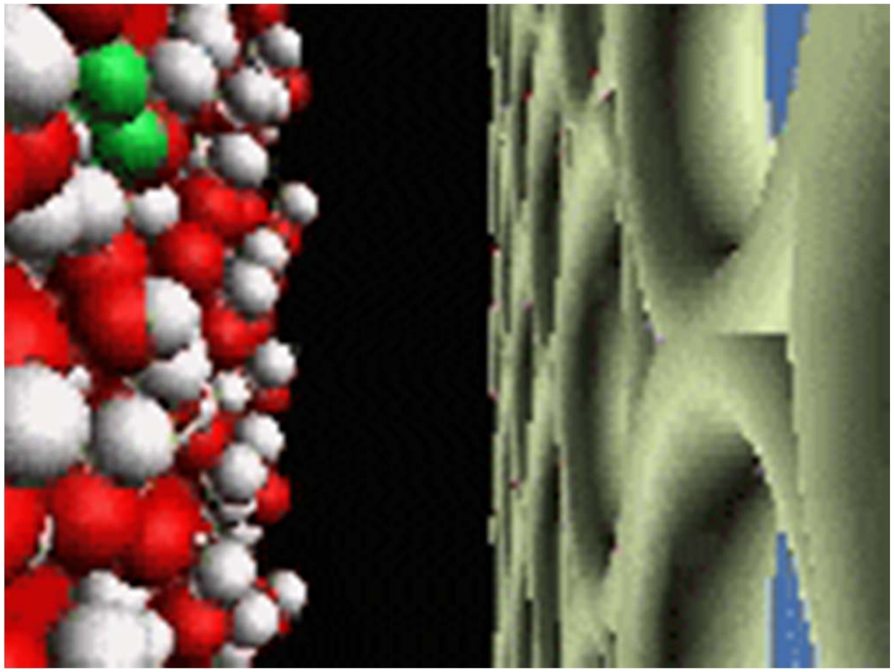
Modular Treatment Systems

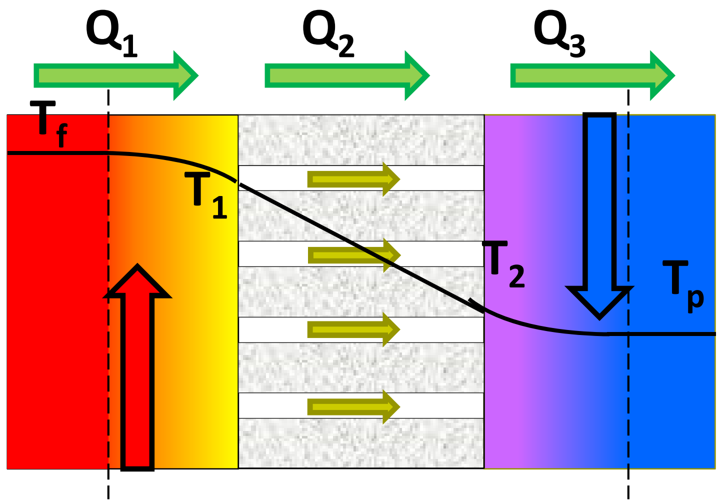
Match treated water quality to intended use



- High Performance Modules
- Lower Chemical Consumption
- Lower Electrical Energy Requirements
- Less Waste Residuals
- Flexible and Adaptive to Varying Source Waters

Example: Enhancing Membrane Distillation





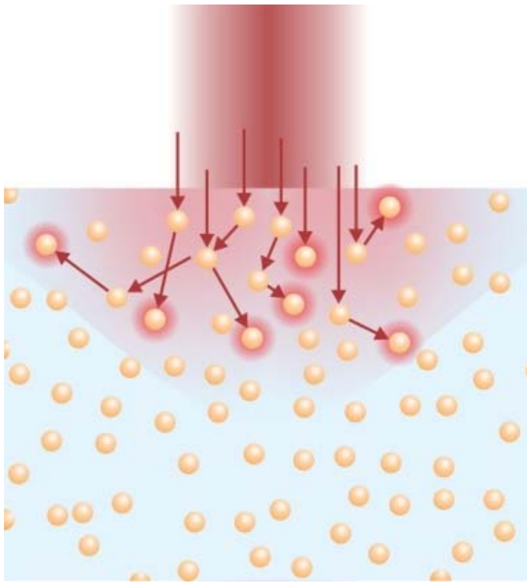
Temperature polarization:

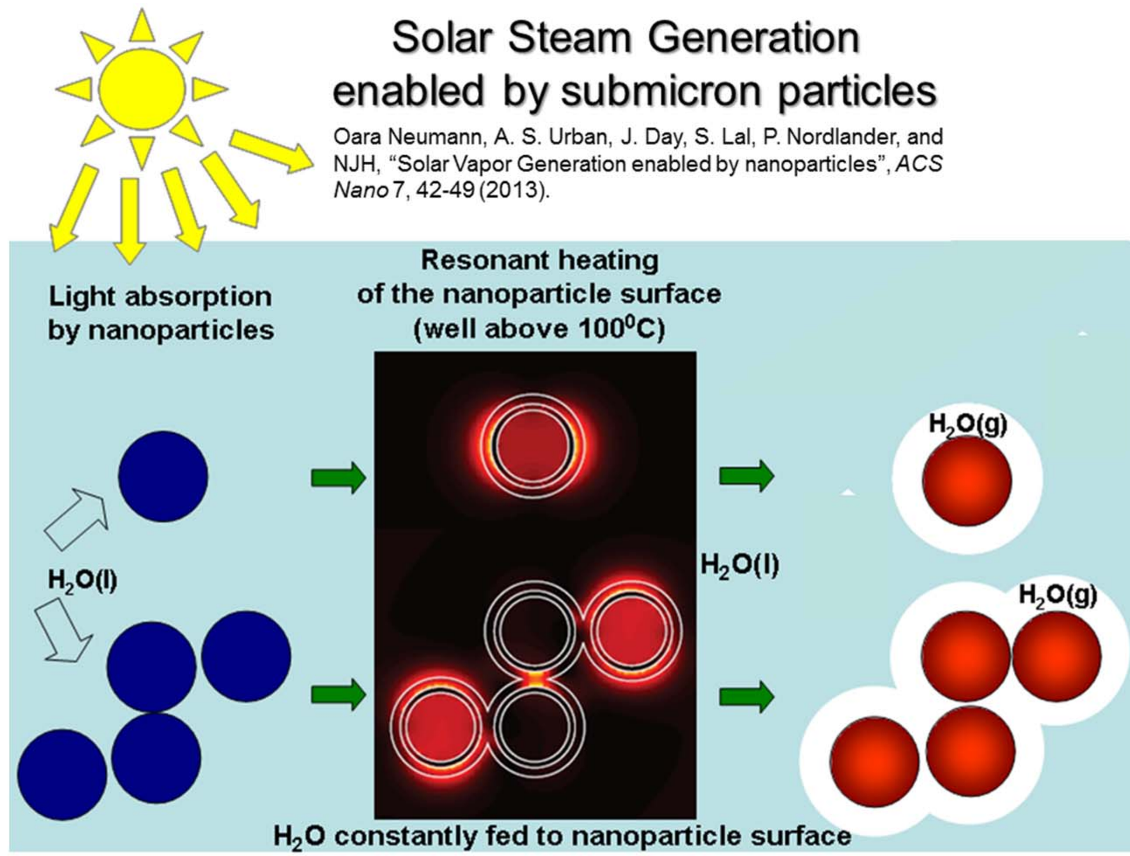
$$\alpha = \frac{T_1 - T_2}{T_f - T_p}$$

Can reduce transmembrane temperature gradient by up to 70%

www.desalination.biz

Photonics of Nanoparticles for Solar-Thermal Applications



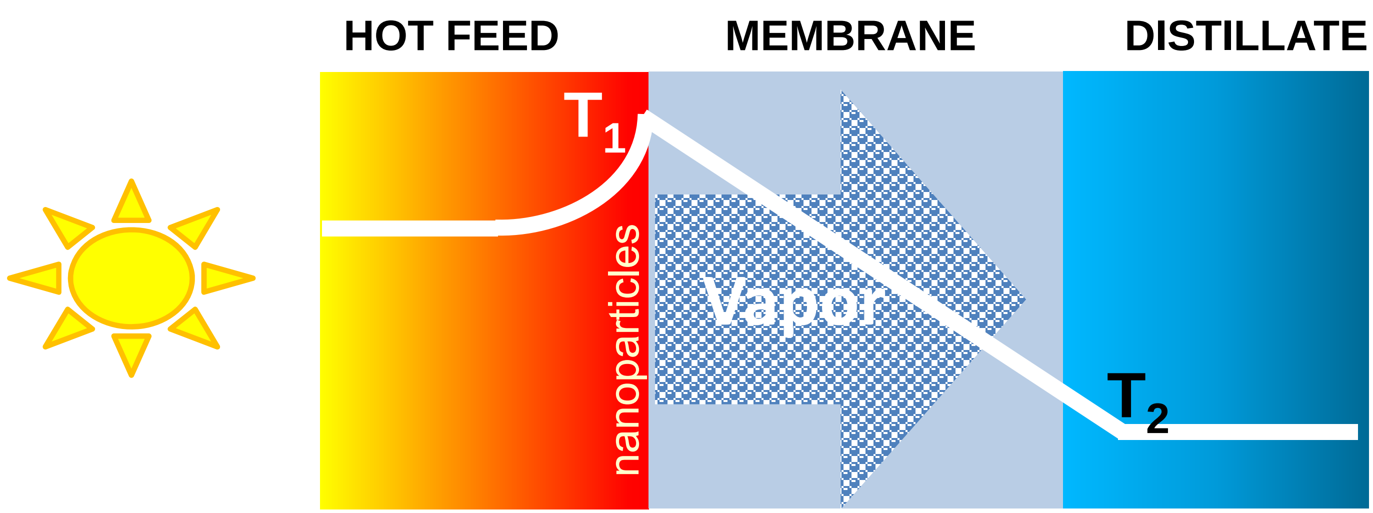


Light localization by multiple scattering confines solar energy, enabling high efficiency heat transfer

(Hogan et al., *Nano Lett.* **2014**, *14*, 4640-4645)

Enabling Technology

Direct solar membrane distillation for low-energy desalination

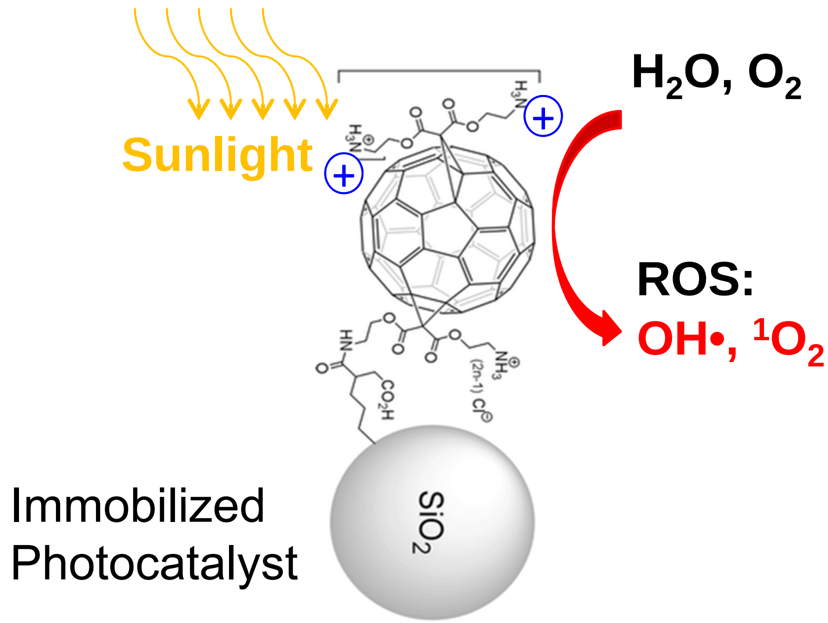


Higher T gradient = higher flux

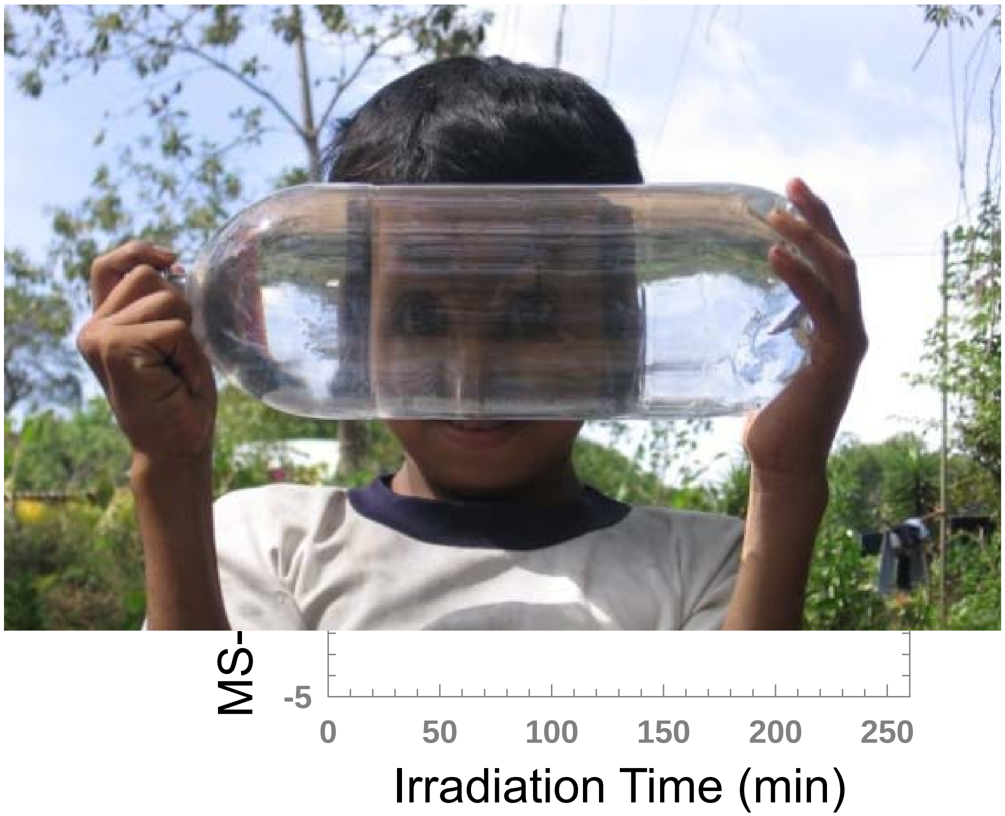
Multifunctional membranes: Fouling-resistant, High-flux Self-cleaning

Enabling Technology
(Photo)Disinfection & Advanced Oxidation

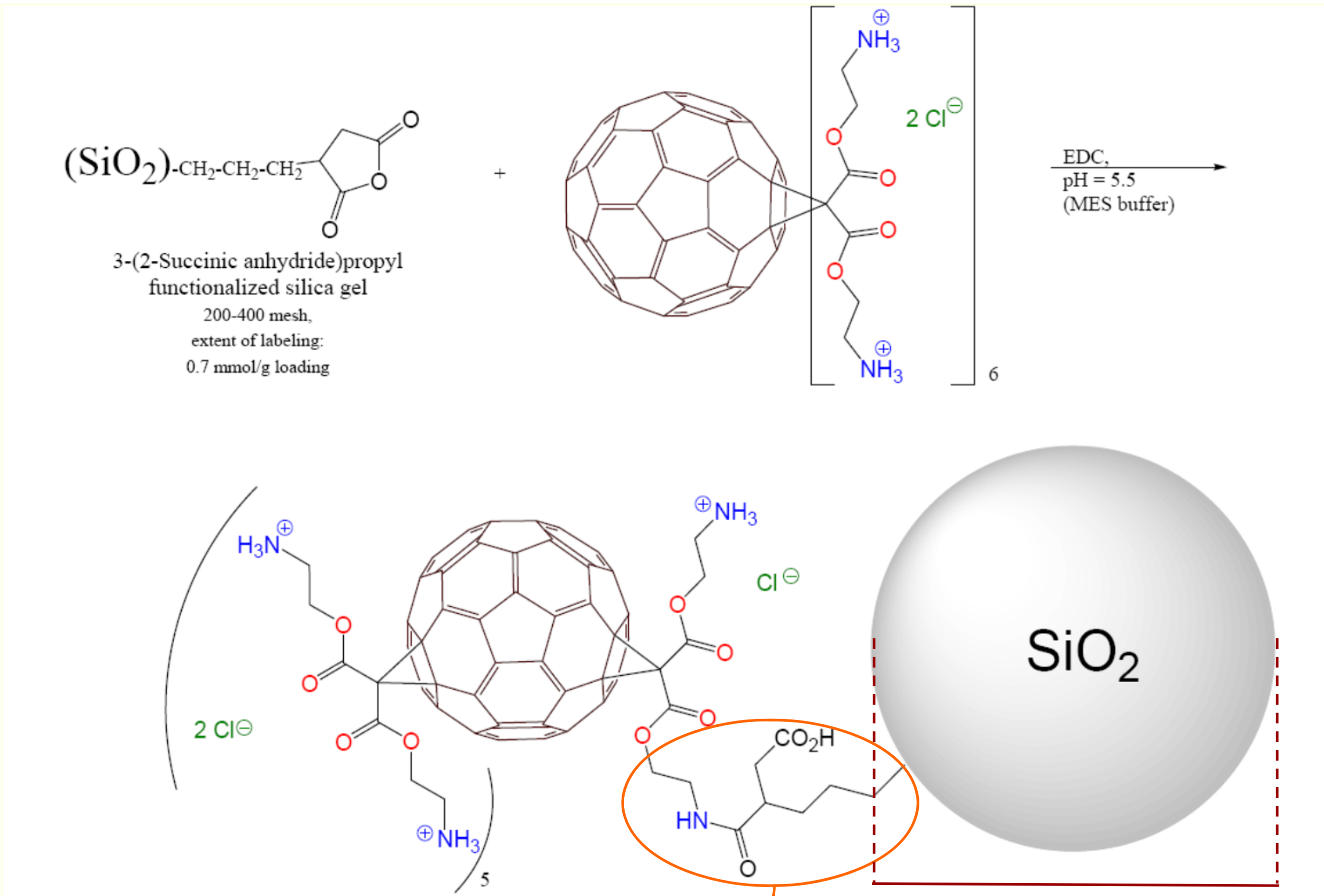
Nano(photo)catalysts that use solar radiation to generate ROS that destroy resistant microbes and recalcitrant pollutants without generating harmful disinfection byproducts



Advantages of Amino-C_{60} as Photocatalytic Disinfectant

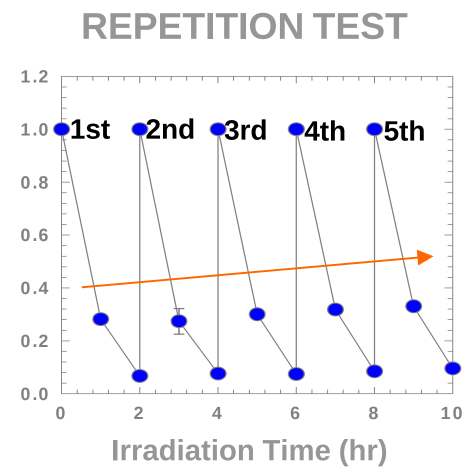


Immobilization of aminofullerene onto silica beads facilitates separation, reuse and recycling



0.2 - 0.3 mm
EASILY SEPARABLE

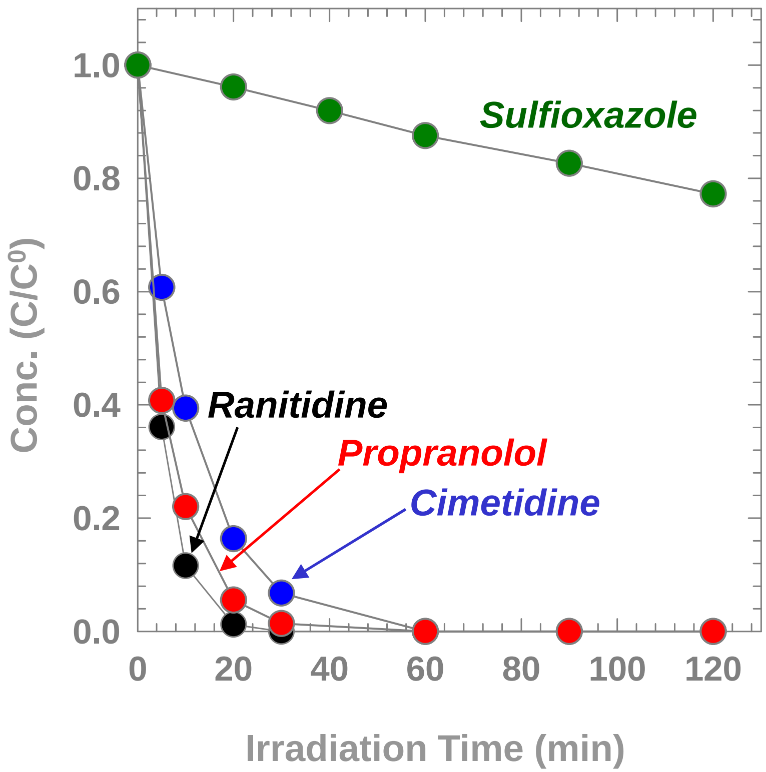
NO C_{60} AGGREGATION ON THE SILICA SURFACE (HIGHER CATALYTIC AREA)



No loss of photo-activity

Lee, Mackeyev, Cho, Wilson, Kim and Alvarez (2010). *Environ. Sci. Technol.* 44: 9488–9495.

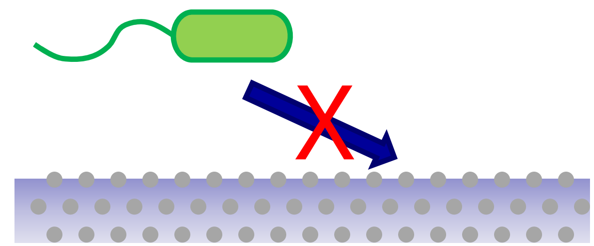
Photocatalytic treatment of emerging contaminants (pharmaceuticals, endocrine disruptors)



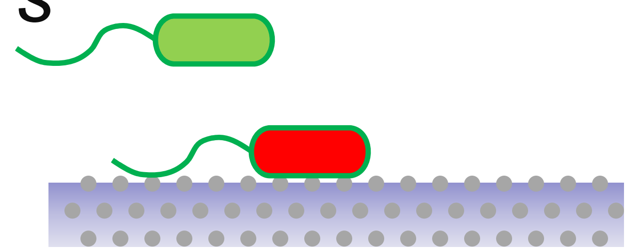
Lee J., S. Hong, Y. Mackeyev, C. Lee, L.J. Wilson, J-H Kim and P.J.J. Alvarez (2011). Environ. Sci. Technol. *45*: 10598–10604.

Nanotechnology for Biofouling Control

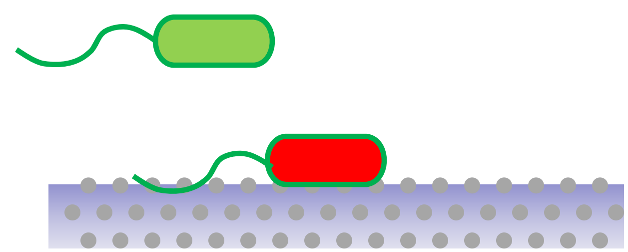
- *Discourage adhesion*
  - Nano-patterned topology
  - Surface chemistry
  - Interrupt quorum sensing



- *Incorporate antimicrobial NPs*
  - Nano silver
  - Carbon nanotubes
  - Porous nano-carriers

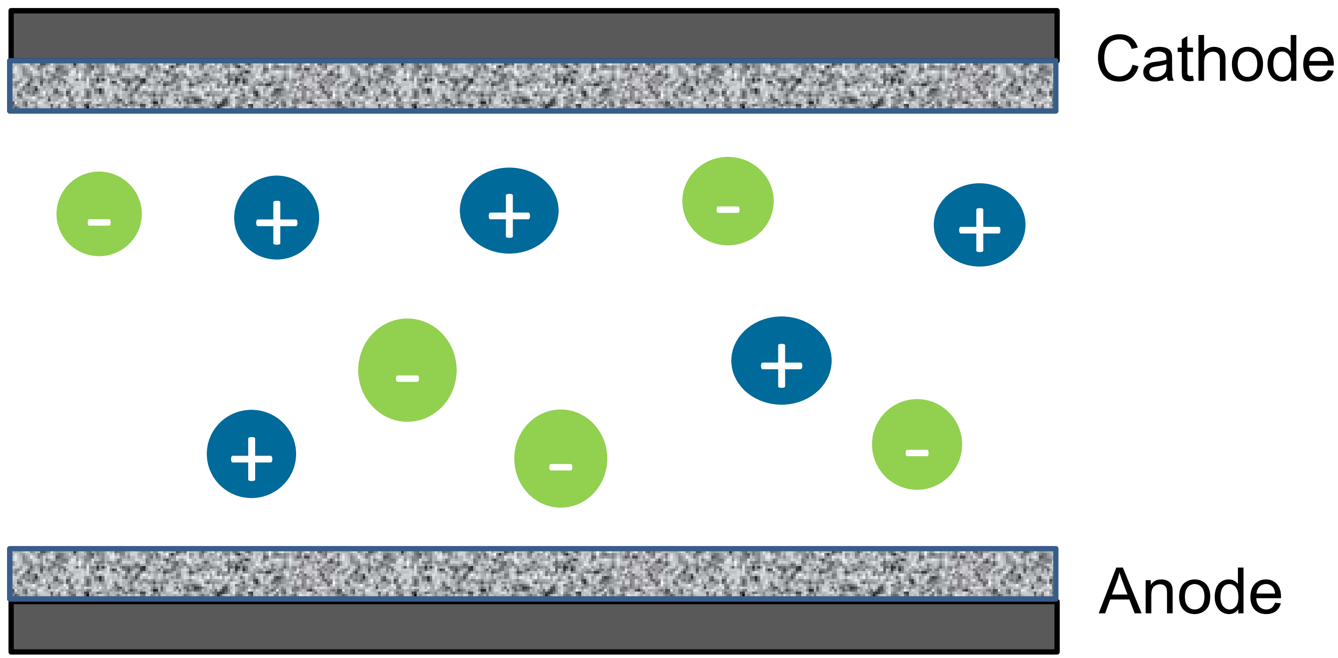


- *Photocatalytic ROS*
  - Semiconductors, e.g., TiO_2
  - Fullerene derivatives (self-cleaning surfaces)

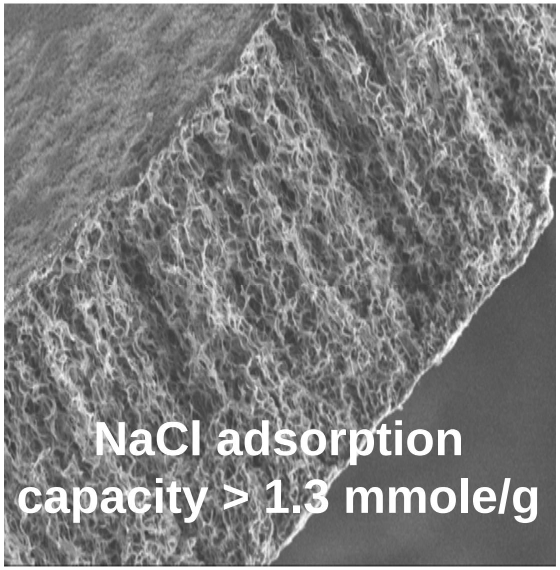


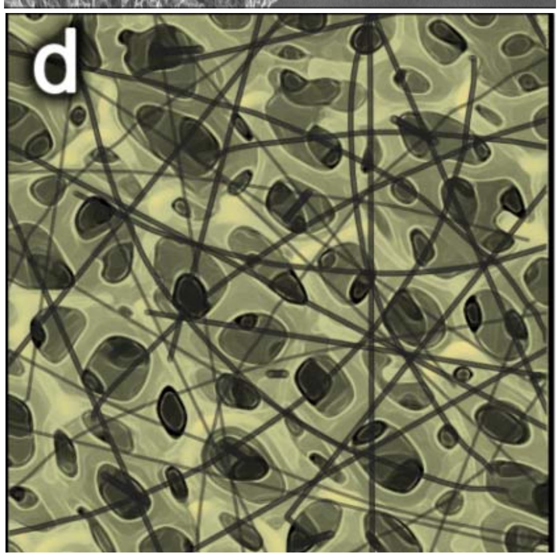
Enabling Technology
Electrosorption for Scaling Control

Nanocomposite electrodes to remove multivalent ions from brines, and generate smaller waste streams

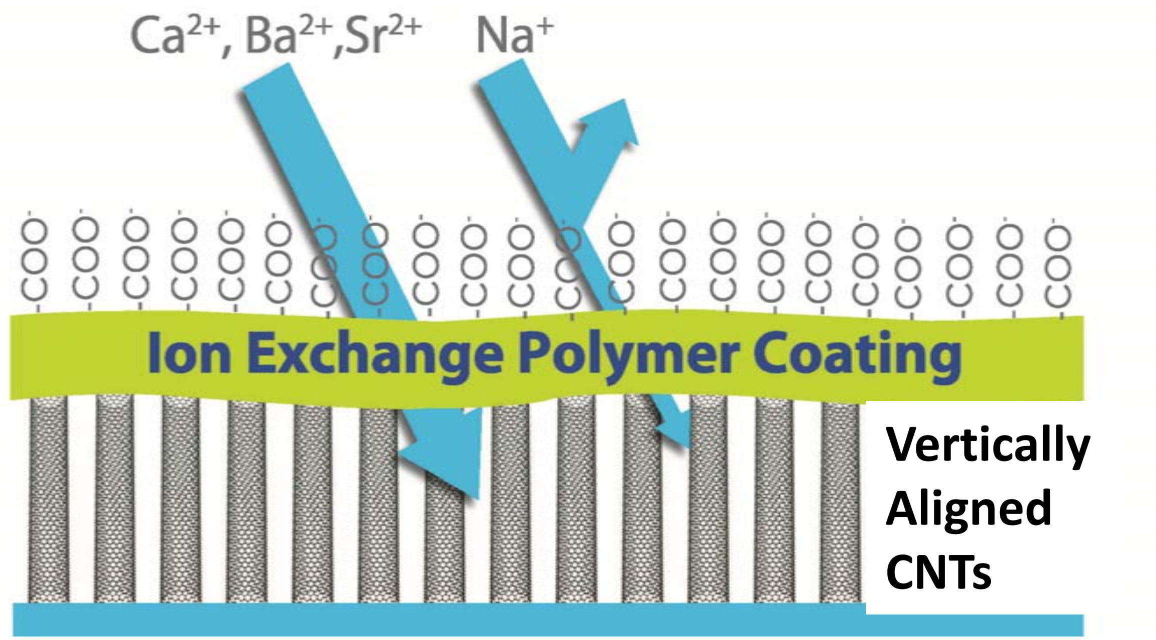


Nano-Enabled CDI for Scaling Control





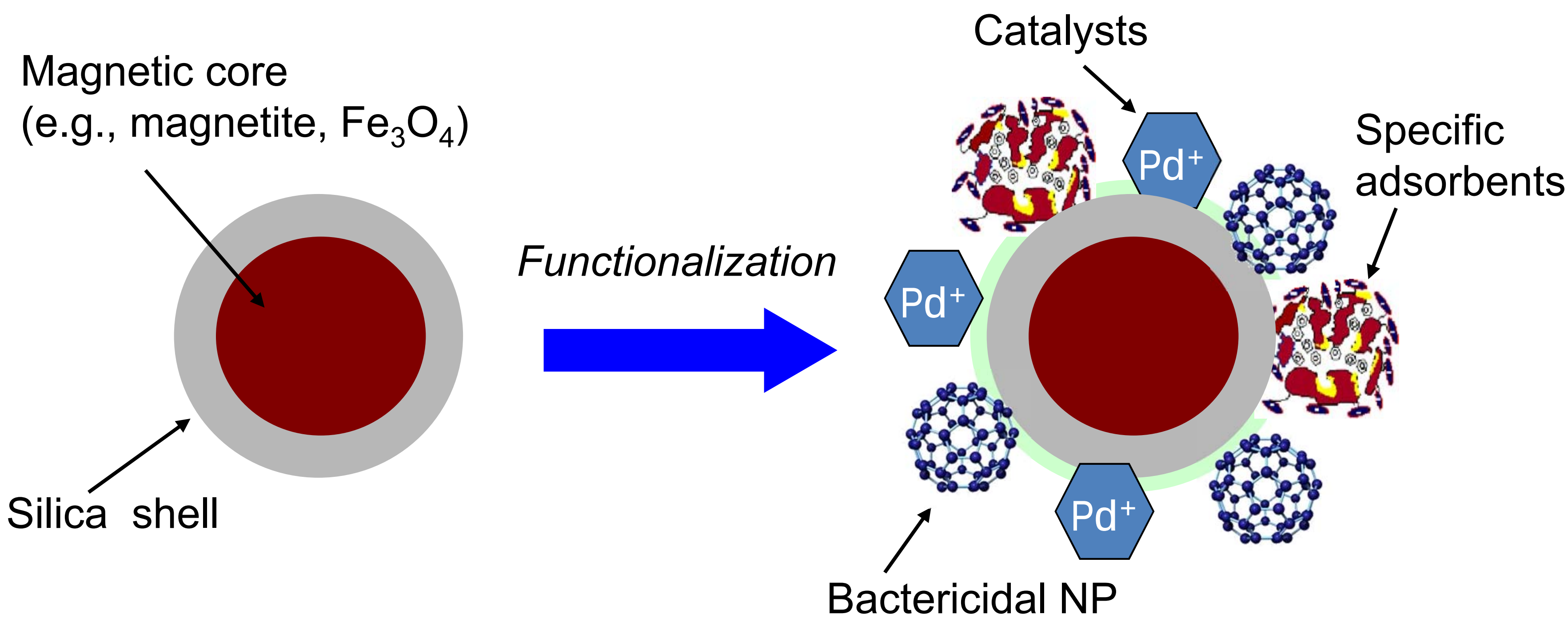
IX polymers enable preferential removal of divalent cations that cause scaling



CNTs/graphene enhance sorption capacity, kinetics, mechanical strength and electrical conductivity.

Enabling Technology
Multifunctional nanosorbents

Selective removal of target contaminants by functionalized nanoparticles supported in macroscale structures or subject to magnetic separation for enhanced removal kinetics and easier reuse



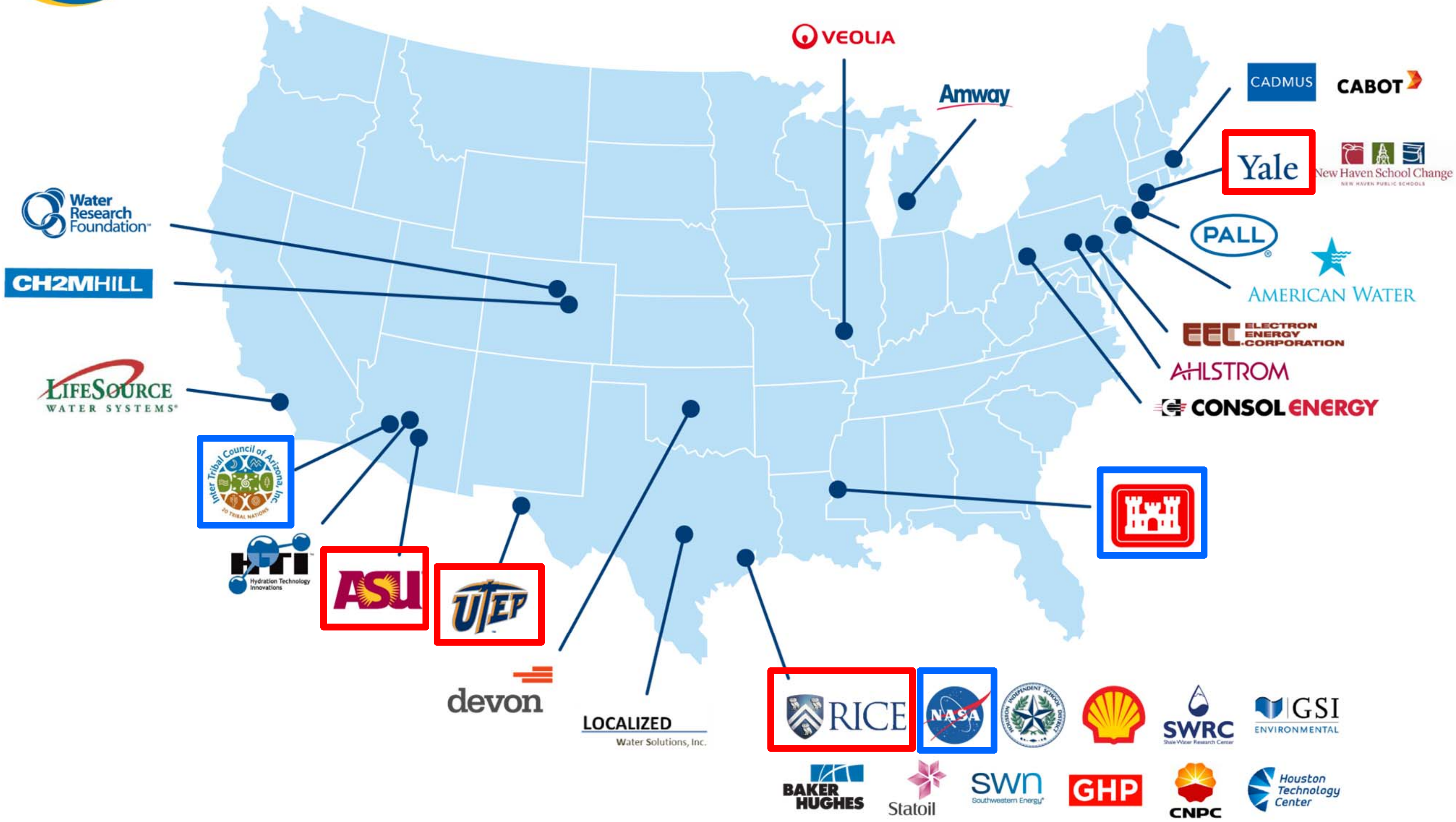
SUMMARY OF APPLICATIONS

- Low-energy desalination by nanophotonic MD or electrosorption
- DBP-free disinfection
- Advanced (photo)oxidation
- Selective nano-sorbents
- Multi-functional membranes
- Fouling- & corrosion-resistant surfaces

"People don't know what they want until you show it to them"

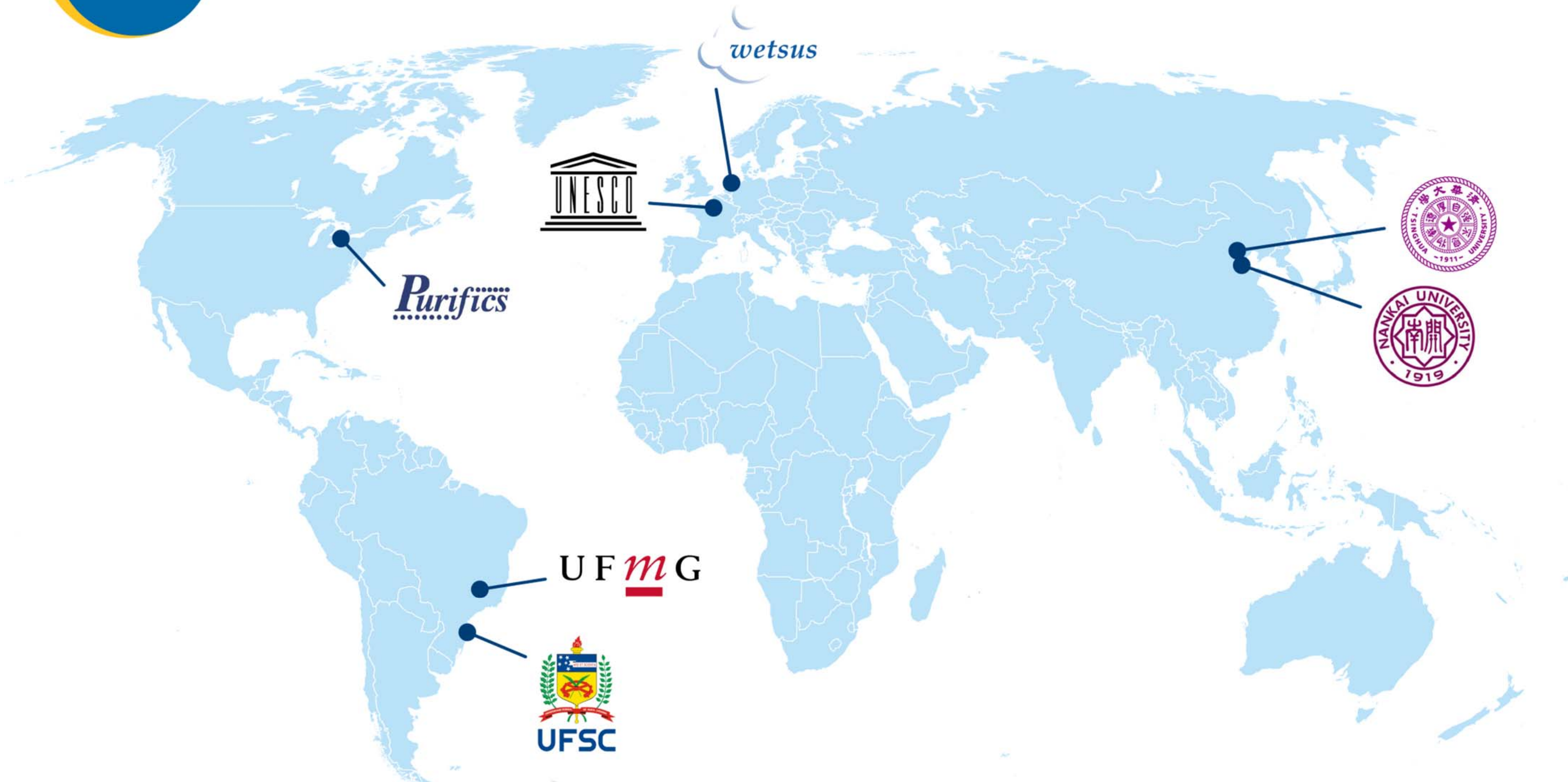
– Steve Jobs

Some of Our NEWT Partners



- Innovation across value chain (nanomaterial and equipment manufacturers, service providers, R&D and deployment partners, and users)

International Partners



- Co-development and production of advanced multifunctional materials
- Globally-relevant research and education experiences for students
- Testbed sites for applications in fast-growing water markets

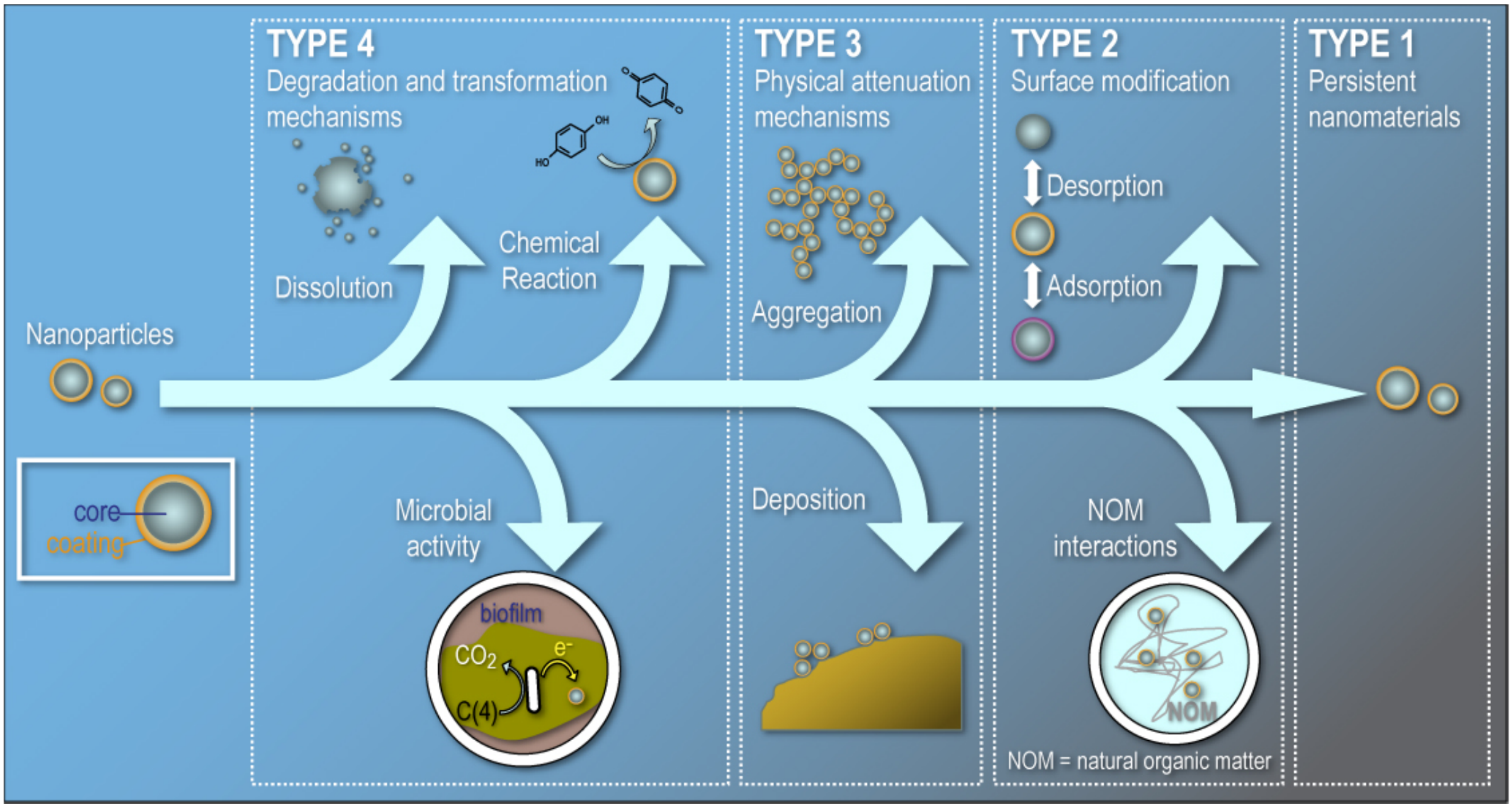
Responsible Nanotechnology

"With Great Power, Comes Great Responsibility"

Uncle Ben to Peter Parker in Spider Man

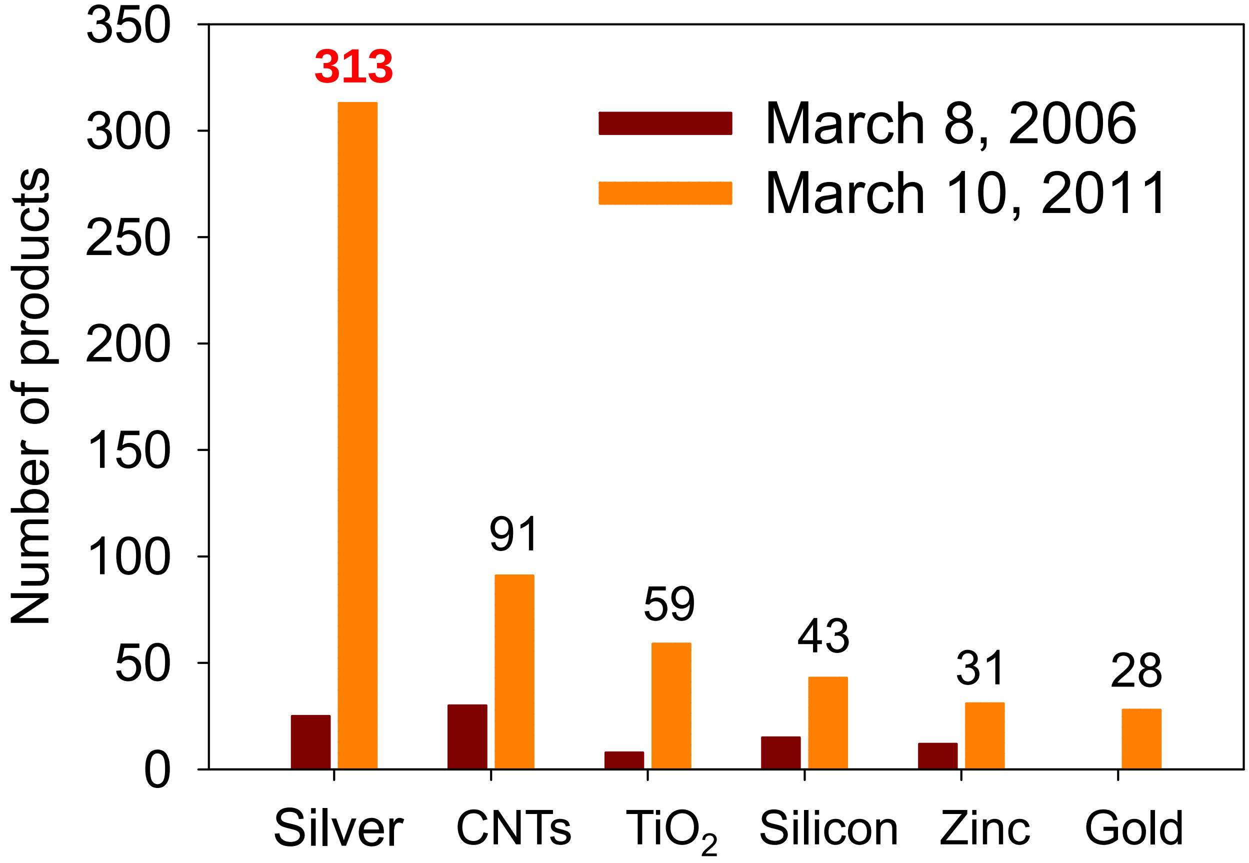
Paul Hermann Muller
Thomas Midgley

Nanoparticle Modifications in the Environment



Alvarez P.J.J., V. Colvin, J. Lead and V. Stone (2009). Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano 3(7): 1616-1619.

Example: Silver Nanoparticles



Most Widely Used Nanomaterials In Commercial Products

Source: Woodrow Wilson-The project on emerging nanotechnologies

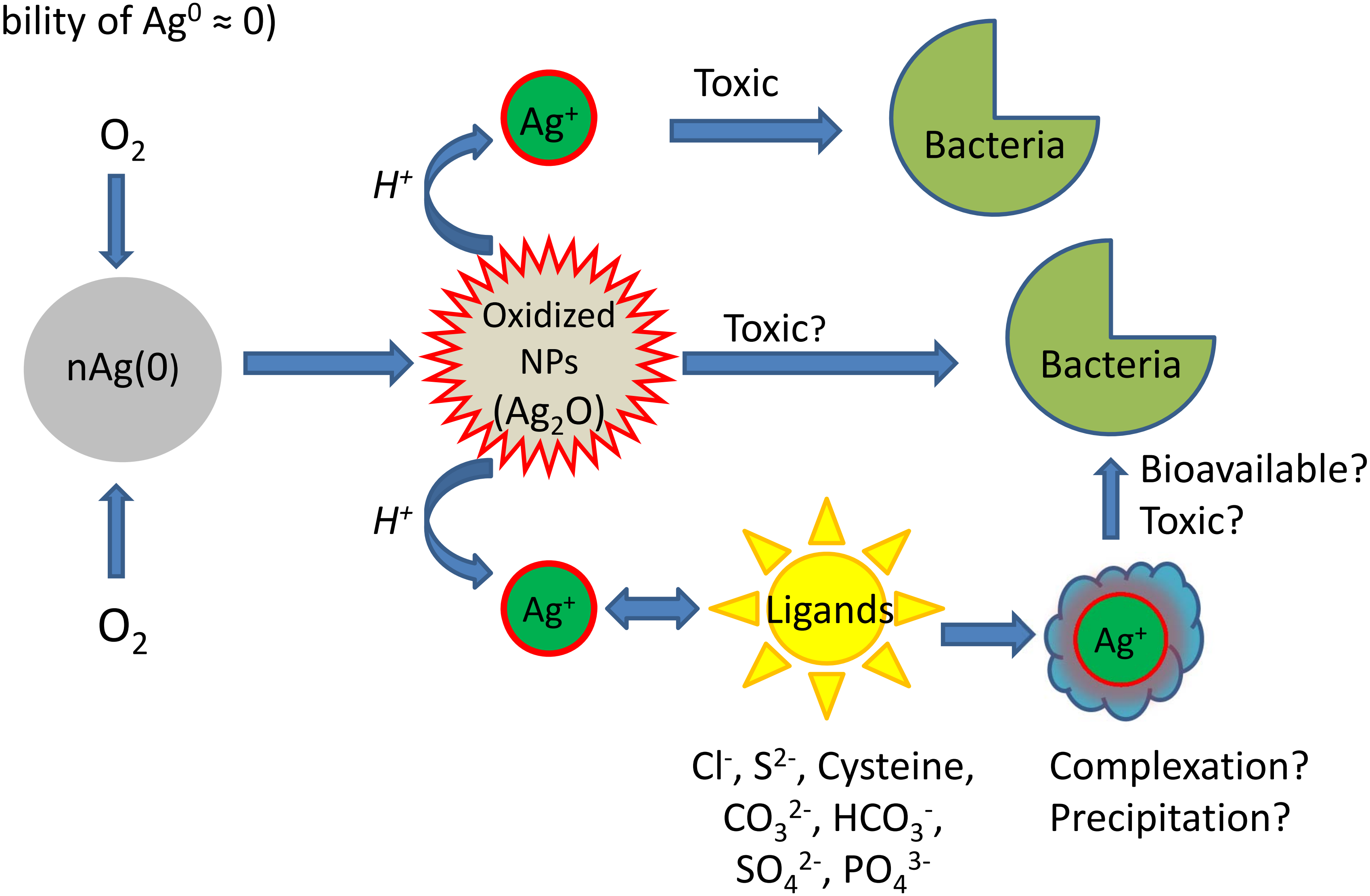
Is the antimicrobial activity of silver due to the nanoparticles themselves, or to the released Ag^{+} ions, or both?

- And how do environmental conditions affect their relative influence?

Bioavailability and Toxicity of AgNPs

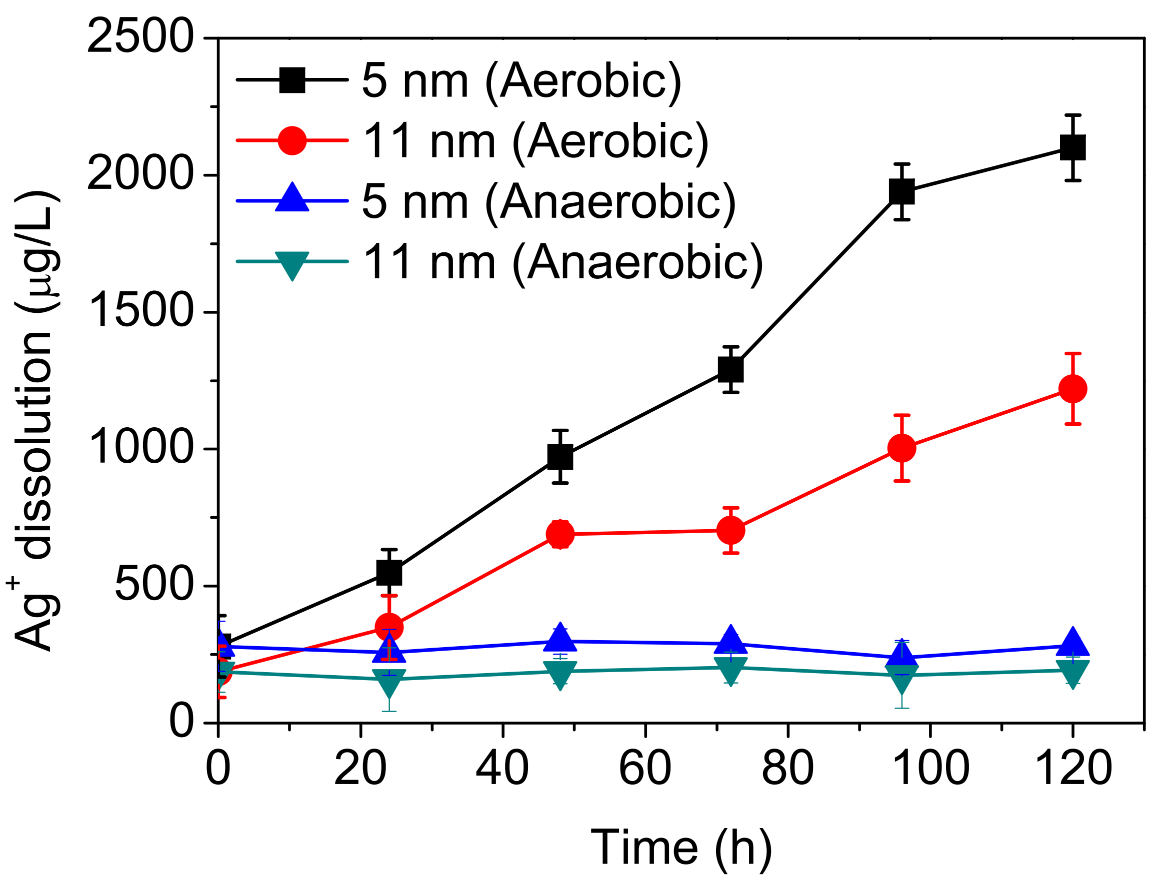
Ag^+ is released only if Ag(0) is oxidized: $4Ag^0 + O_2 + 4H^+ \leftrightarrow 4Ag^+ + 2H_2O$

(Solubility of $Ag^0 \approx 0$)



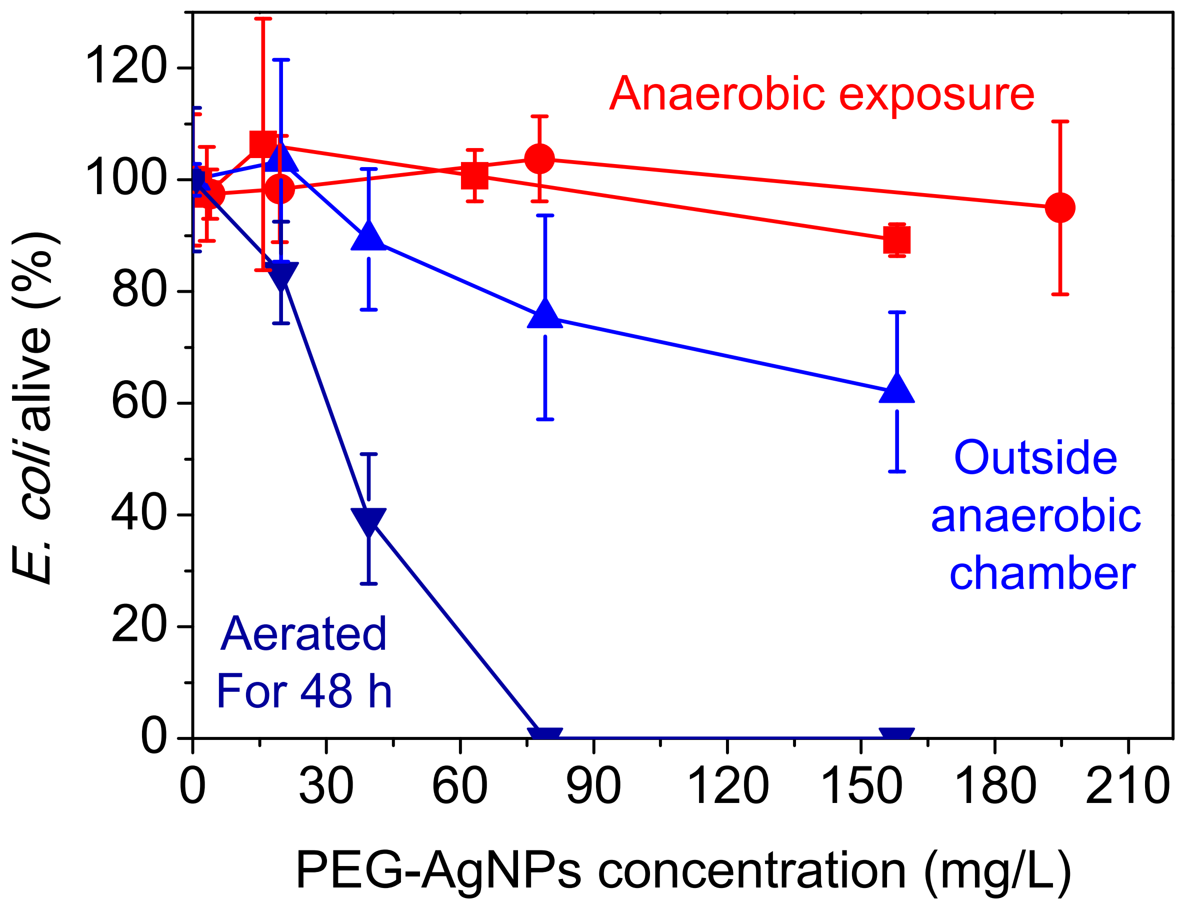
No Ag^+ release under Anaerobic Conditions

(Faster release for air-exposed smaller particles)



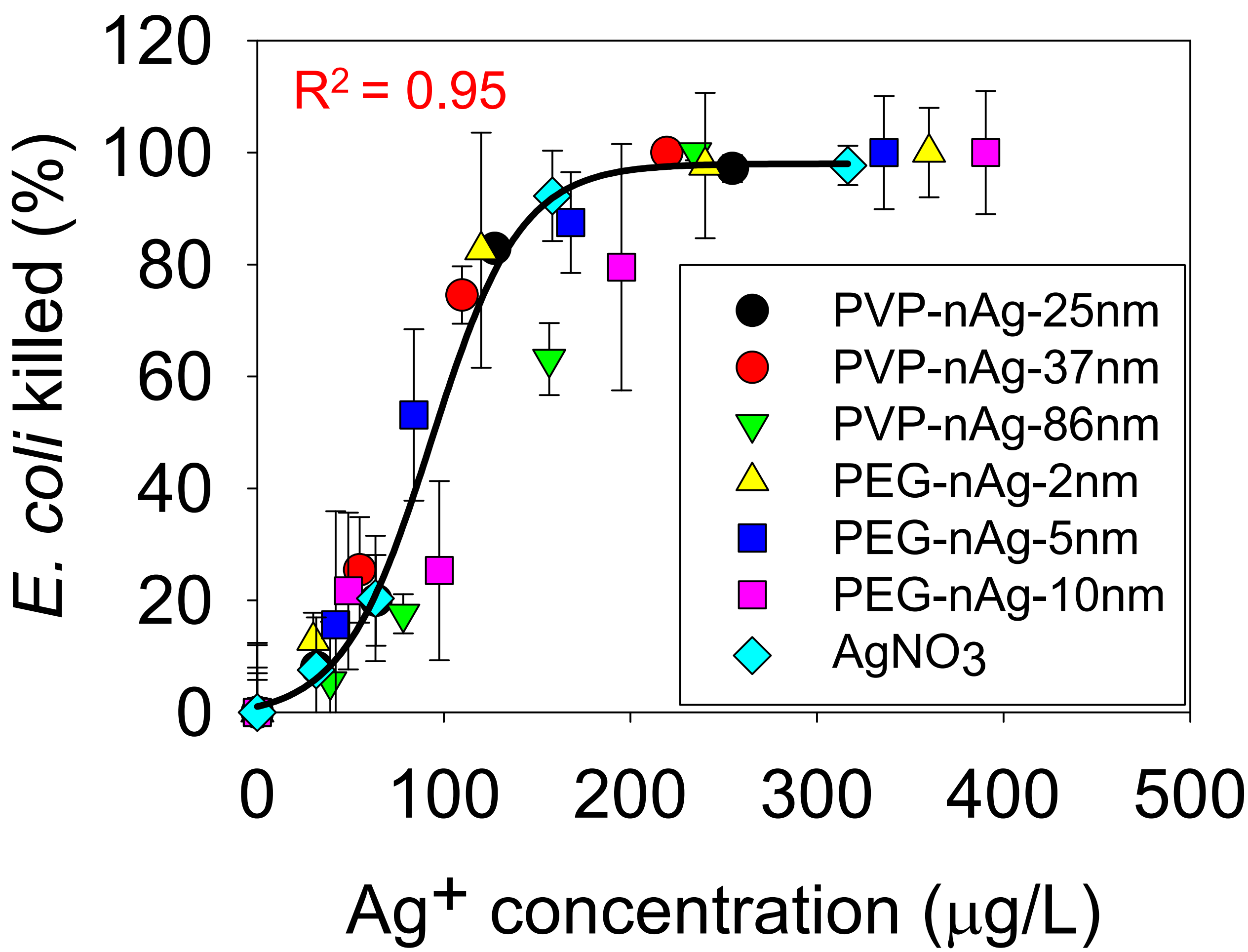
Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

No Toxicity Without Ag^+ Release



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

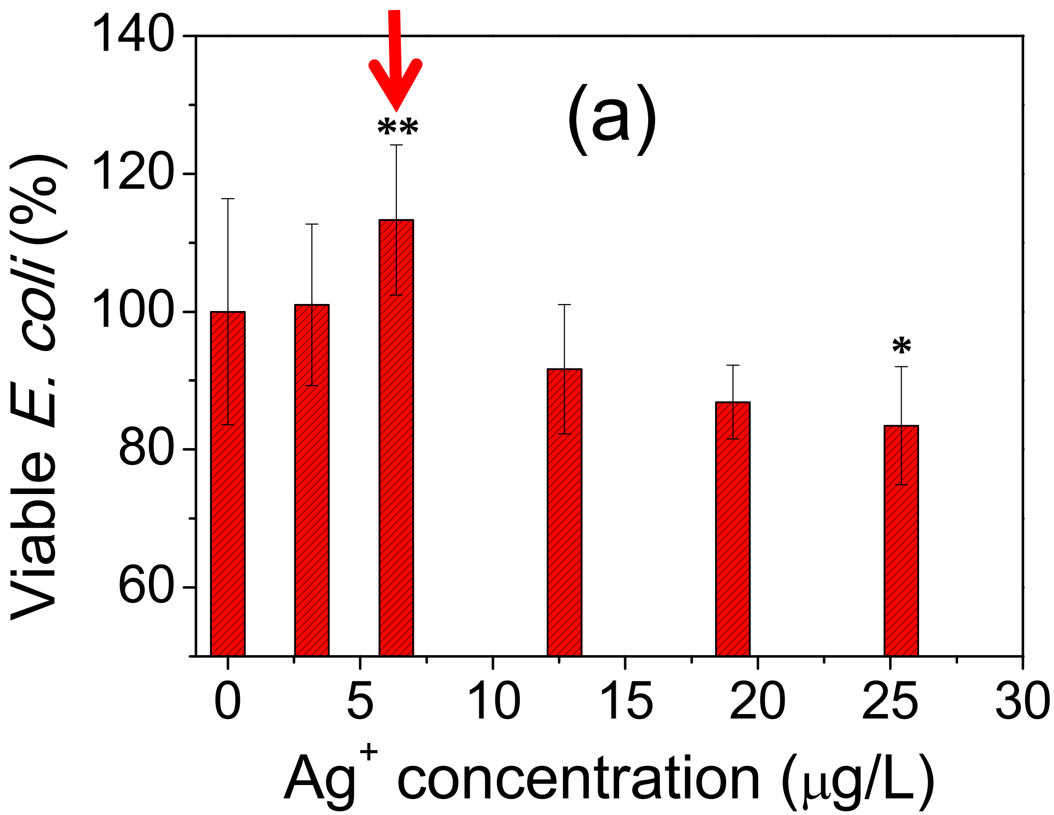
AgNP Toxicity Can Be Explained by Dose-Response of Released [Ag^+]



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

“What does not kill you makes you stronger”

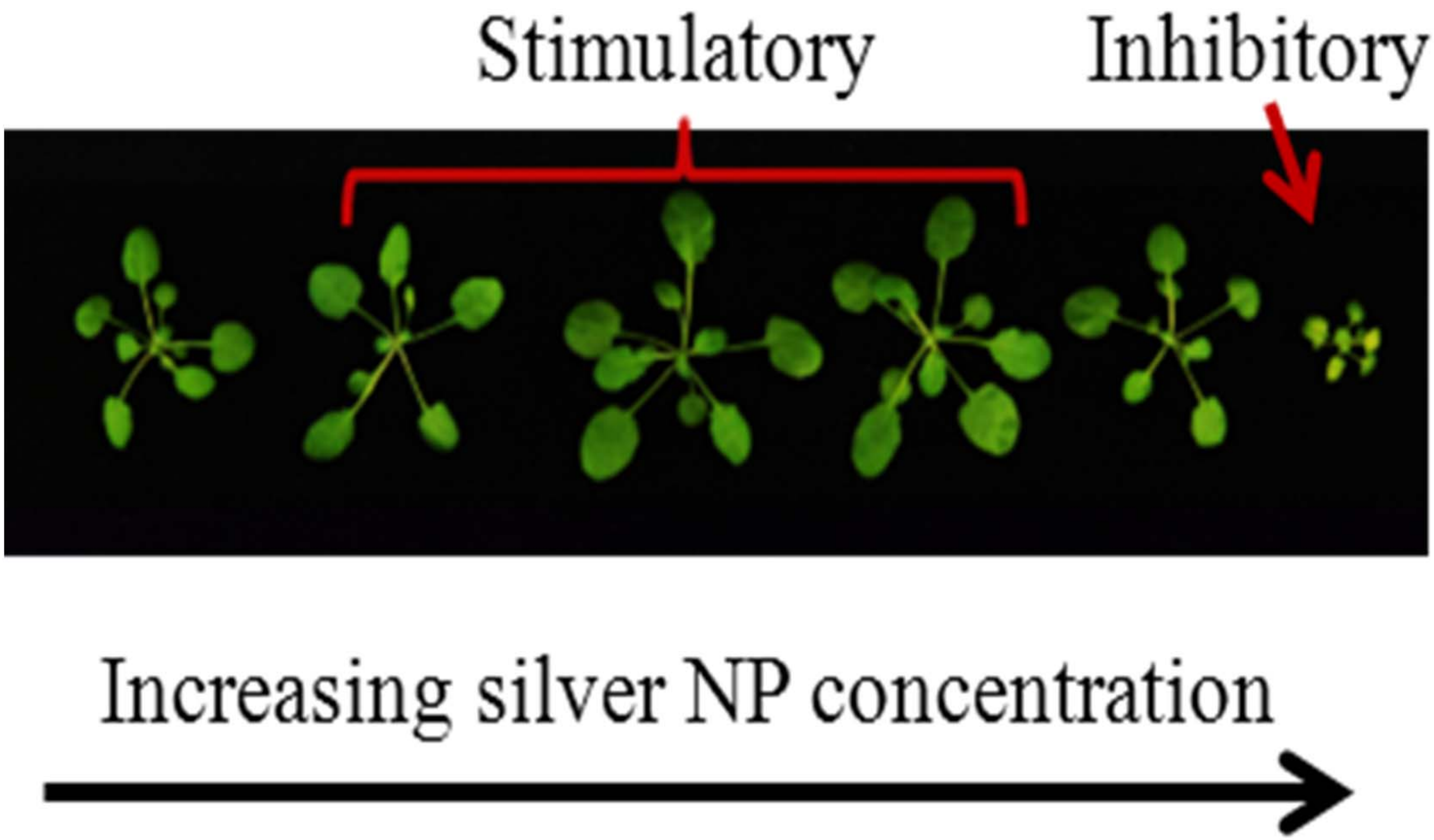
Friedrich Nietzsche



Stimulatory effect after 6 h exposure to low Ag$^+$ concentration **(Hormesis?)**

Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271−4275.

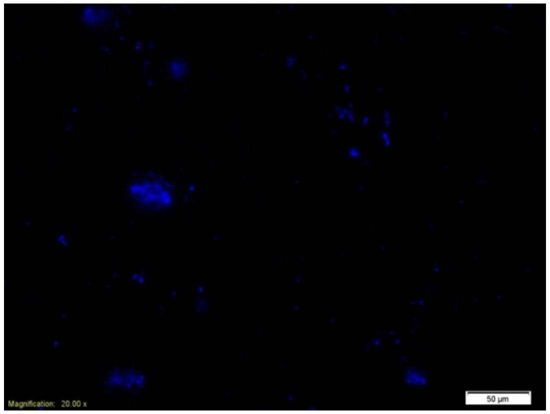
Sub-Lethal Concentrations of AgNPs Could Also Stimulate Plants



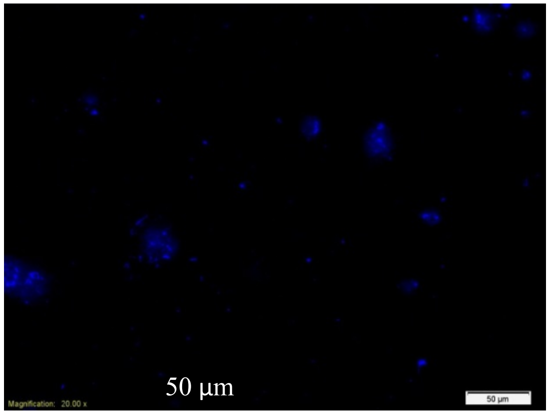
Wang J., Y. Koo, A. Alexander, Y. Yang, S. Westerhof, Q. Zhang, J. Schnoor, V. Colvin, J. Braam, and P.J. Alvarez (2013). Environ. Sci. Technol. 47 (10): 5442–5449.

Sublethal Exposure to AgNPs (but not Ag^+) stimulated biofilm development

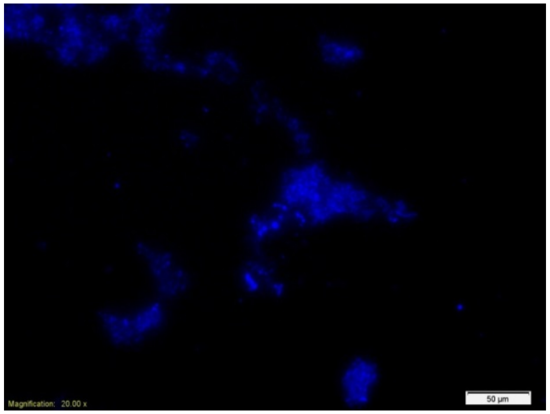
Mixed culture from the effluent of a WWTP, forming biofilm on a glass slide



Control



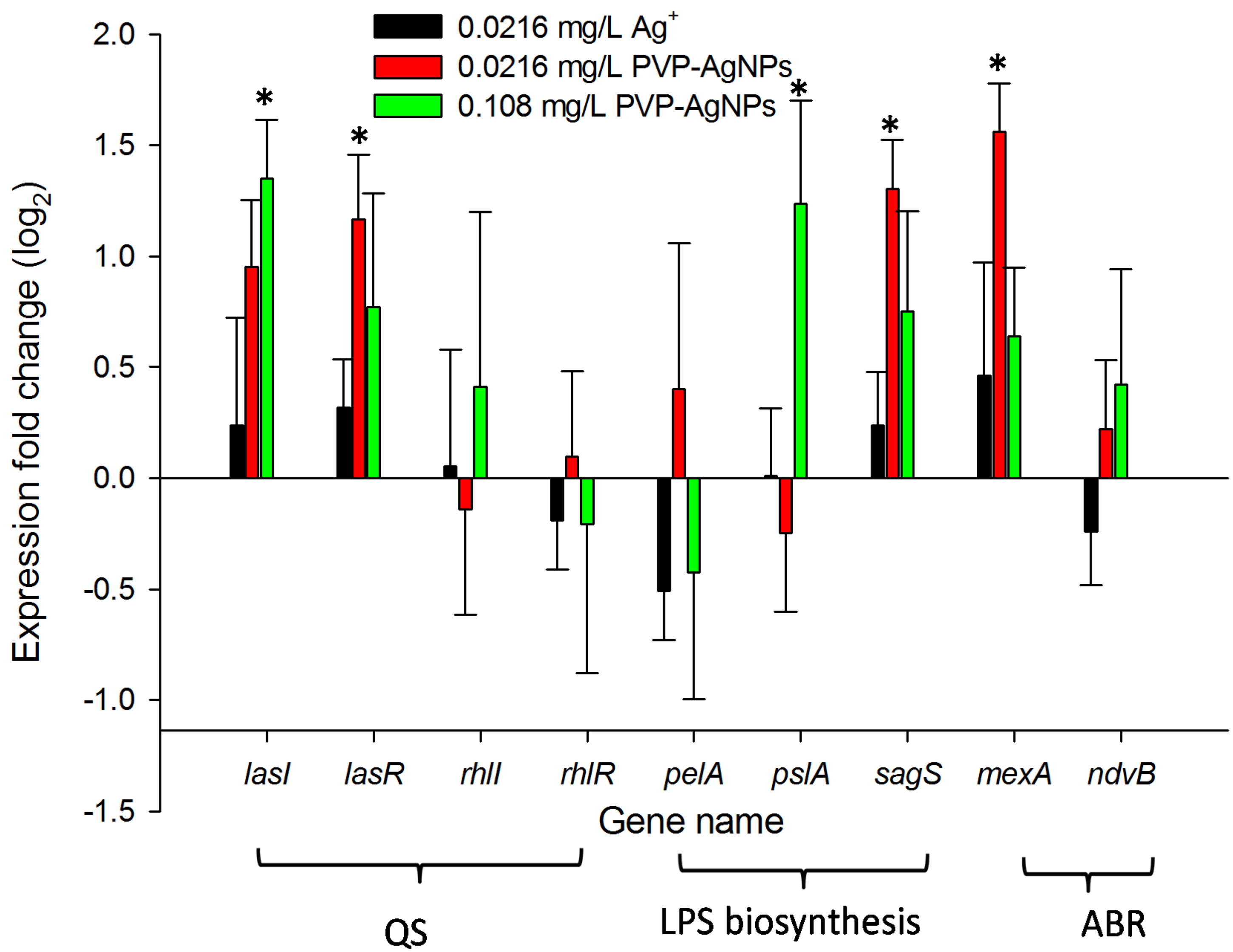
0.02 mg/L of Ag^+



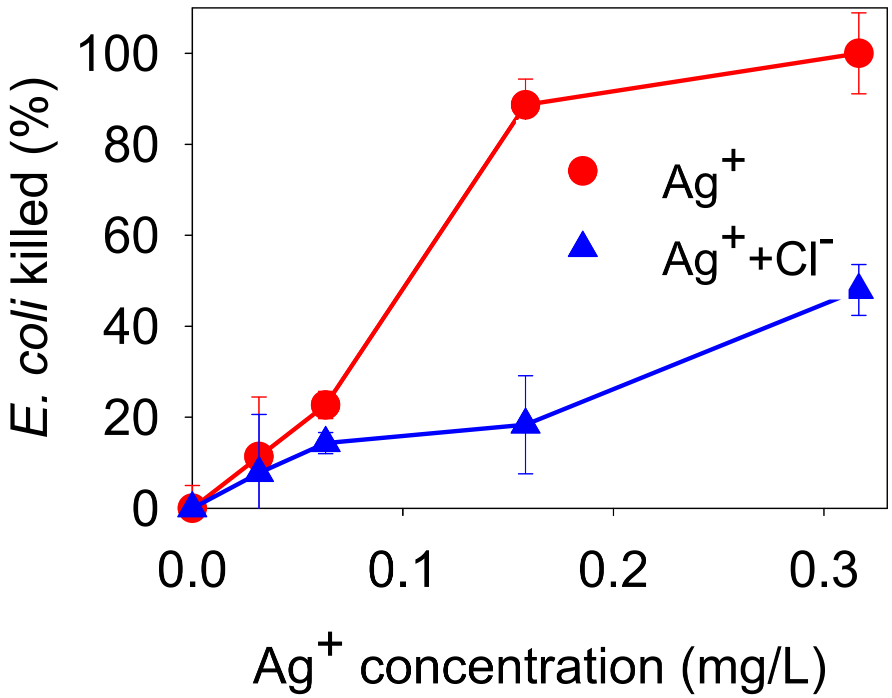
0.02 mg/L of AgNPs

Yang & Alvarez (2015). ES&T Letters. DOI: 10.1021/acs.estlett.5b00159

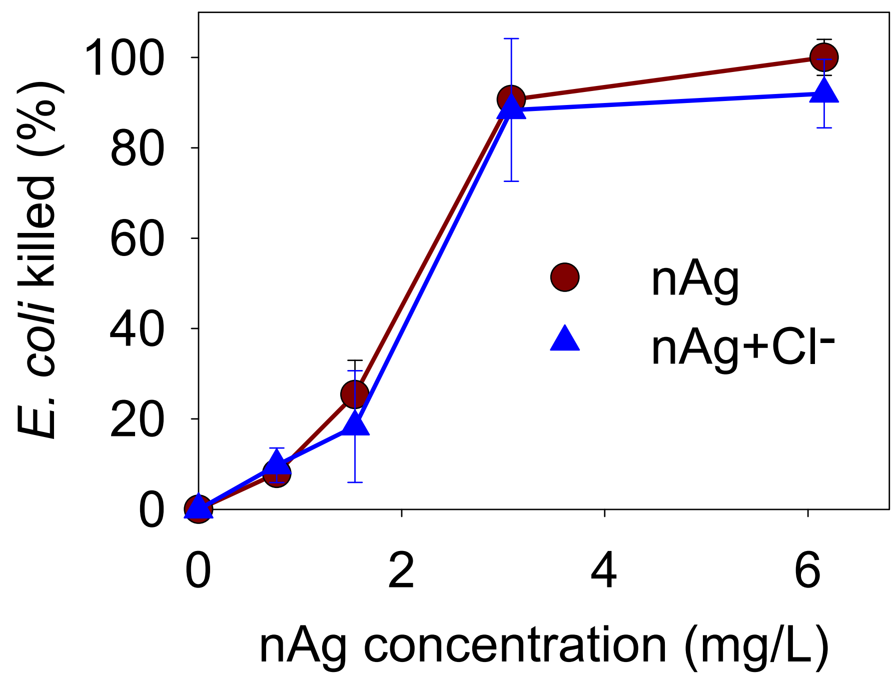
Sub-lethal Exposure of PAO1 to AgNPs also Upregulates Quorum Sensing, LPS, and Antibiotic Resistance Genes



Why is nAg sometimes a stronger bactericide?



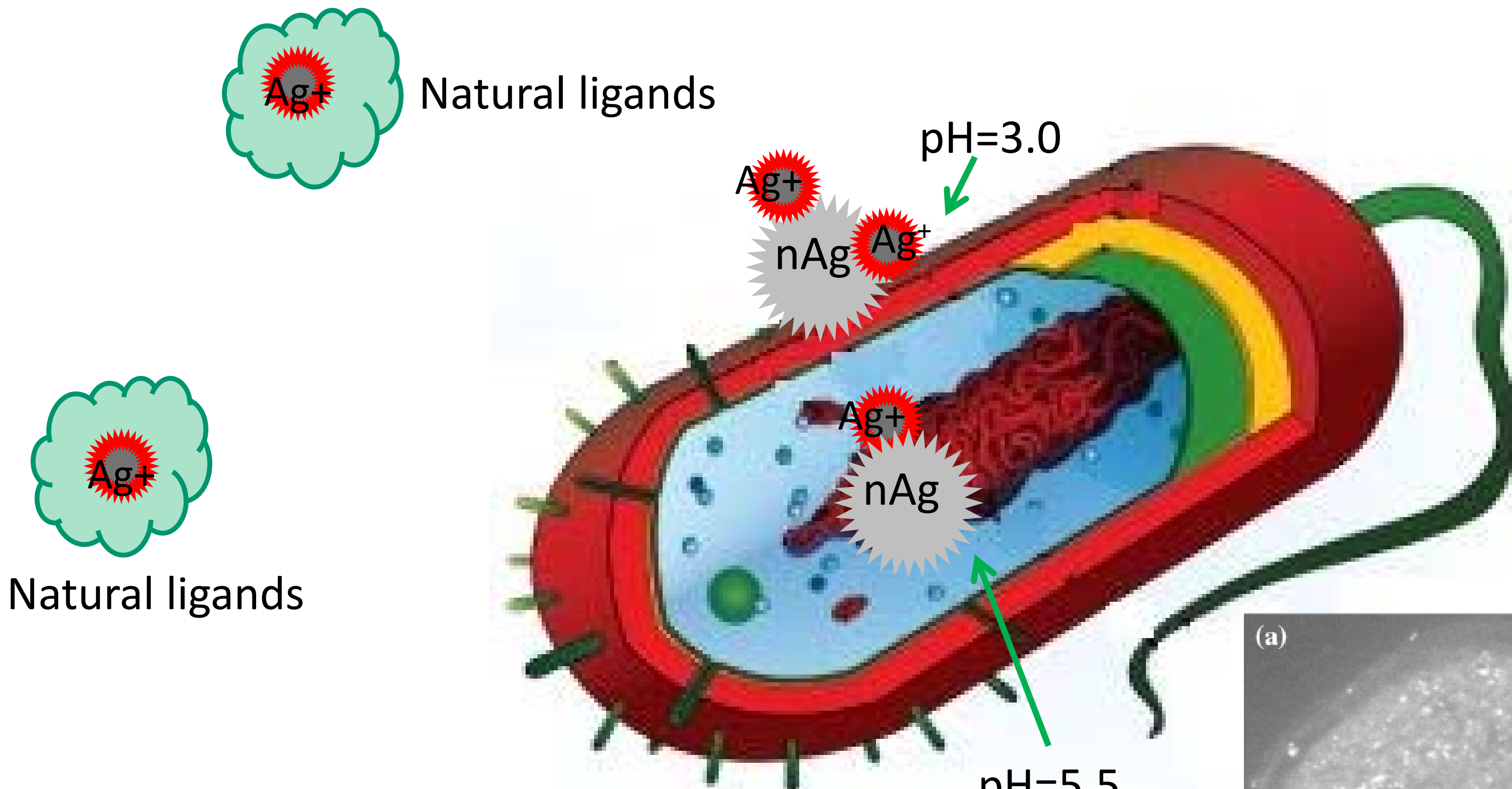
Max [Ag^+]: 3µM; [Cl^-]: 3µM

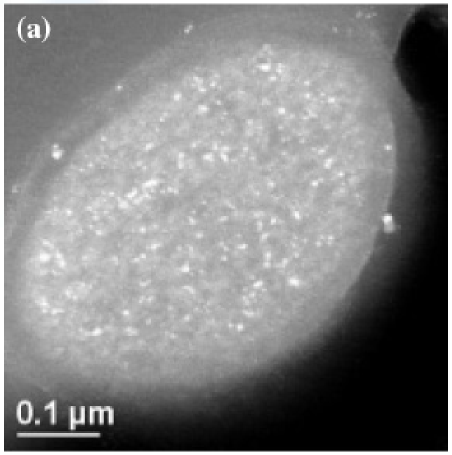


Max [nAg]: 57µM; [Cl^-]: 57µM

- Cl^- (& other ligands, NOM) reduce Ag^+ bioavailability and preferentially decrease its toxicity, even without precipitation
- nAg may then be more bioavailable & effectively deliver Ag^+

More Effective Delivery of Ag^+ to Membrane and Cytoplasm





Morones et al.,2005

Risk = Hazard × Exposure

Hazard, but no exposure

Exposure but no hazard

Hazard as well as exposure

Safer Use of ENMs

Risk = Hazard x Exposure

Hazard

- Prioritize use of ENMs of benign, low-cost, and earth-abundant compositions (GRAS); Green Chemistry and Green Engineering
- Experts panel to select ENMs before incorporation into products
- Interface with TSCA in the US and REACH in the EU

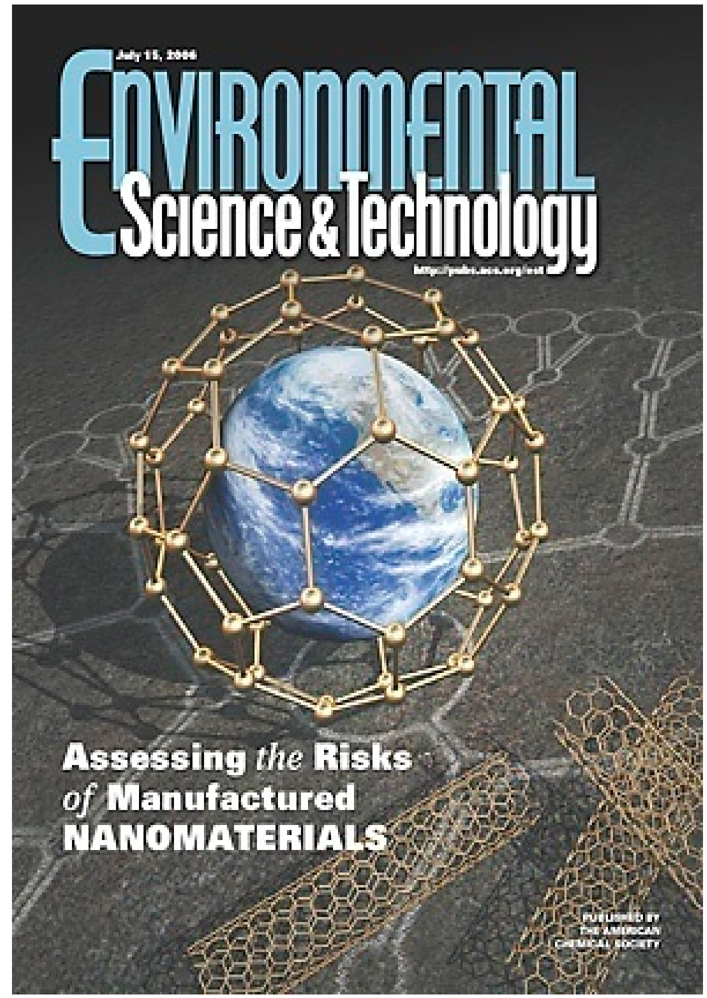
Exposure

- Immobilize ENMs to minimize release and exposure and enable reuse (no free NPs)
- Model & monitor treated water for leaching
- Foster safety in manufacturing by iterating with OSHA on best practices
- Independent certification for meeting health & safety stds.

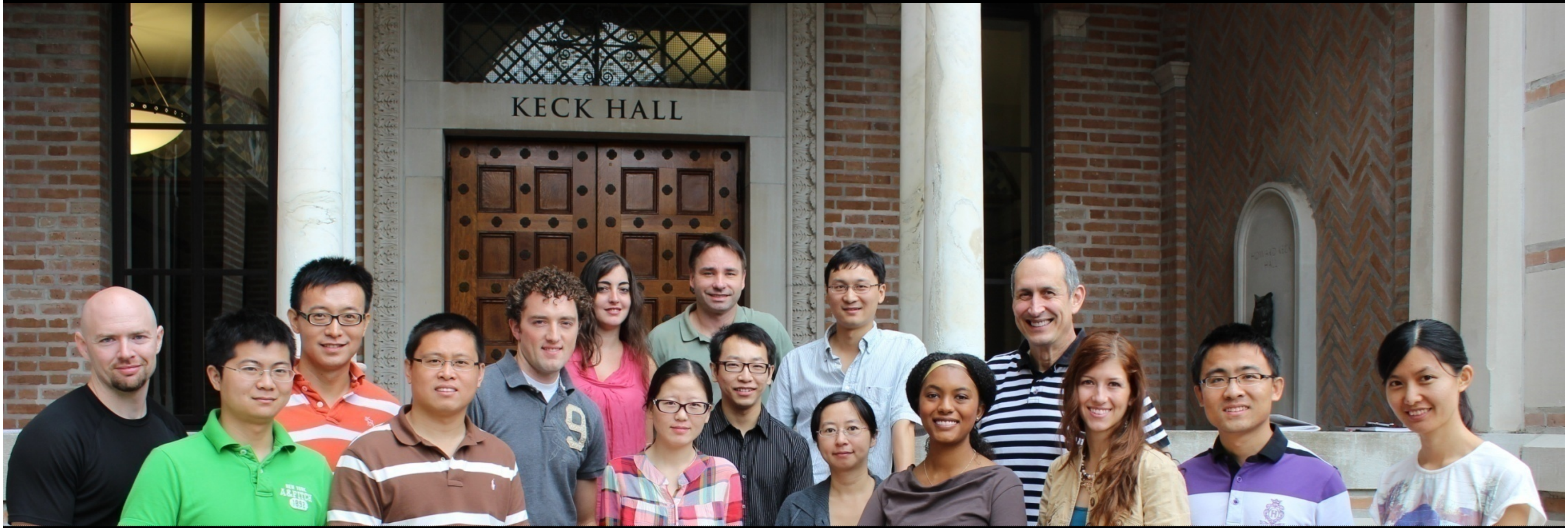
CONCLUSIONS

- Implications: Ecotoxicology- Ecosystem services (primary productivity, food webs, nutrient cycling?) biodiversity? Toxicity to higher organisms? *Mitigated by NOM, salts*

- Applications: DBP-free disinfection, advanced (photo) oxidation processes, anti-fouling/corrosion coatings? functionalized membranes



Thanks! - Graduate Students and Postdocs
NSF, EPA, CBEN, FAO, NERC, BP



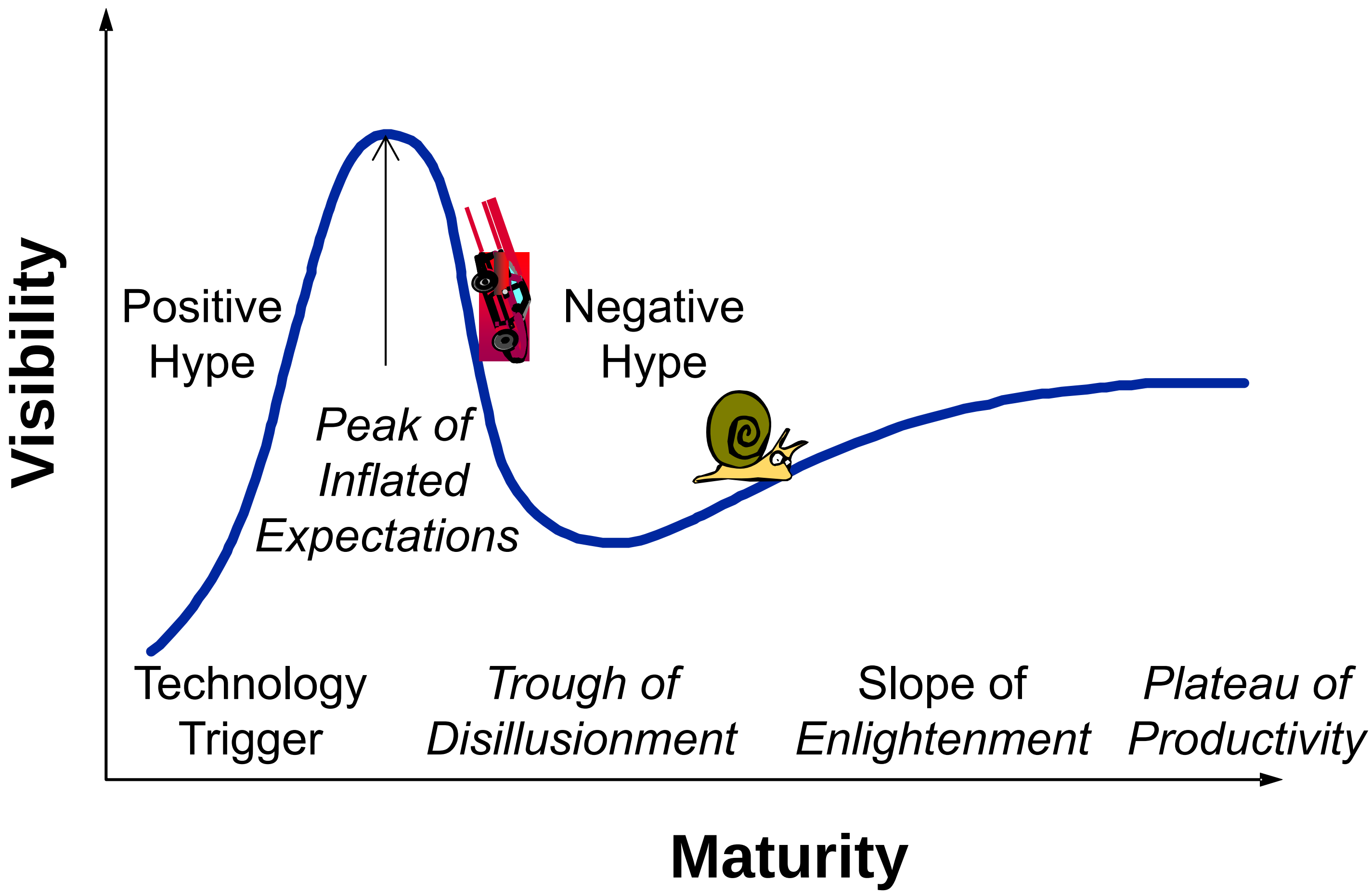
Ph.D. M. Vermace; Craig Hunt; Marcio da Silva; Nanh Lovanh; Alethia Vazquez; Roopa Kamath; Michal Rysz; Natalie Capiro; Delina Lyon; Rosa Dominguez, Dong Li; Diego Gomez, Jacques Mathieu, Leti Vega, Xiaolei Qu, **Jon Brame,** Jiawei Ma, Pingeng Yu, Mengyan Li, Jing Wang, Ana McPhail, O. Monzon

M.S.E. Gary Chesley; Sang-Chong Lieu; Pete Svebakken; Phil Kovacs; Rod Christensen; Marc Roehl; Ken Rotert; Brad Helland; Leslie Cronkhite; Annette Dietz; Bill Schnabel; Ed Ruppenkamp; Leslie Foster; Bryan Till; Nahide Gulensoy; Rebecca Gottbrath; Matt Wildman; Chad Laucamp; Todd Dejournet; Sascha Richter; Nanh Lovanh; Sara Kelley; Eric Sawvel; Jennifer Ginner; Sumeet Gandhi; Richard Keller; Jennifer Wojcik; Anitha Dasappa; Leslie Sherburne; Brett Sutton; Russ Sawvel; Andrea Kalafut; Roque Sanchez; Amy Monier; Isabel Raciny; **Katherine Zodrow**; Robert O'Callaham; Bill Mansfield

Postdocs Graciela Ruiz; Jose Fernandez; Byung-Taek Oh; D. Kim; Joshua Shrout; Laura Adams, Sufia Kafy; Lena Brunet; **Jaesang Lee**, Jiawei Chen; Shaily Mahendra; **Zongming Xiu; Yu Yang**

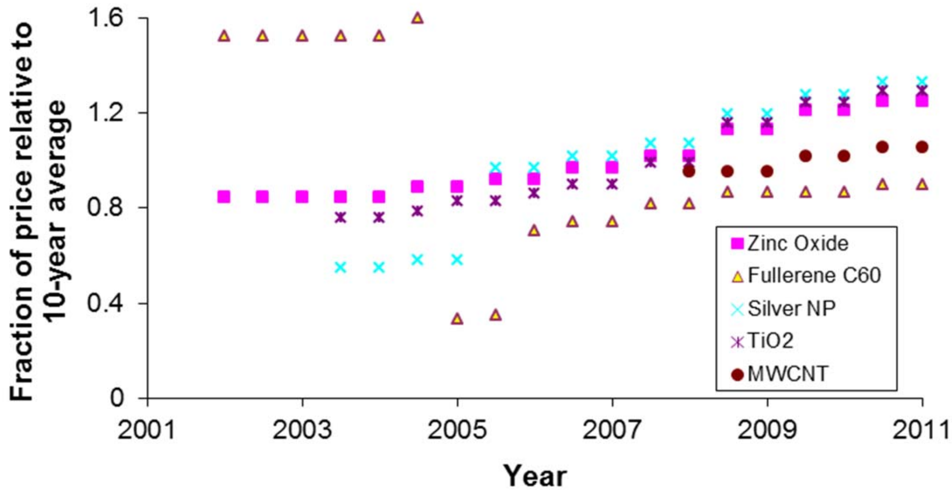
Any Questions?

Quo Vadis, Nano?

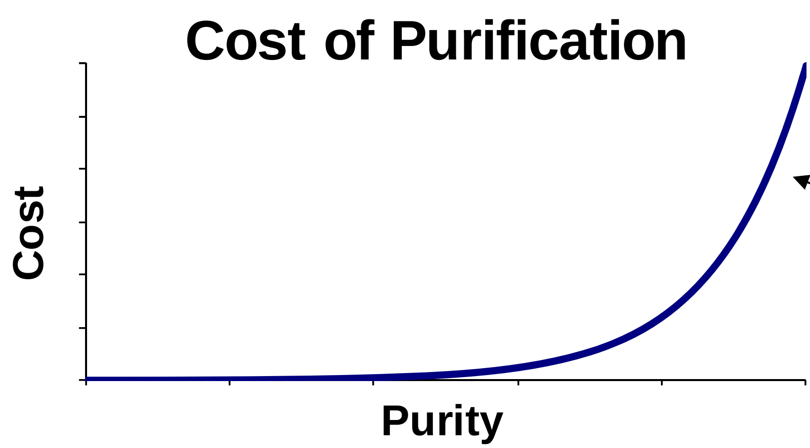


"Nanohype" - Berube

Need market-driven decrease ENM price



Few commercial applications
= low supply
→ prices stay high

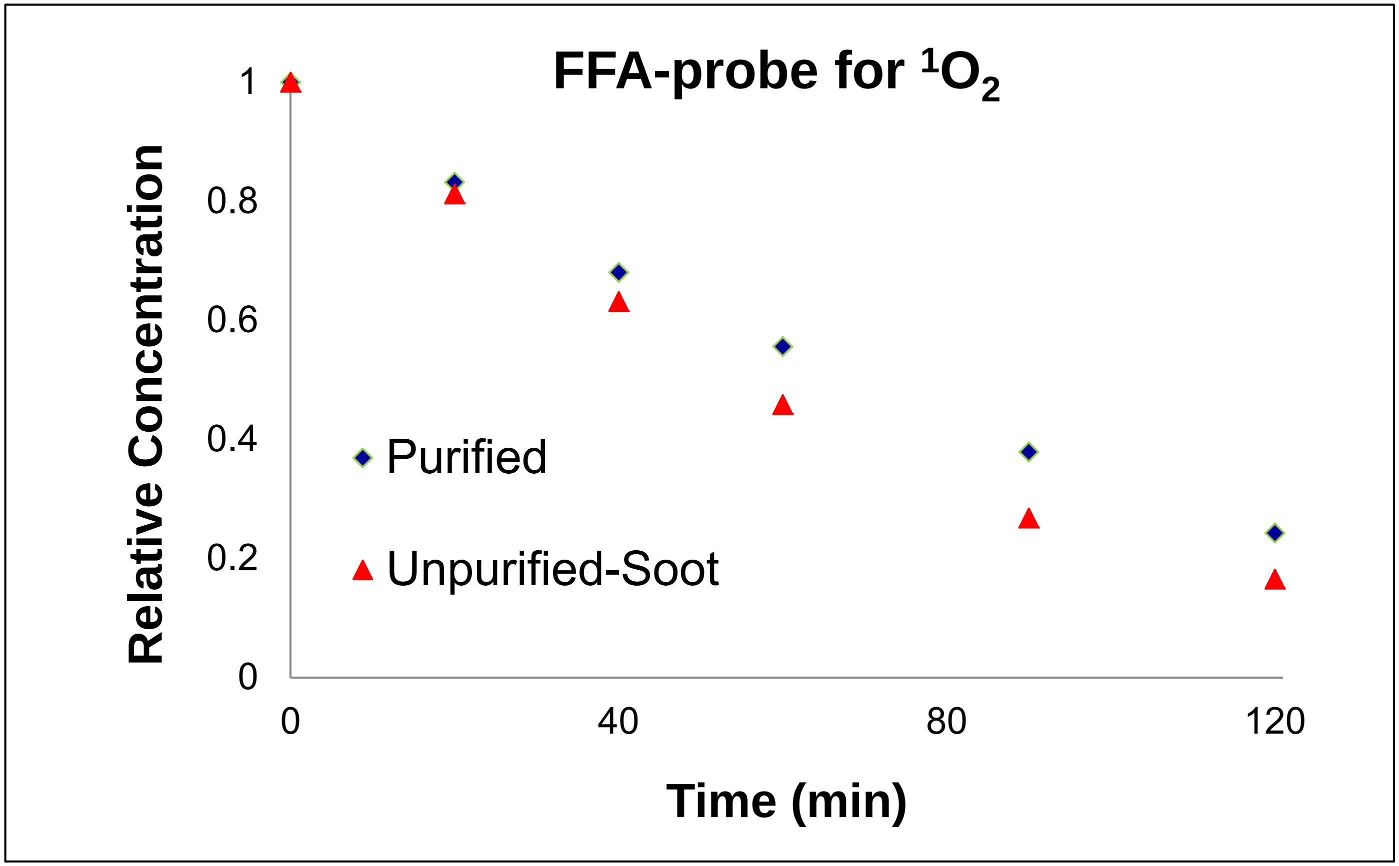


Most production is done for research (small quantities of highly purified material)

High purity requirements increase **separation cost** due to higher energy, solvent, & process time requirements

Avoid the diminishing returns of ultra high purity

Less pure amino-C_{60} cost less (20x) without significantly sacrificing reactivity



Outlook for Developing Nations

Despite current barriers (technical capacity, cost) the use of ENMs will increase in developing nations *(similar to cell phones)* for point-of-use water treatment and reuse, due to:

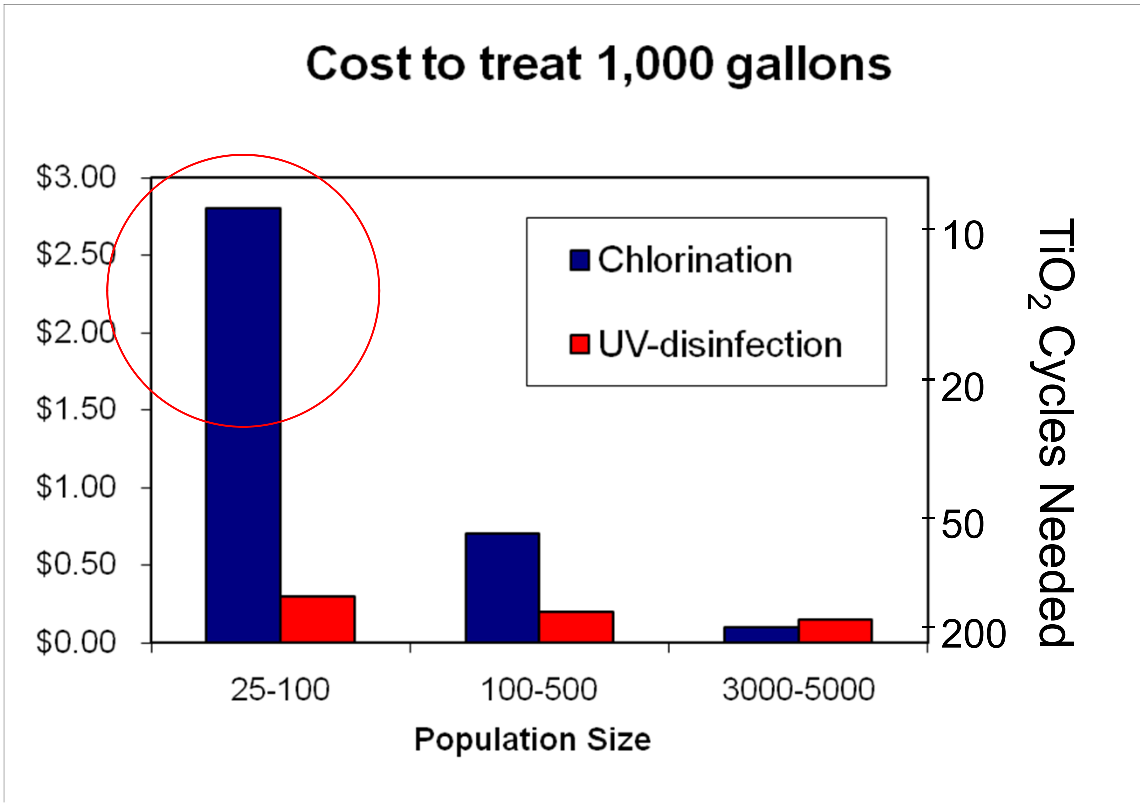
- Decreasing cost:
  - *Economy of scales*
  - *Recyclability of immobilized NPs*
  - *Avoid diminishing returns of ultra high purity*
  - *Valuable properties imparted at low additive ratios*
- Savings on capital investment for new infrastructure in expanding mega-cities

When Does NEWT Make Sense?

- Where current technologies **do not meet** current or upcoming DWT or WWT **regulations**;
- To treat **recalcitrant compounds** (e.g., pharmaceuticals) that escape WWTPs and hinder reuse (e.g., irrigation);
- Where there is **insufficient infrastructure** and one must rely on POU devices
- When NEWT **enhances cost-effectiveness** (e.g., faster, less energy, and less material)

Feasibility Is within Reach

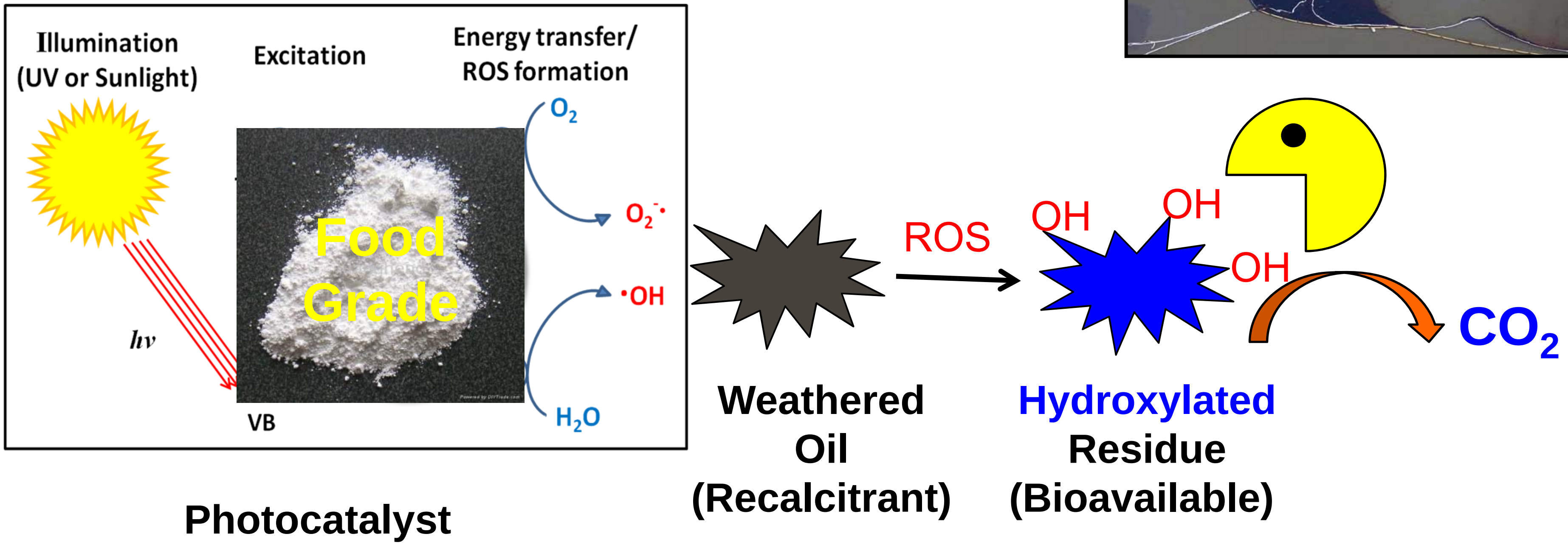
(Photo-disinfection with TiO_2 is feasible for small villages if recycled)



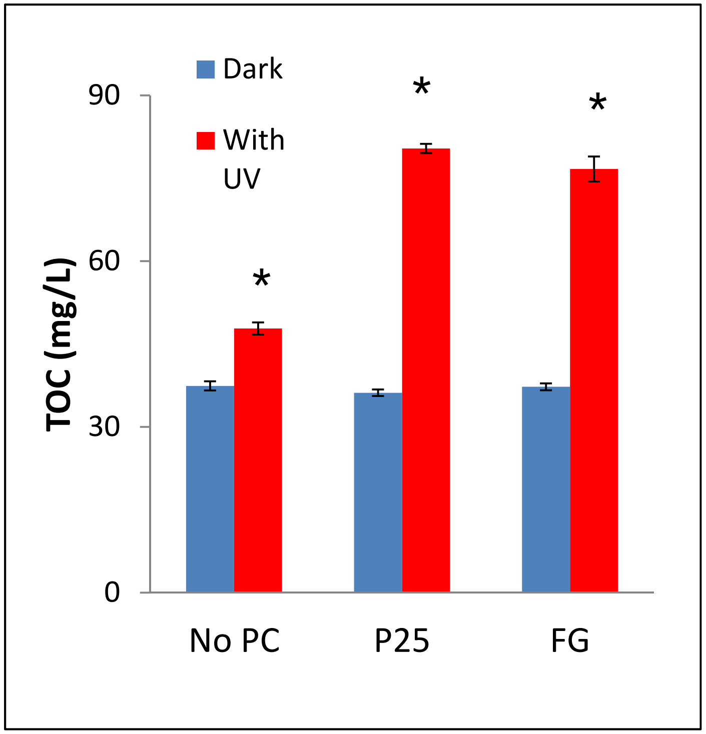
Recycling makes photo-disinfection with TiO_2 competitive with traditional treatment processes *at small scales*

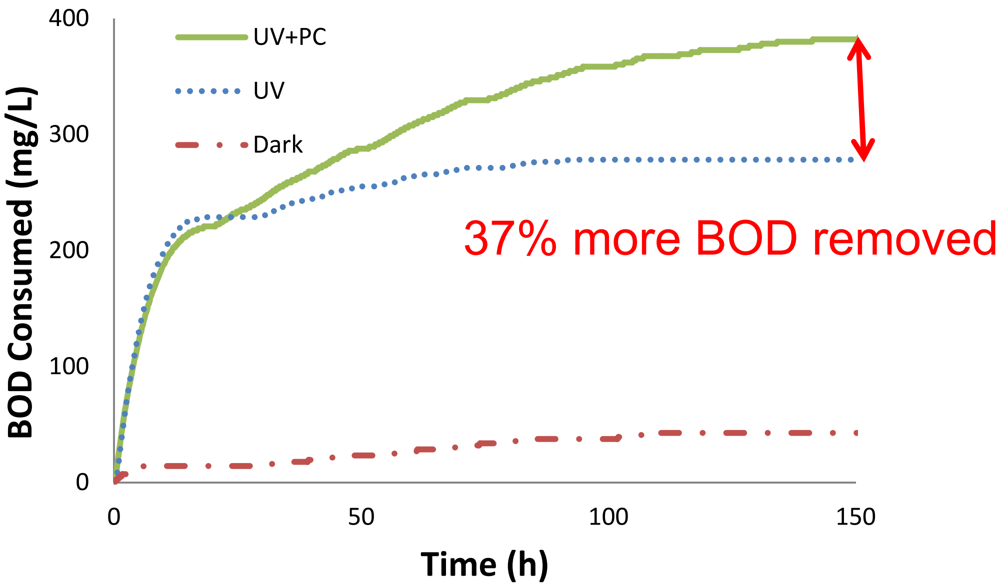
(Assumes \$0.15/g TiO_2, 50 g/L used for treatment)

Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation



Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil

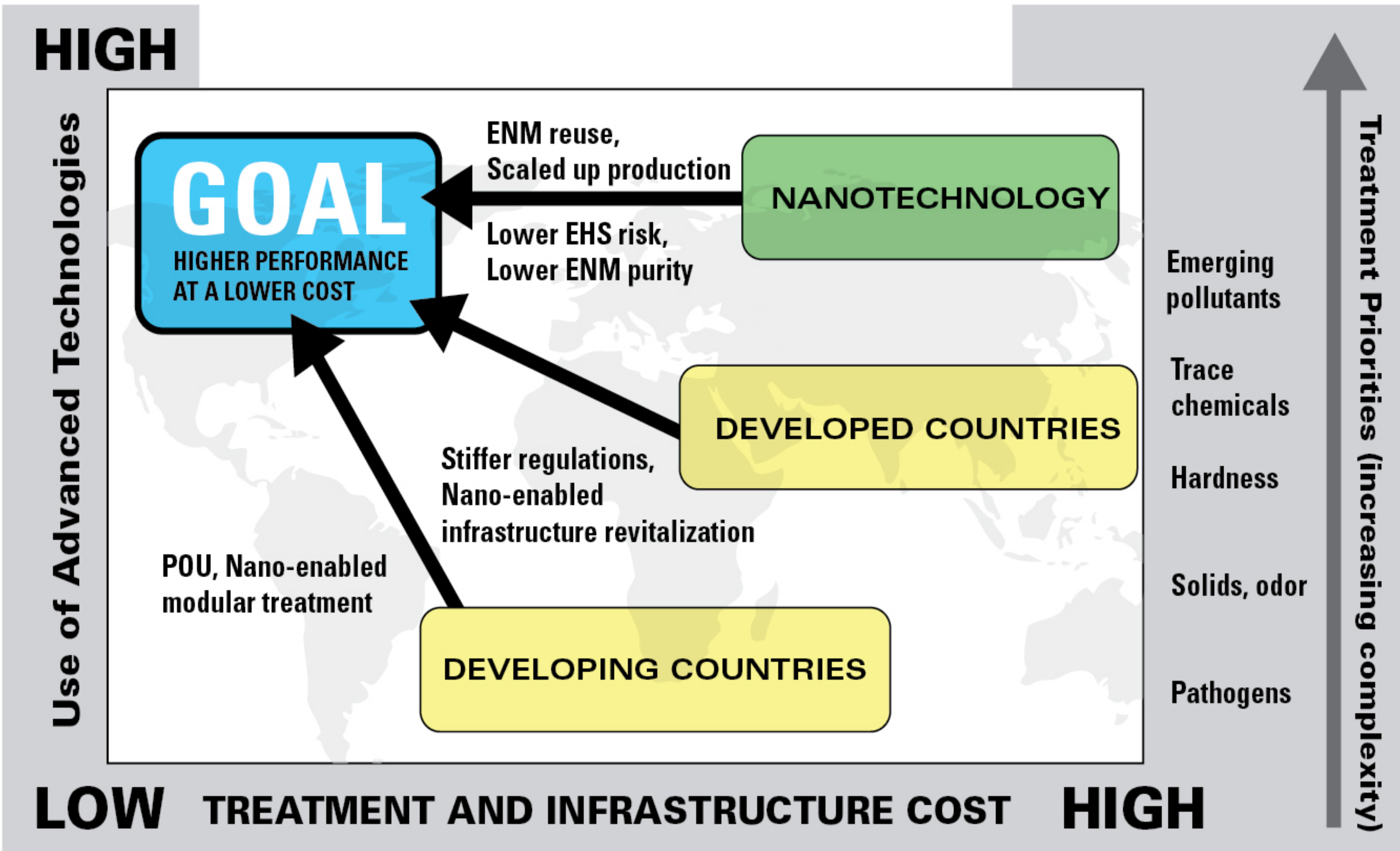




* statistically significant (p <0.05) after 1-day exposure

Brame J., S.W. Hong, J. Lee and P.J.J. Alvarez (2013). *Chemosphere* 90: 2315–2319.

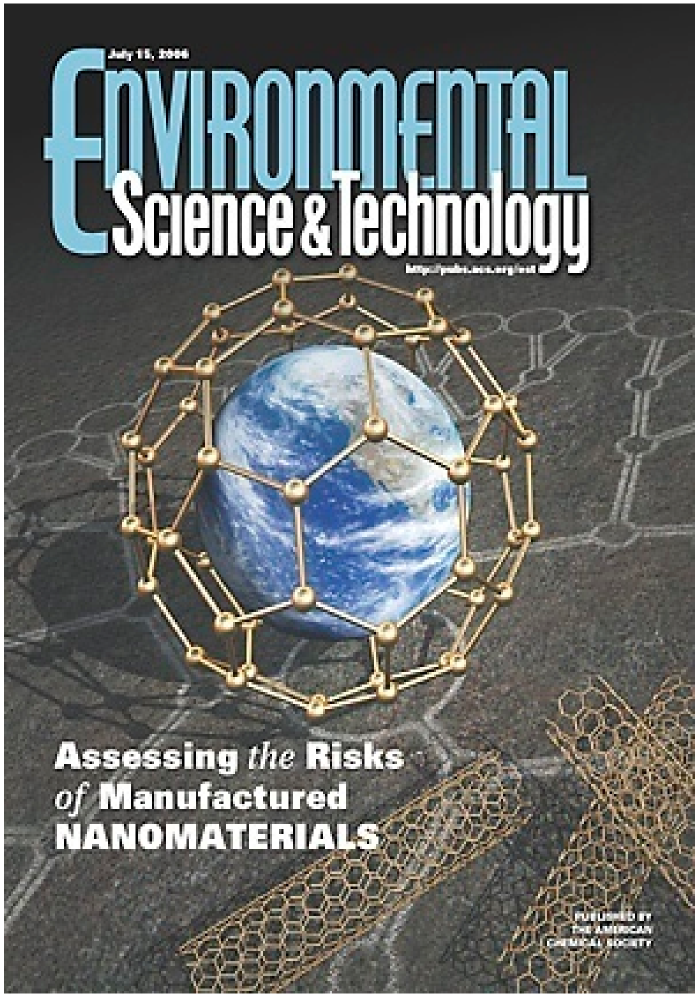
Conceptual Improvements to Water Treatment Through Nanotechnology

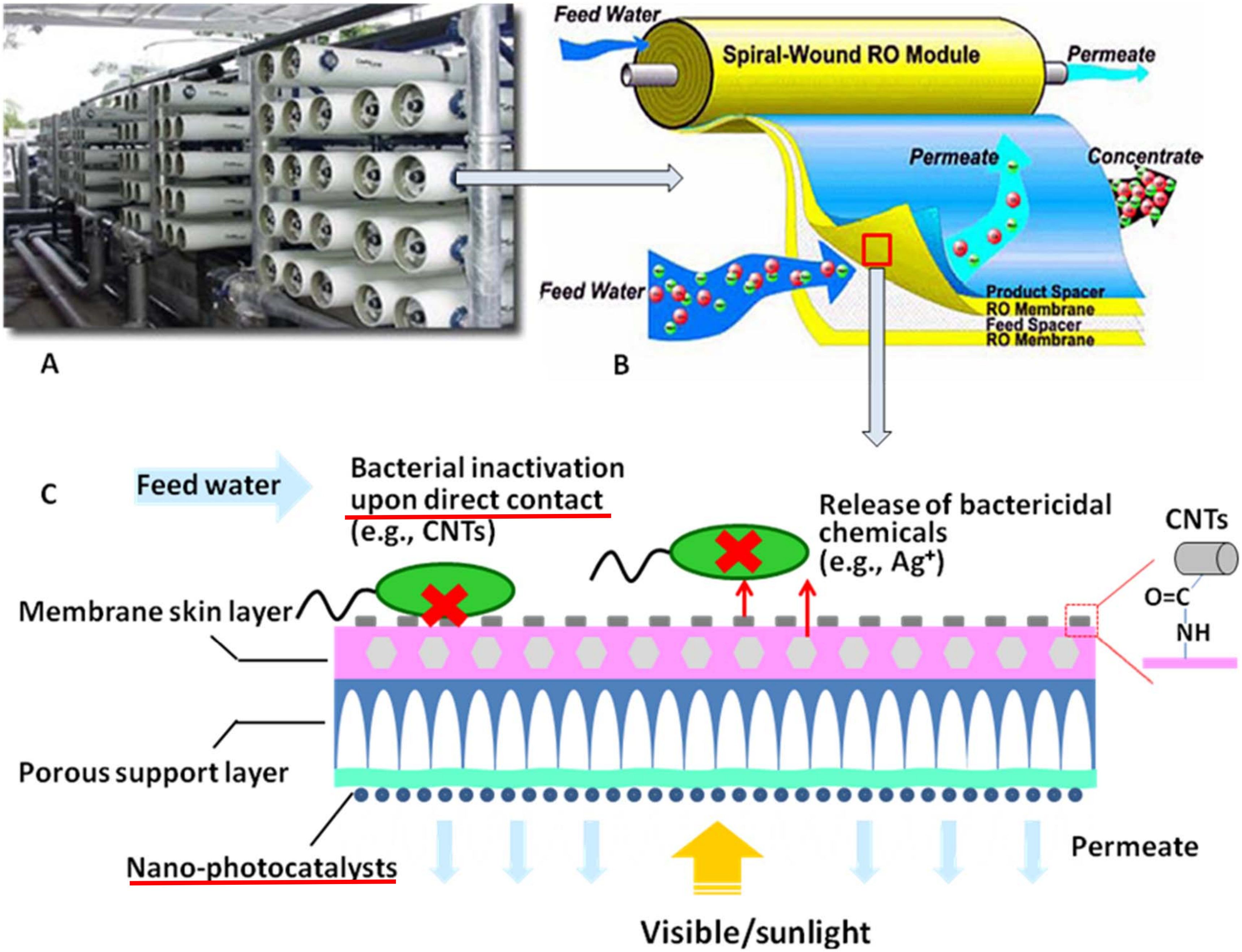


Qu X., J. Brame, Q. Li and P.J.J. Alvarez (2012). Acc. Chem. Res. doi:10.1021/ar300029v

SUMMARY

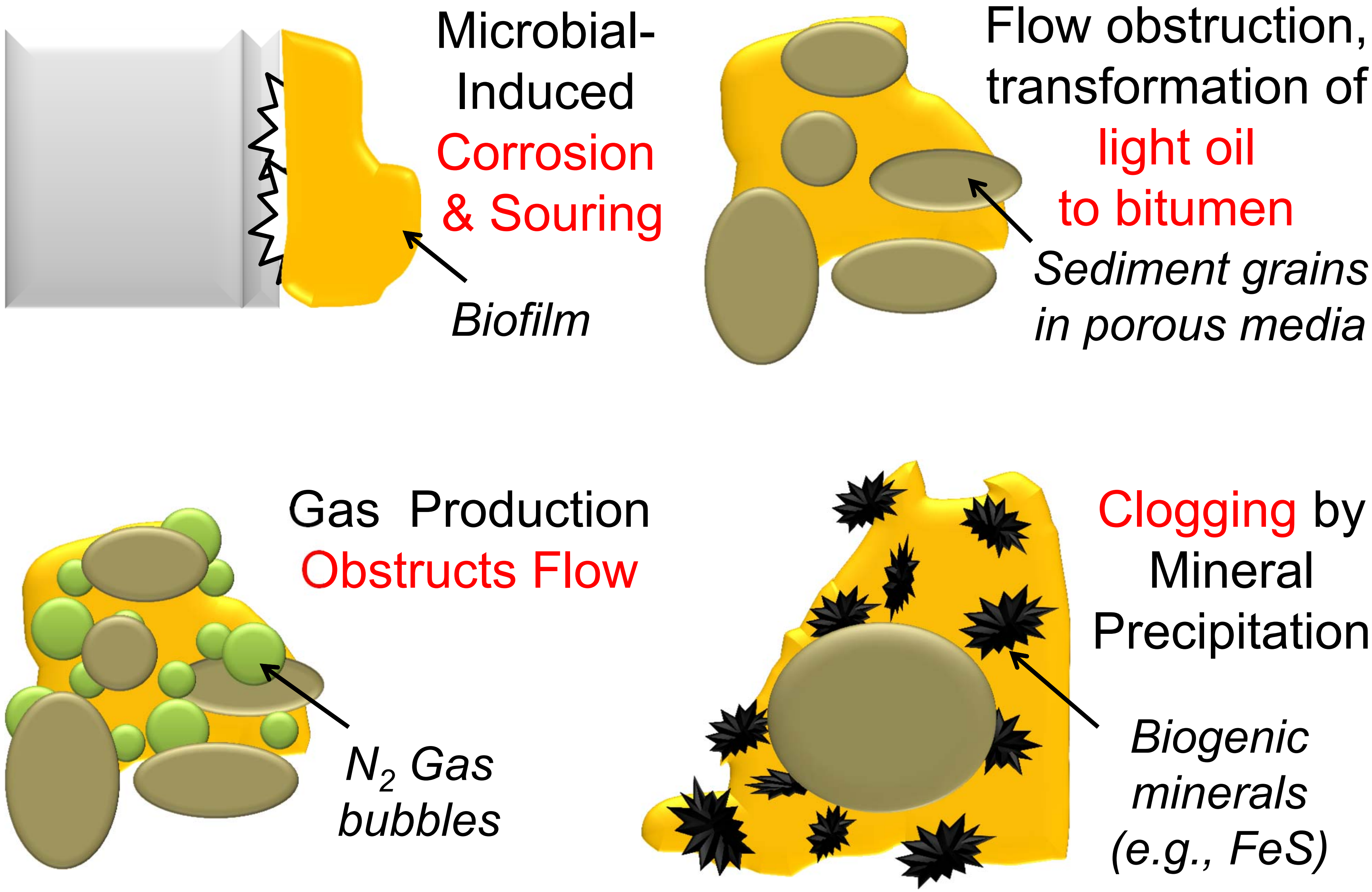
- Antimicrobial NPs can enable microbial control (e.g., DBP-free disinfection, fouling resistant surfaces and membranes, etc.)
- Sub-lethal concentrations of Ni^{2+} and Cd^{2+} hinder biofilm formation by inhibiting quorum sensing at the transcription level.
- Nanotechnology could offer opportunities for controlled released of bactericidal or QS-interrupting metals



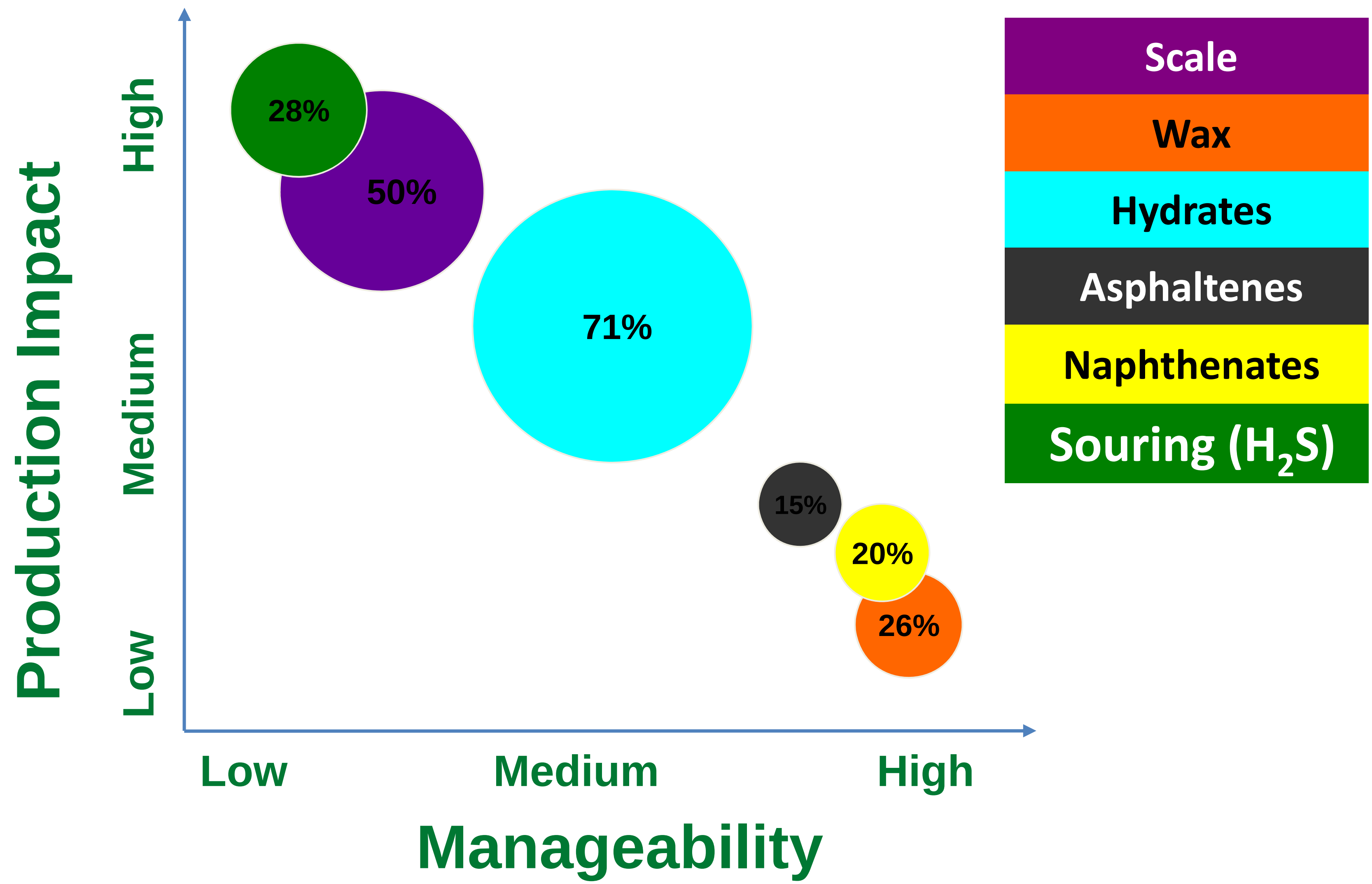


Qu X., J. Brame, Q. Li and P.J.J. Alvarez (2012). *Acc. Chem. Res.* doi:10.1021/ar300029v

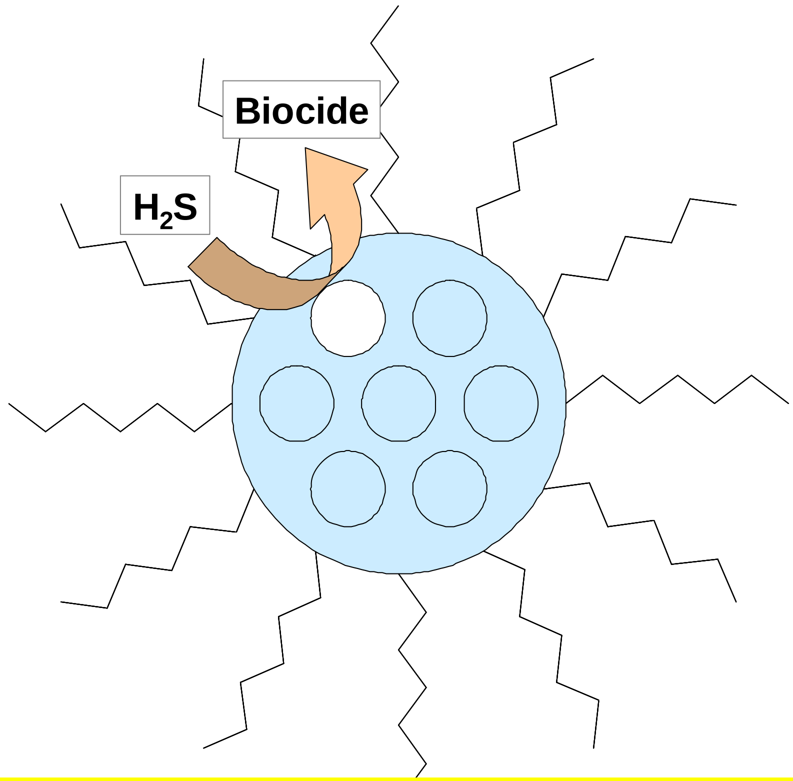
Microbial Processes of Concern to the Oil and Gas Industry



3. O&G Reservoir Souring Control

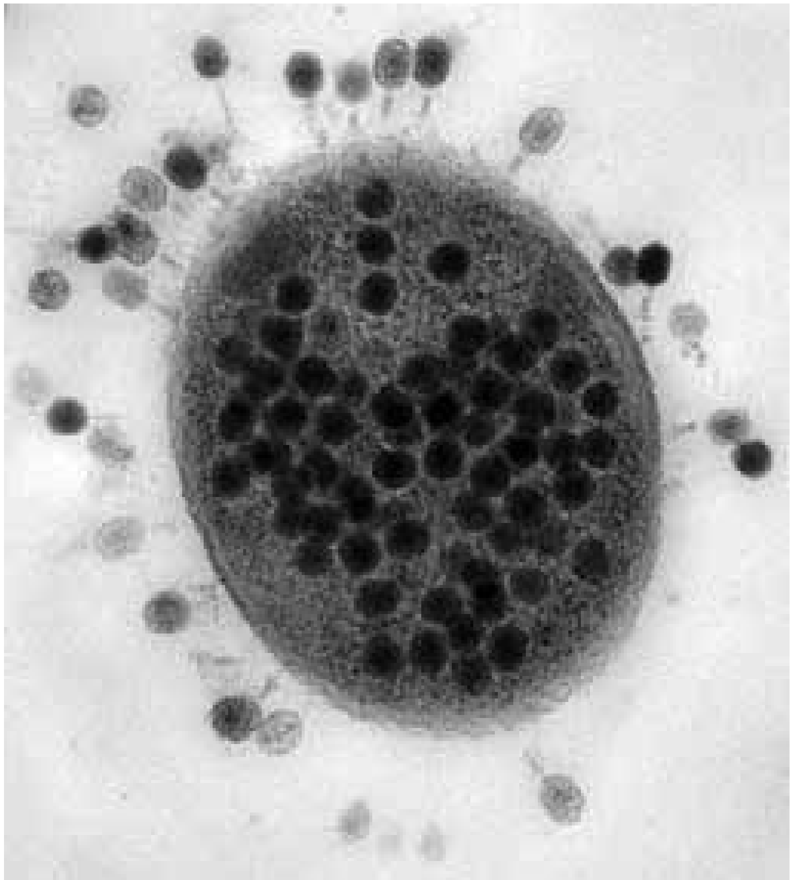


Responsive NPs for Selective Biocide Delivery



- Mesoporous silica filled with biocides & coated with polymers to enhance stability under high salinity/temperature
- Trapdoors made by Mike Wong (hexahydro-s-triazines) fall off due to nucleophilic attack by H_2S, to release the biocide
- This triggers a burst release of biocide **"on demand"**

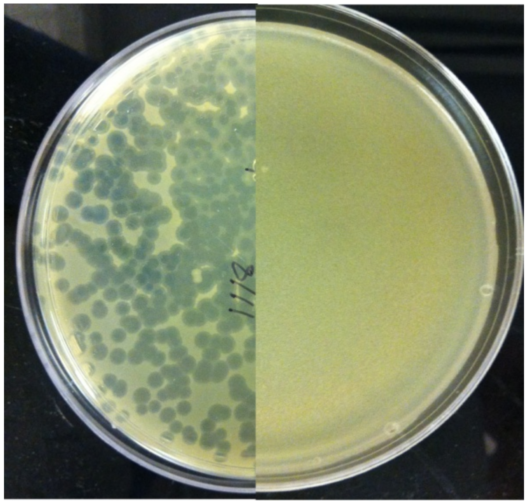
In Situ Control of Sulfidogens with Bacteriophages (Reservoirs & Pipelines)



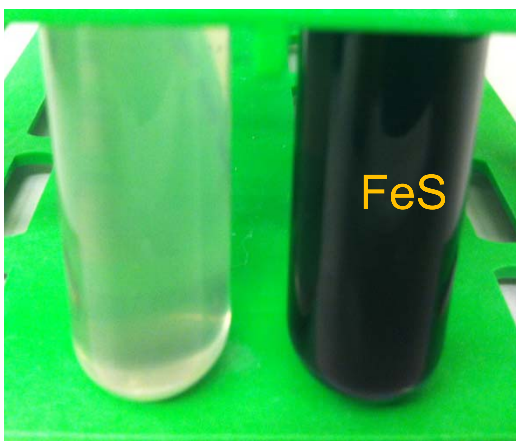
- Prevent souring by H_2S, corrosion, & clogging by FeS_2
- Advantages
  - o **Self-replicating** → low production costs, persistent protection
  - o **Penetrating** → degrade biofilms, can enhance transport properties
    - encapsulation
    - targeting through triggered release (increased local MOI)
  - o **Green** technology

Strategy: isolate and enrich **<u>polyvalent</u>** (broad-host-range) phages for "vaccination" inoculation of reservoirs.

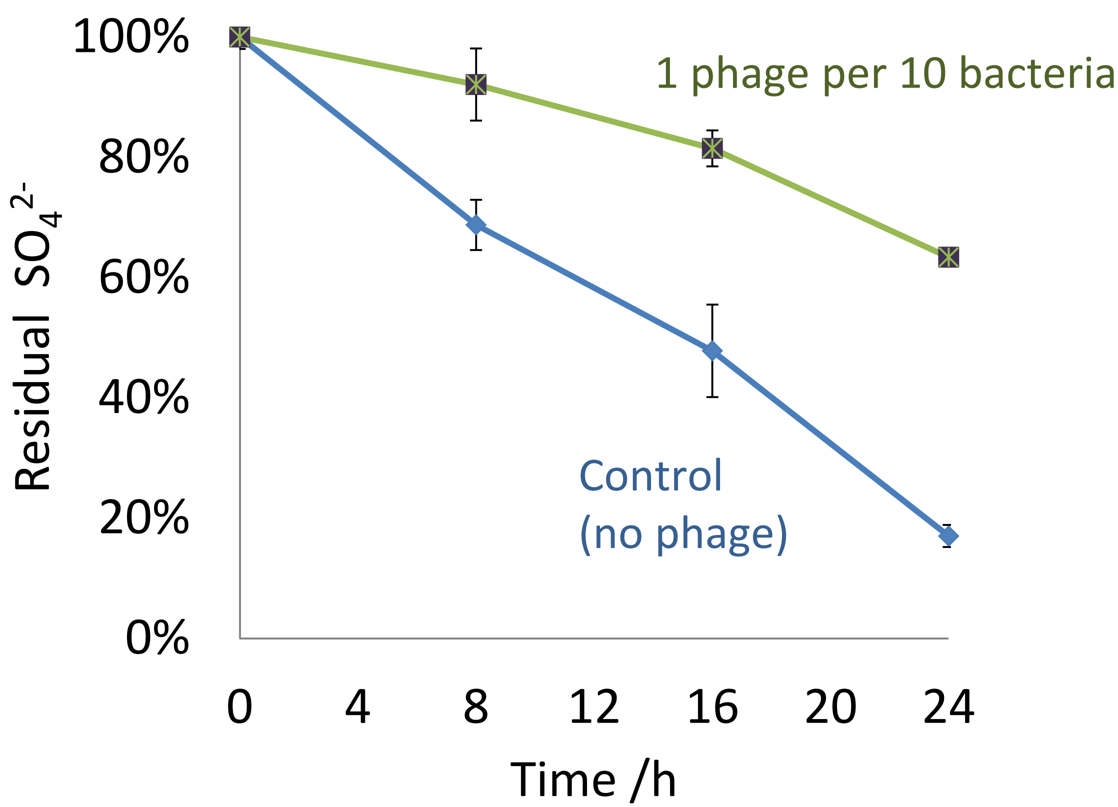
Inhibition of *Desulfovibro salexigens* ATCC 14944 by a phage from WWTP



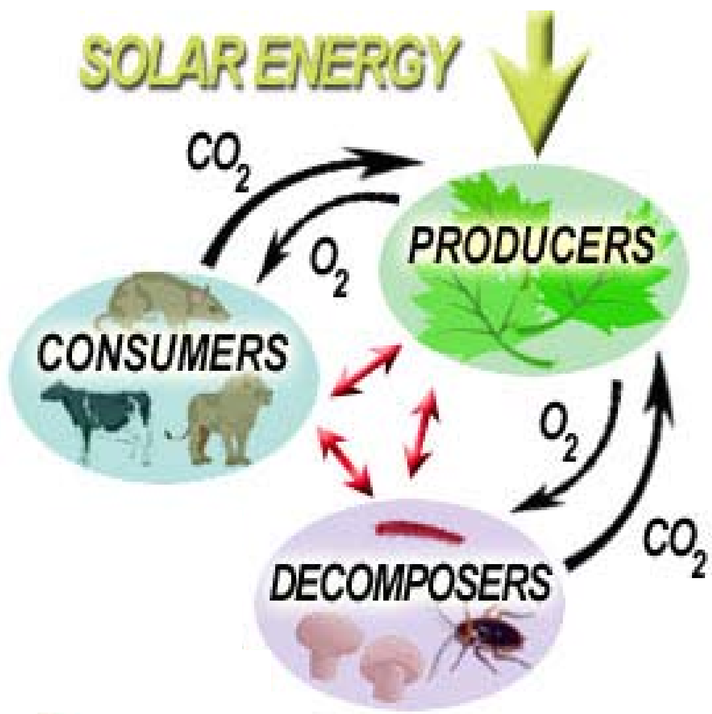
With and without phage



With and without phage

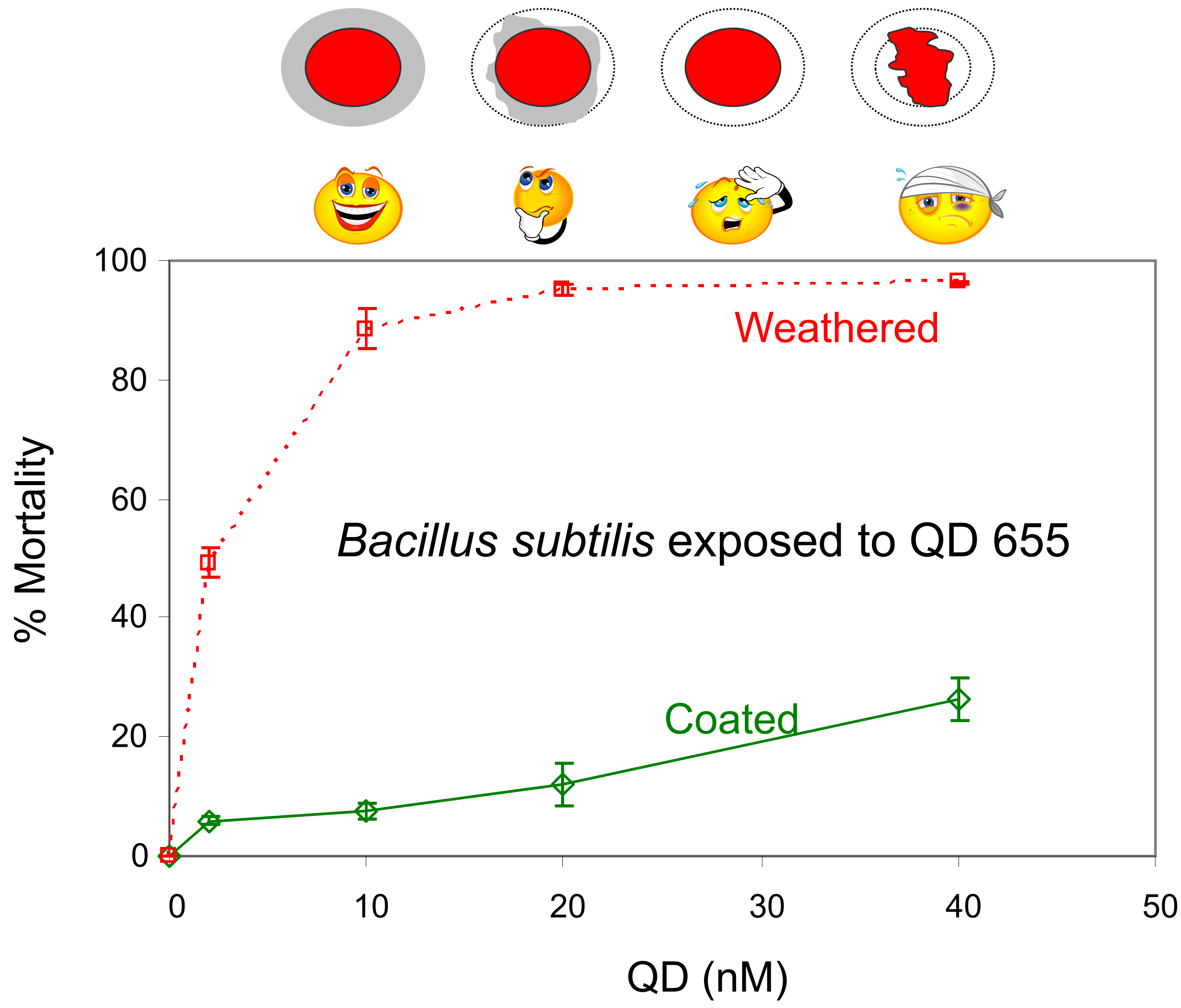


Microbial-nanoparticle Interactions to Inform Risk Assessment

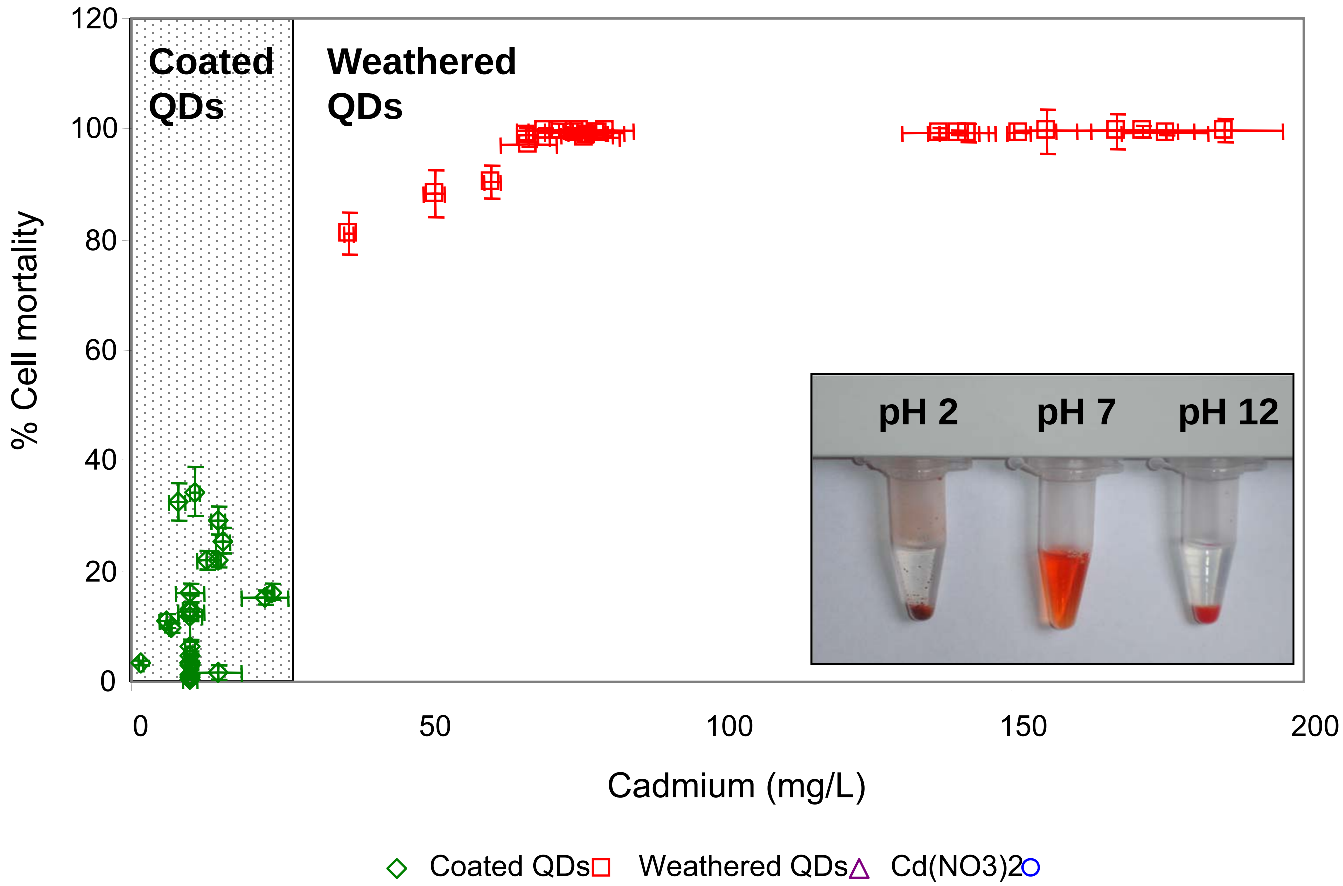


- Bacteria are at the foundation of all ecosystems, and carry out many ecosystem services
- Disposal/discharge can disrupt primary productivity, nutrient cycles, biodegradation, agriculture, etc.
- Antibacterial activity may be fast-screening indicator of toxicity to higher level organisms (*microbial sentinels*?)

Example 2. Artificial Coatings: Quantum Dot Weathering

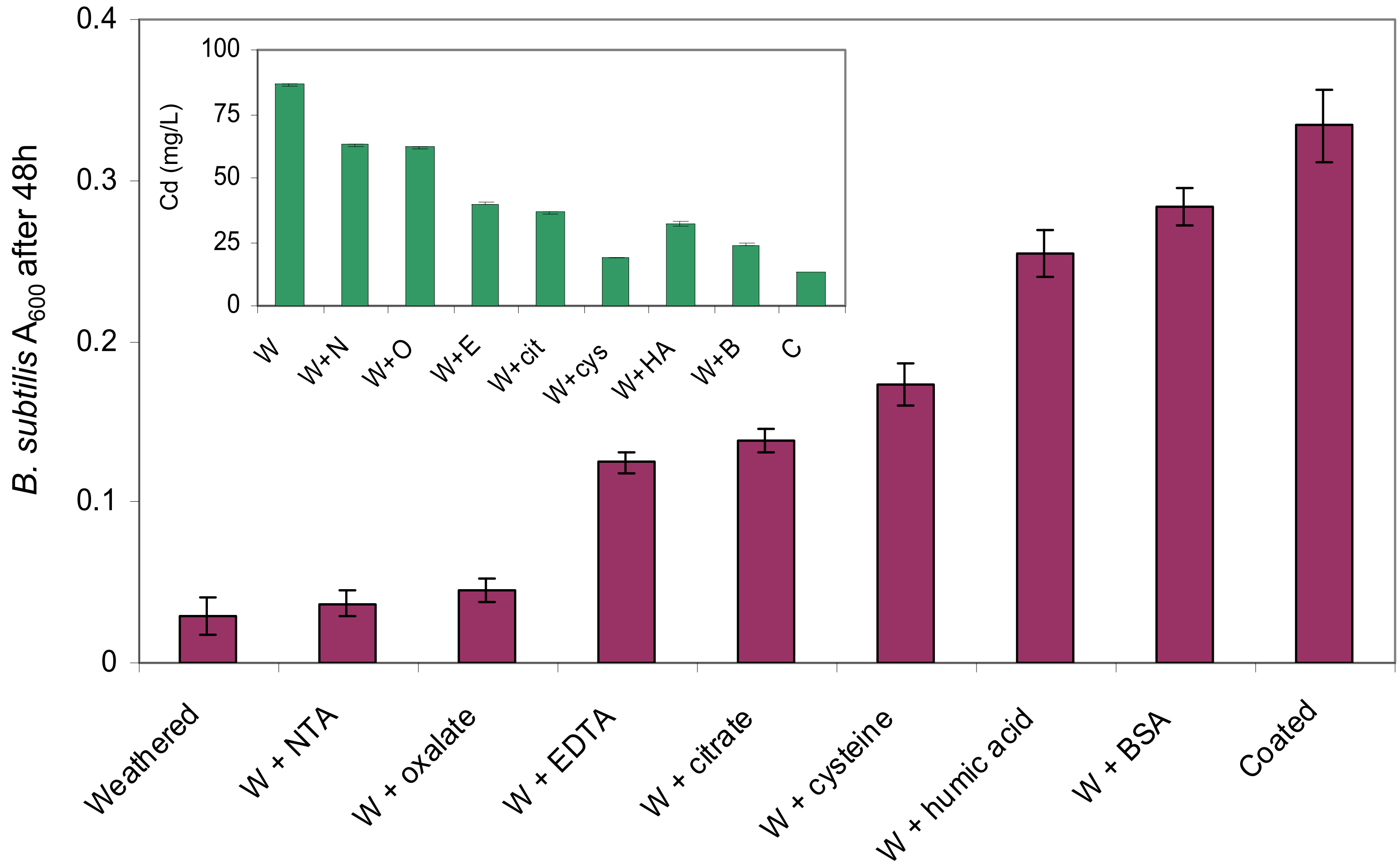


Cd^{2+} and Selenite Release after pH change (pH <4 & pH >10) Explains Dose-Response



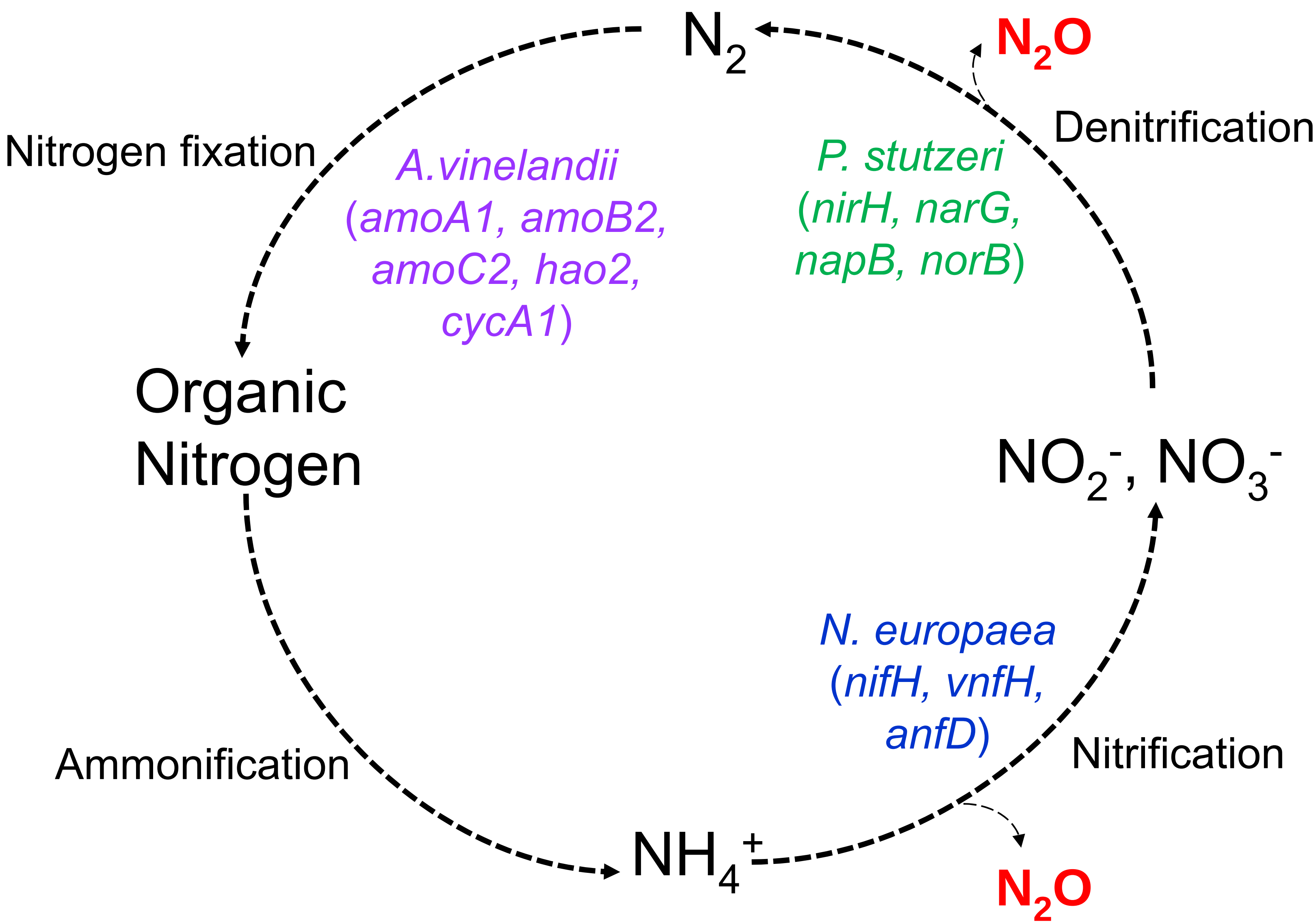
Mahendra S., H. Zhu, V. Colvin and P. J. J. Alvarez (2008). Environ. Sci. Technol. 42 (24), 9424-9430

Organic ligands mitigate toxicity

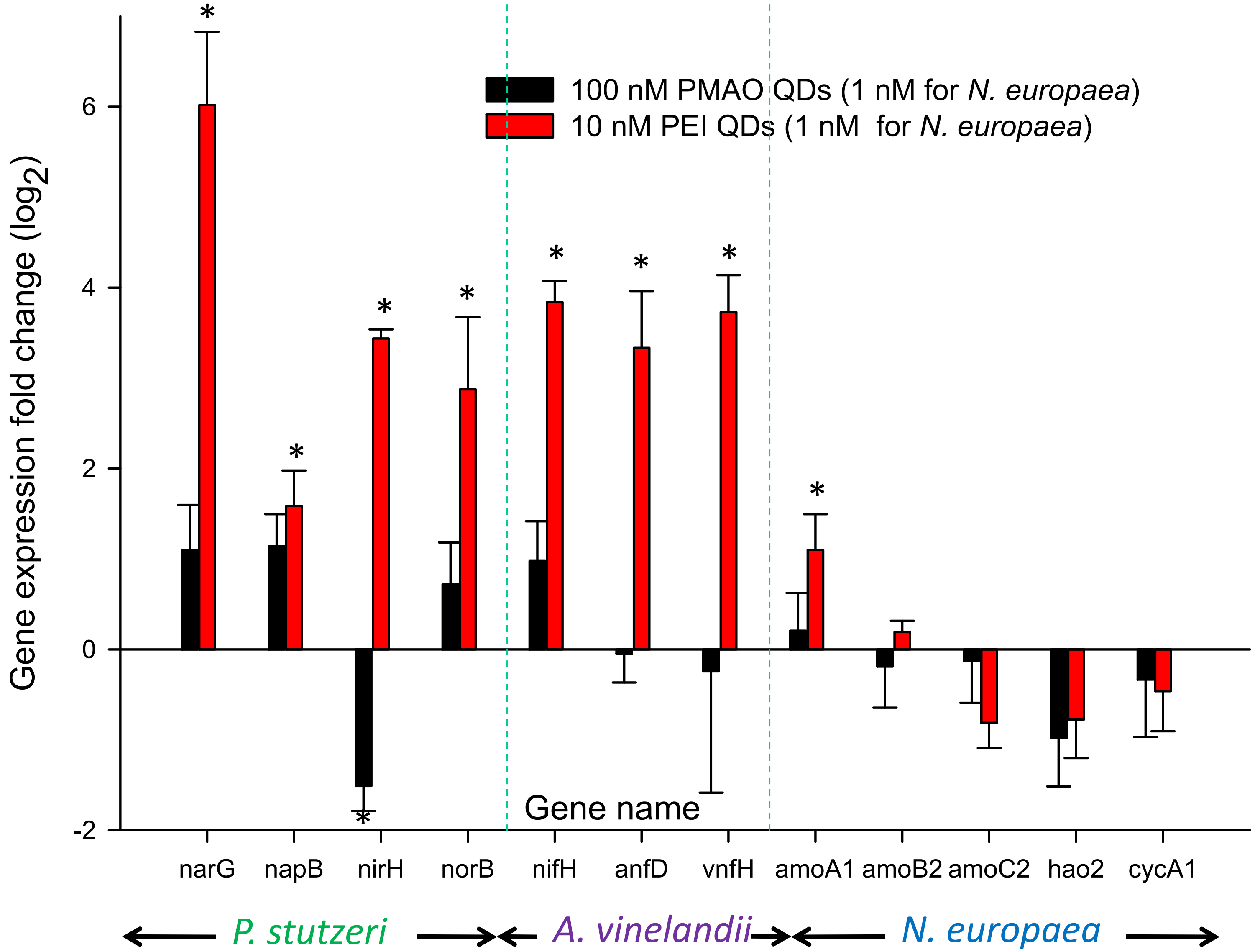


Mahendra S., H. Zhu, V. Colvin and P. J. J. Alvarez (2008). Environ. Sci. Technol. 42 (24), 9424-9430

Potential Impacts to the N cycle:



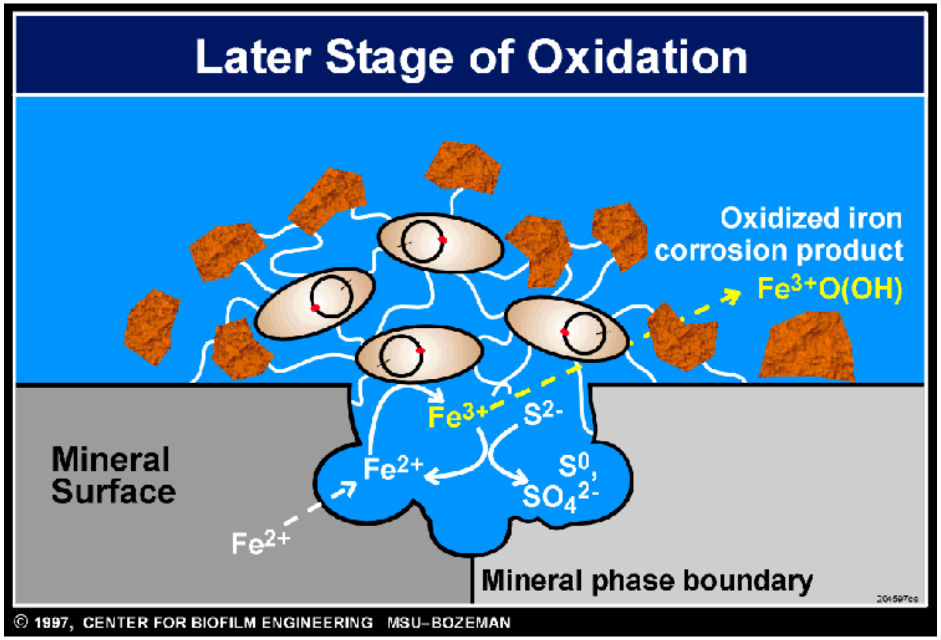
Sub-lethal concentration of PEI QDs up-regulated denitrification and N_2 fixation genes



Yang Y., J. Wang, H. Zhu, Vicki L. Colvin and P.J.J. Alvarez (2012). Environ. Sci. Technol. 46(6): 3433−3441

Biofilms and Biofouling Control

- Attached microorganisms in a “slimy” matrix that are very difficult to eradicate.
- Preferred lifestyle of microorganisms in the environment
- Can **harbor pathogens** and increase energy consumption (headloss)
- Can cause **corrosion** through
  - production of organic acids
  - cathodic depolarization
  - direct oxidation of metal

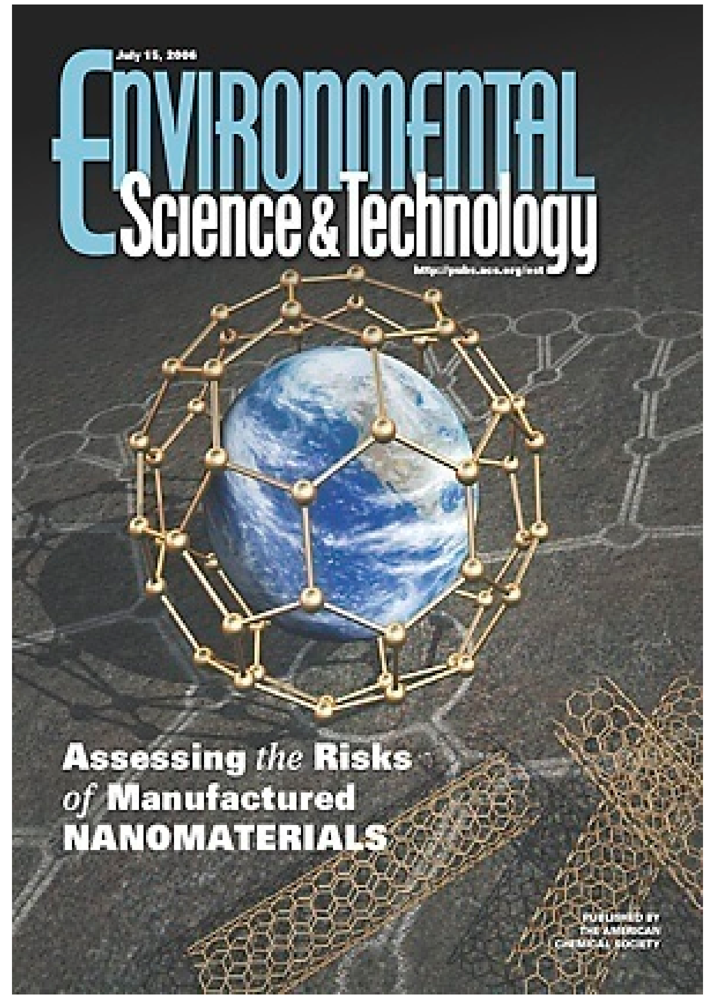


Source: http://www.biofilm.montana.edu/resources/images/biofilms-nature/oxidation-late-stage.html

Conclusions

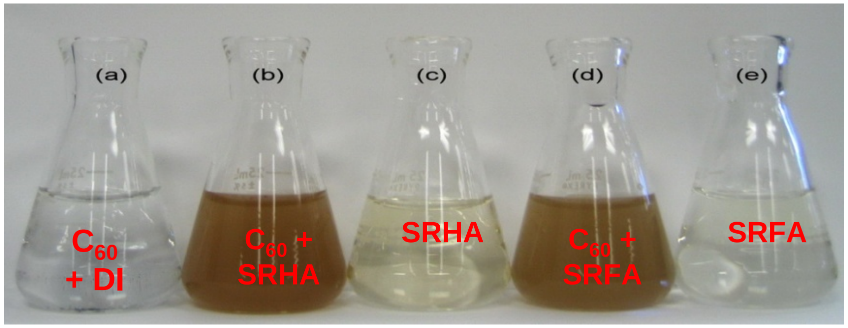
Nanotechnology offers great potential for meaningful disruptive innovation in water & wastewater treatment and reuse:

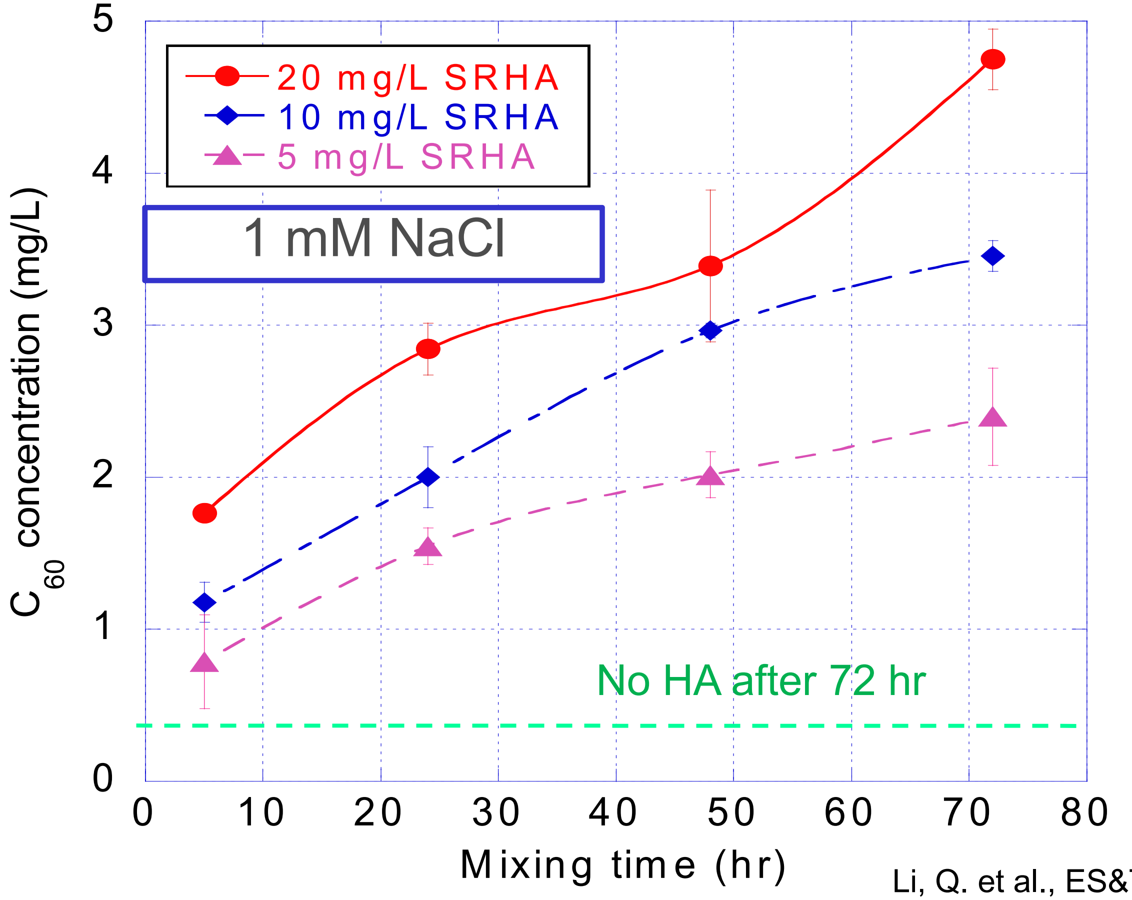
- DBP-free disinfection
- Advanced (photo) oxidation
- Selective adsorption and energy-efficient desalination
- Fouling- and corrosion-resistant surfaces
- Multi-functional membranes
- Responsive materials



Dissolved NOM Enhances C_{60} Dispersion

- *Dispersed C_{60} was measured as dissolved TOC*

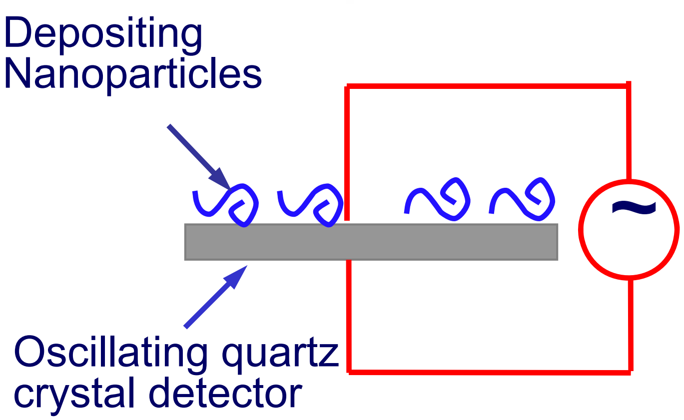


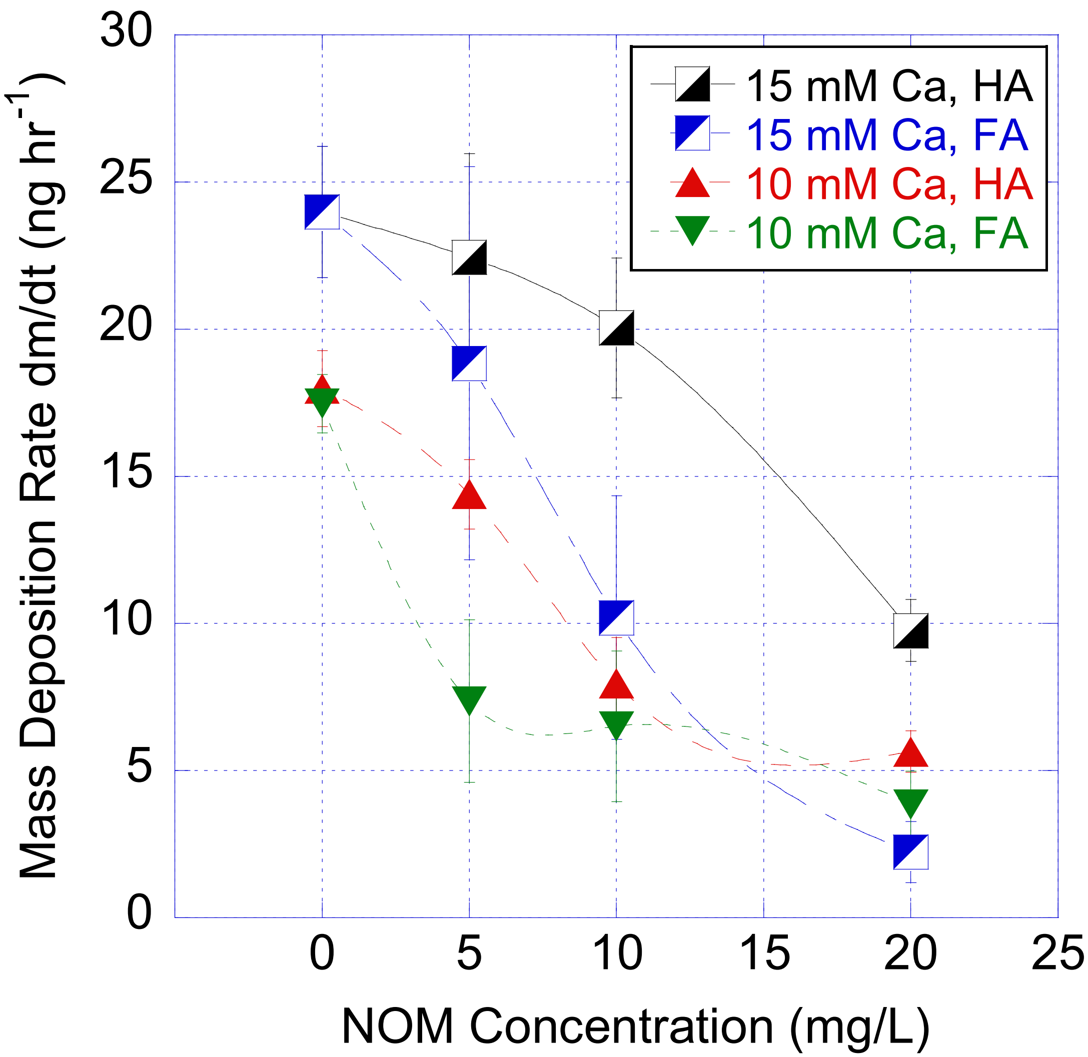


Li, Q. et al., ES&T, 2009, 43(10): 3574-3579.

Dissolved NOM Decreases nC_{60} Deposition onto a Quartz Surface, Increases Mobility in Water

Quartz Crystal Micro Balance





Four Strategies to Interrupt QS

1. **Block production of autoinducers (repress gene transcription)**

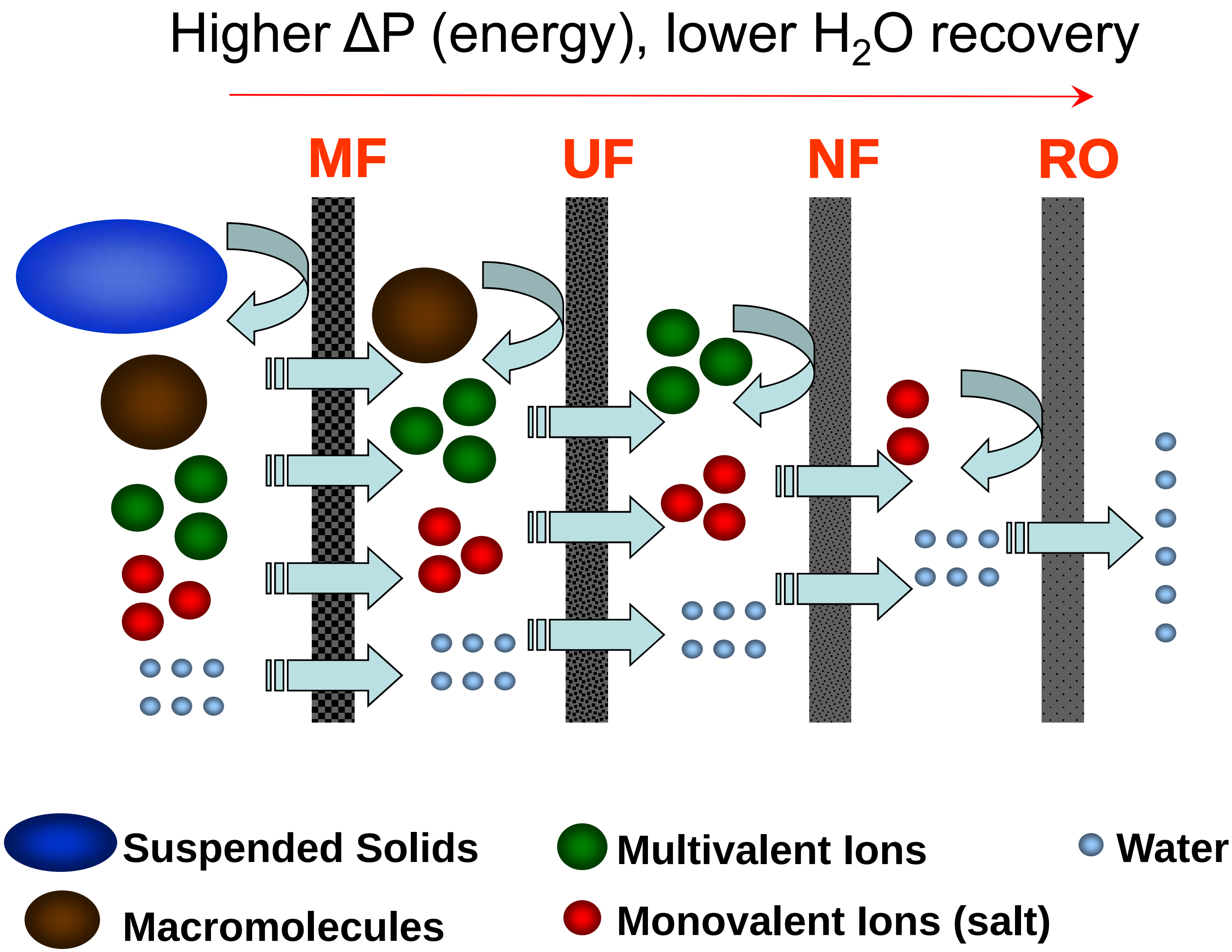
2. Inactivate or degrade autoinducers (enzymes)

3. Use autoinducer analogues to block receptors

4. Disrupt the autoinducer receptor

Autoinducers and receptors are species specific, which makes strategies 2, 3 and 4 narrowly applicable

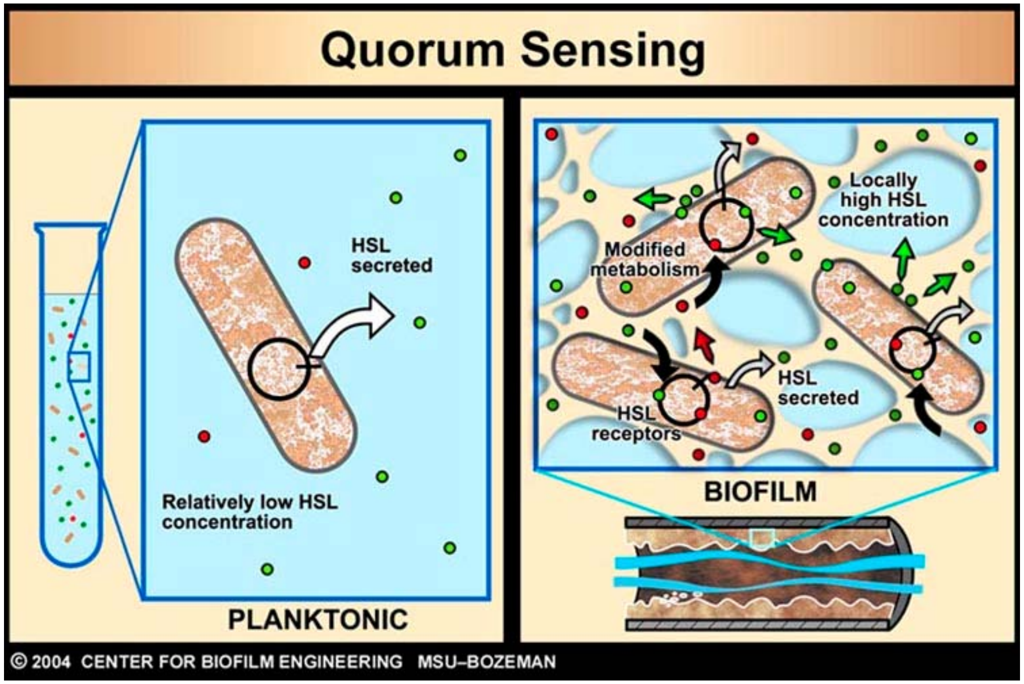
1) Water Treatment Membranes



2) Biofouling Control through Quorum Sensing Interruption

–QS is a cell-to-cell communication via signal molecules (e.g., HSLs)

–Influences
- Bioluminescence
- Sporulation
- <u>Biofilm formation</u>



Source: http://www.biofilm.montana.edu/resources/images/multicellularextracellular/quorum-sensing.html

Serendipitous Finding: Biofouling Resistant Heat Exchanger

- NASA's Service and Performance Check Out Unit Heat Exchanger (SPCU HX)
  - Provides thermal control to the spacesuits before and after a spacewalk
  - Used at International Space Station US Airlock

  – Results from ground testing suggested that biofilm formation was occurring within the on-orbit HX *($CO_2\uparrow$, pH$\downarrow$, metal dissolution$\uparrow$)*

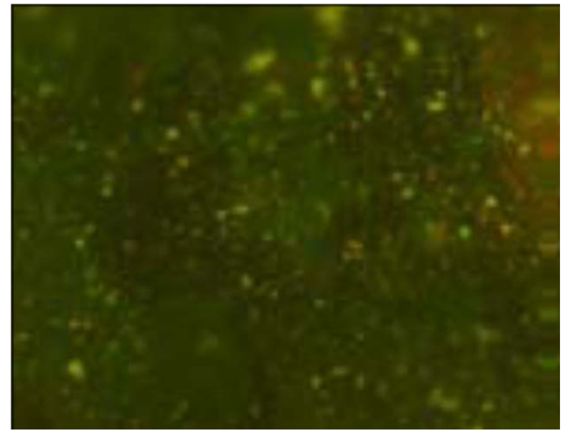
Evaluation of Flight Unit

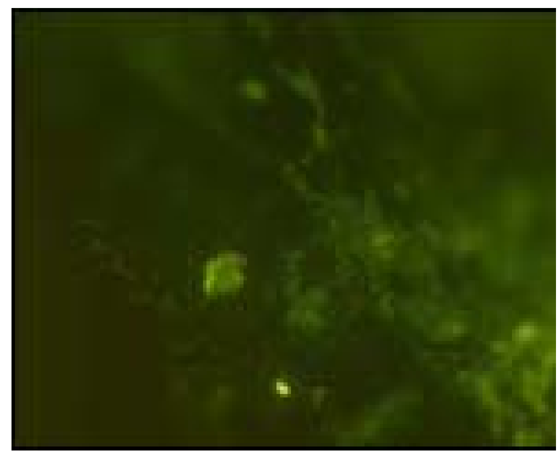
- Heat exchanger was analyzed for biofilm &MIC
  - Expected significant fouling, corrosion
  - Evaluated using scanning electron microscopy (SEM), epifluorescence microscopy, auger microscopy

- Results

–Planktonic growth **<u>without</u> biofilm**

Hypothesis: Trace elements (e.g., Ni) prevented biofouling through QS inhibition





BacLight Live/Dead staining of HX Control (top) and SPCU (bottom) samples. The control sample is fouled with bacteria while the SPCU sample has little growth

Ni^{2+} & Cd^{2+} Inhibit *Burkholderia* Biofilm

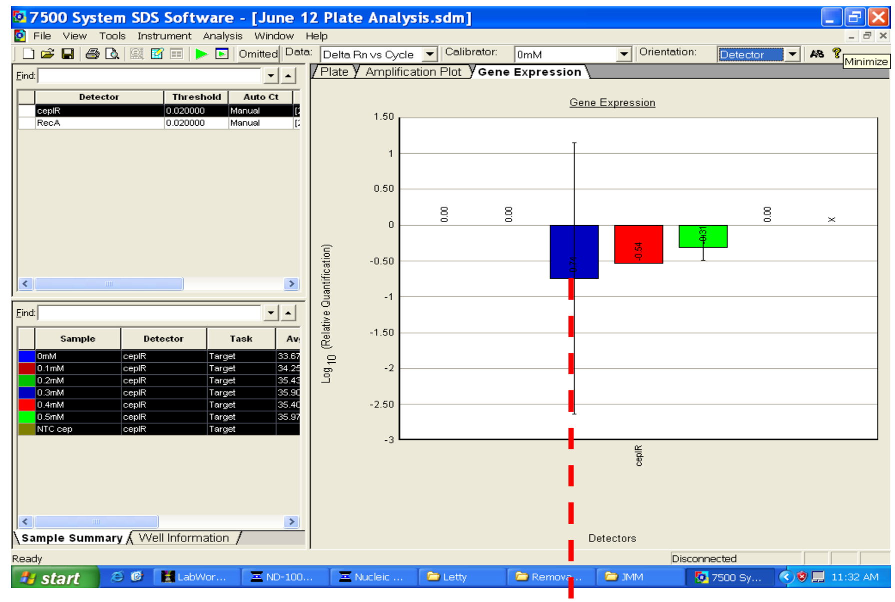
- *B. cepacia* planktonic viability not affected (no bactericidal effect)
- Biofilm formation decreased with increasing Ni conc.
- HSL addition stimulated biofilm formation (no effect on planktonic), implicating QS inhibition

<u>Implication:</u>

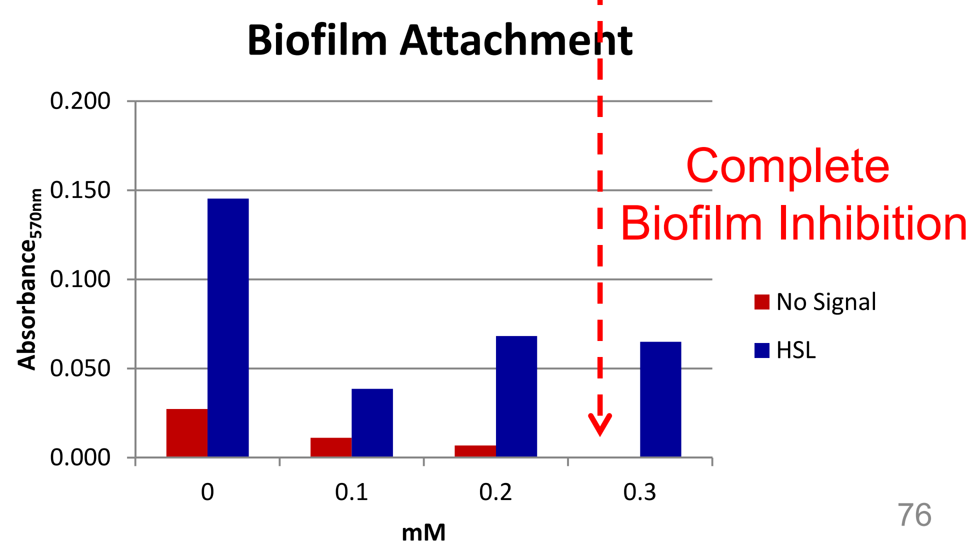
If you can get bacteria to stop HSL production (by repressing QS gene expression) you would mitigate biofilm formation

QS Gene Repression

- Quantified QS gene expression (5x down-regulation of *cep* in *B. cepacia* at 0.3 mM nickel)



- Downregulation of QS gene expression (*cep*) coincided with no biofilm formation



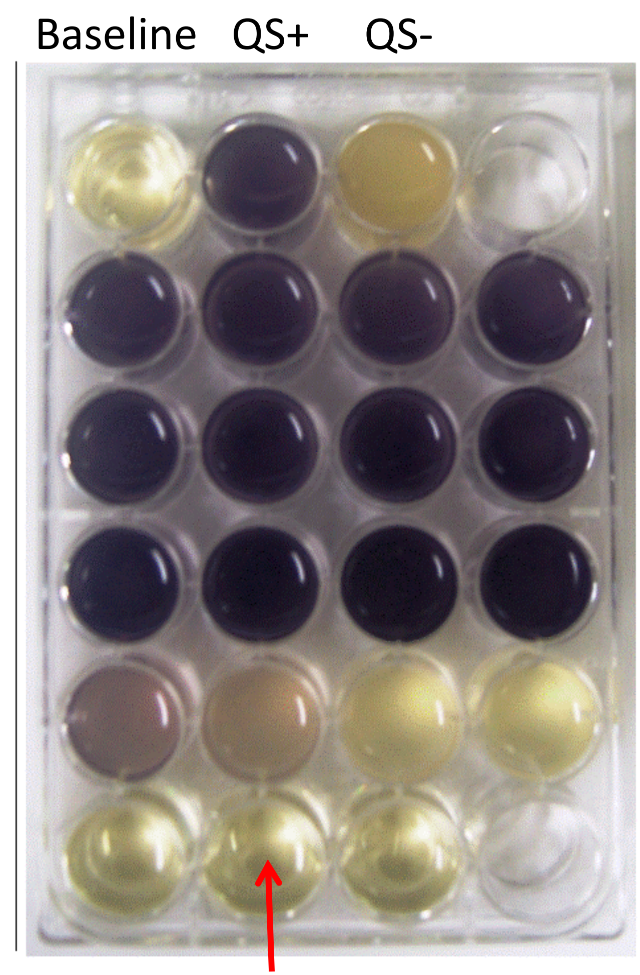
Potential Mechanistic Explanation

- Ni^{2+} and Cd^{2+} are **competitive antagonists** of both Mg^{2+} & Ca^{2+}, which are essential cofactors for many enzymes (including DNA & RNA polymerases, thus QS inhibition at transcription level) and help adhesion by cationic bridging.

Nanotechnology could offer opportunities for controlled released of QS-interrupting metals (e.g., control NP size and coating to modulate dissolution and ion release so that the MCL for the metal is not exceeded)

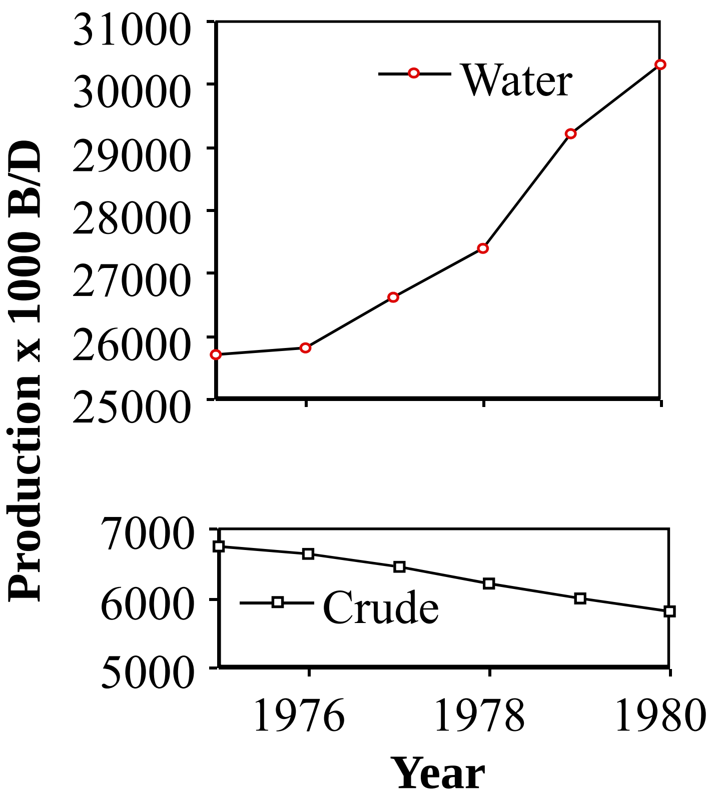
Fast Screening of QS Inhibitors (Microtiter Plate Method)

- Tested different concentrations of Nickel using the model bacterium, *Chromobacterium violaceum* (turns violet when QS is induced)



Quorum Sensing Inhibition (QSI) by **Ni** in *Chromobacterium violaceum*

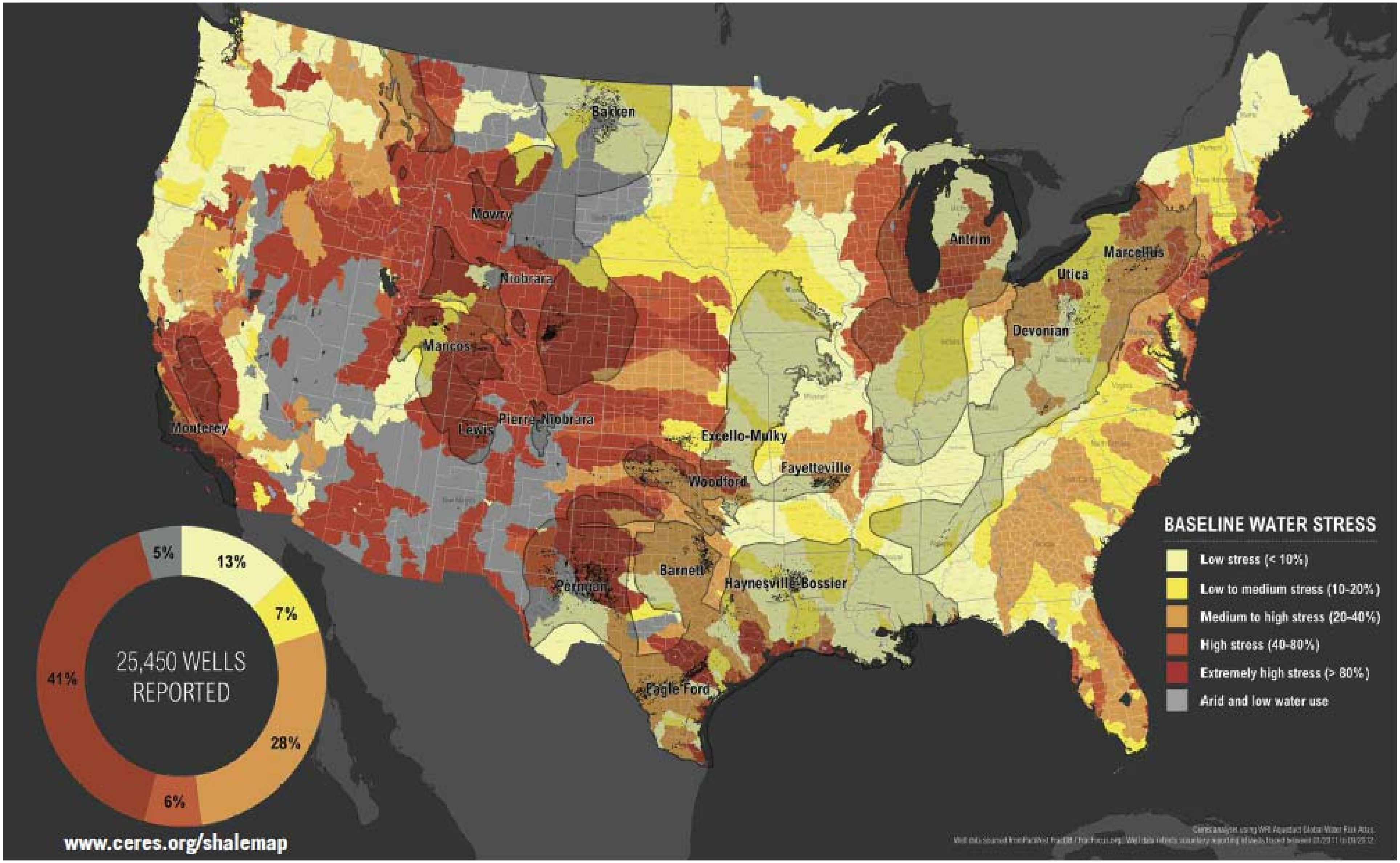
Importance of Water for Energy Production



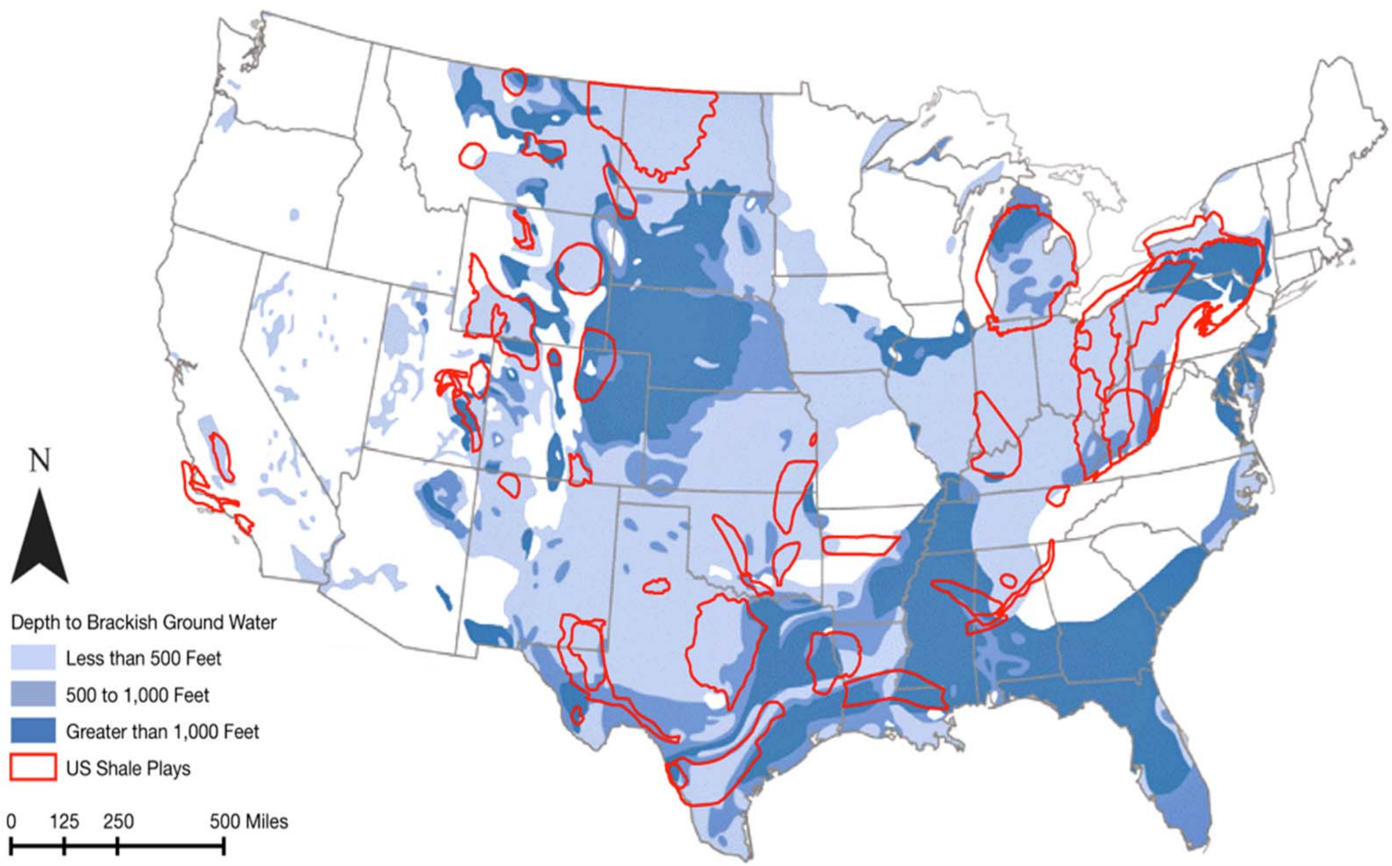
Water is by far the largest byproduct of the fossil fuel industry
Water/Oil Ratio = 10 (US), 14 (Can.) **$1 trillion/yr challenge***

*http://www.twdb.state.tx.us/Desalination/TheFutureofDesalinationinTexas-Volume2/documents/B3.pdf

Fracking in drought-prone regions represents both a water supply and pollution control challenge



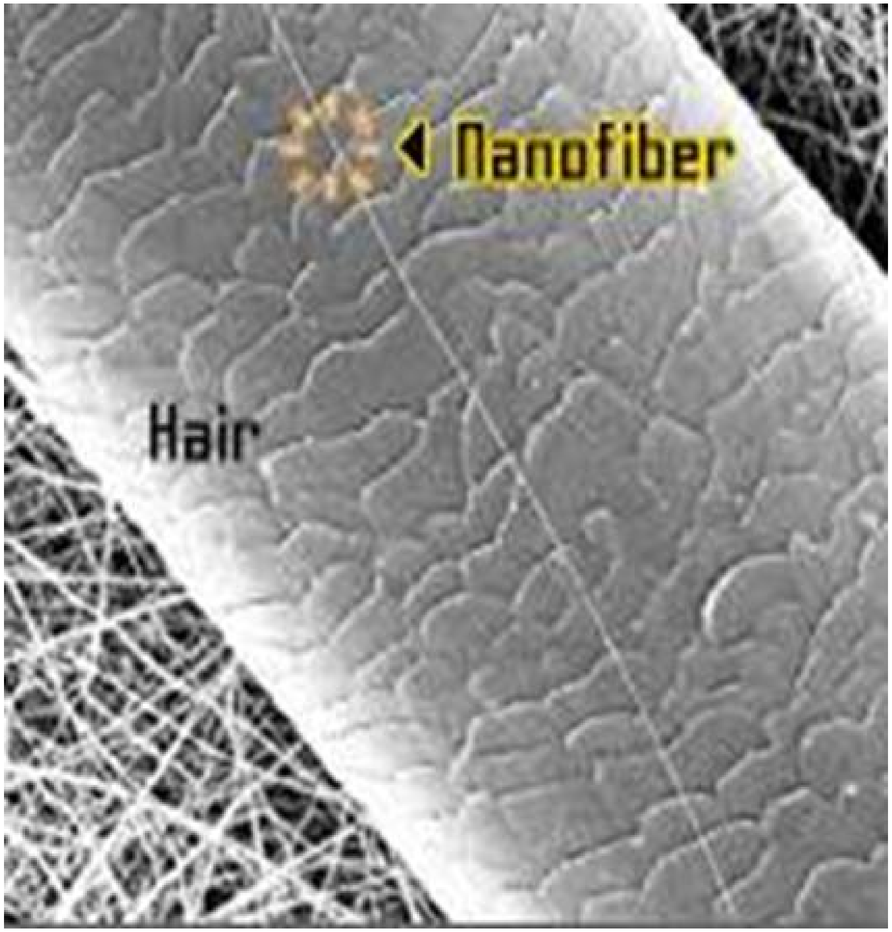
Use Brackish Groundwater for Fracking? (Geospatially consistent)



Nano = Dwarf (Greek) = 10^{-9}

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications."

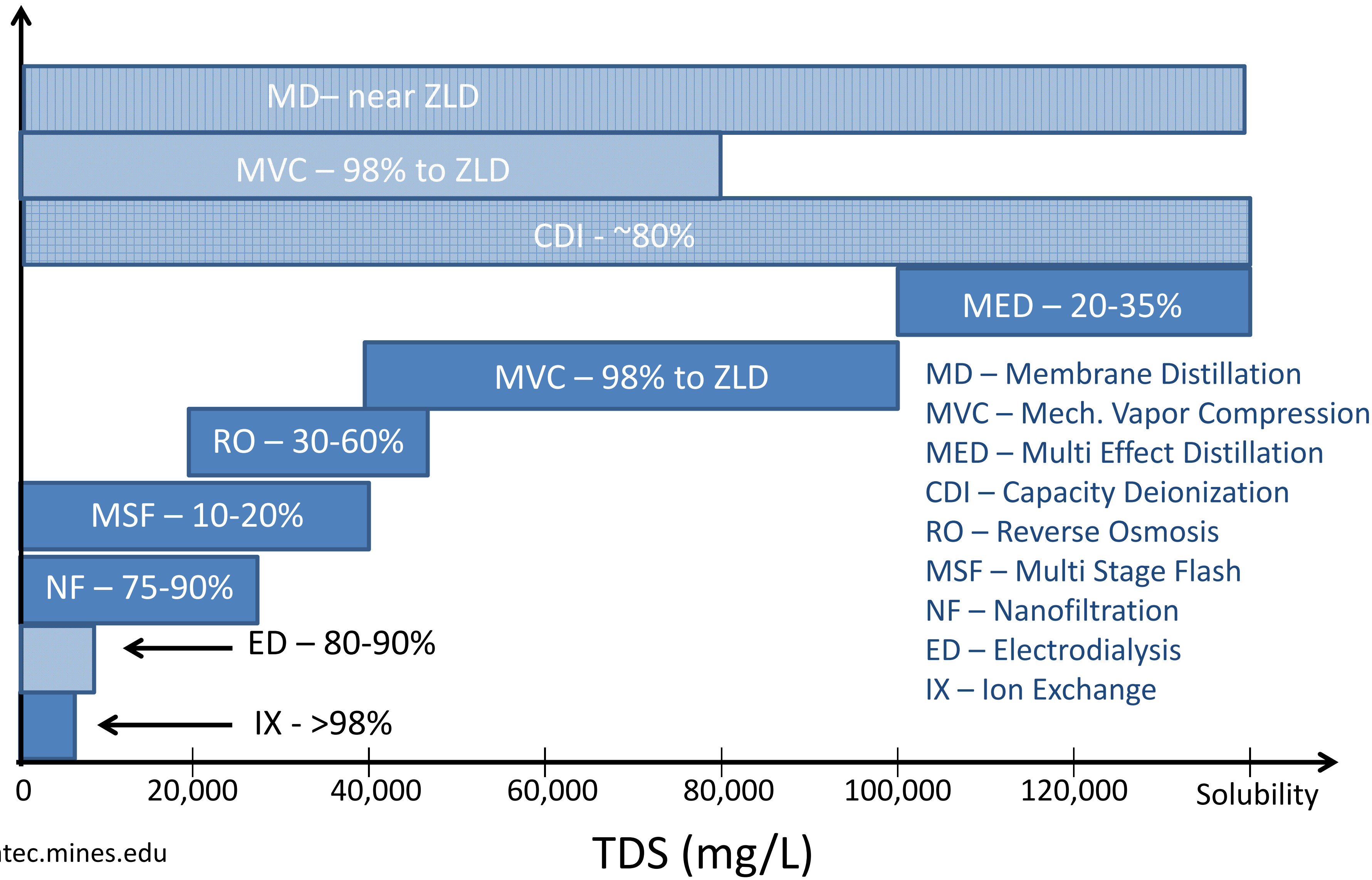
-National Nanotechnology Initiative



1) Need for Low-Energy Desalination

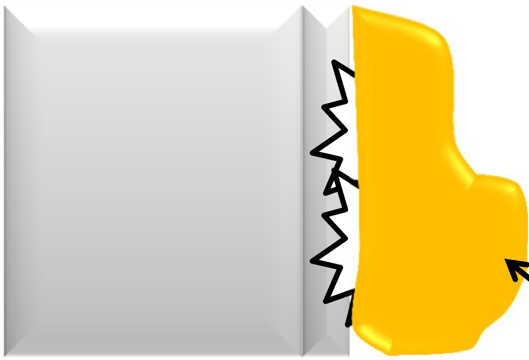
- High TDS represents a beneficial disposition challenge (discharge regulations)
- Multivalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{2+}/Fe^{3+}) interfere with performance of friction reducing polymers and also form scale (flow assurance)
- Naturally occurring radioactive materials
- Toxic inorganic contaminants (e.g., Zn^{2+})

Desalination Technologies: Applicability and Water Recovery



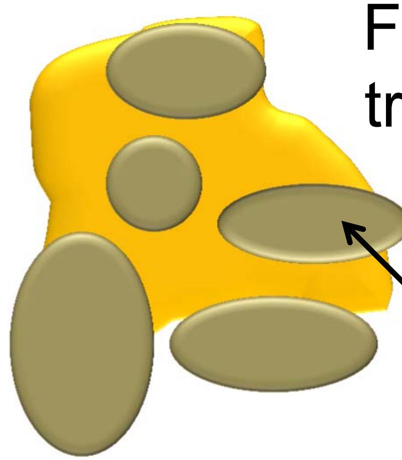
aqwatec.mines.edu

2) Need for Microbial Control



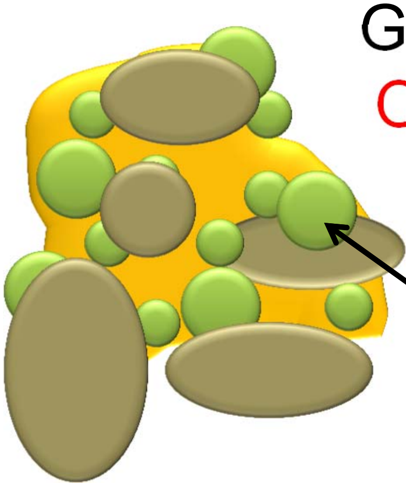
Microbial-Induced Corrosion & Souring

Biofilm



Flow obstruction, transformation of light oil to bitumen

Sediment grains in porous media



Gas Production Obstructs Flow

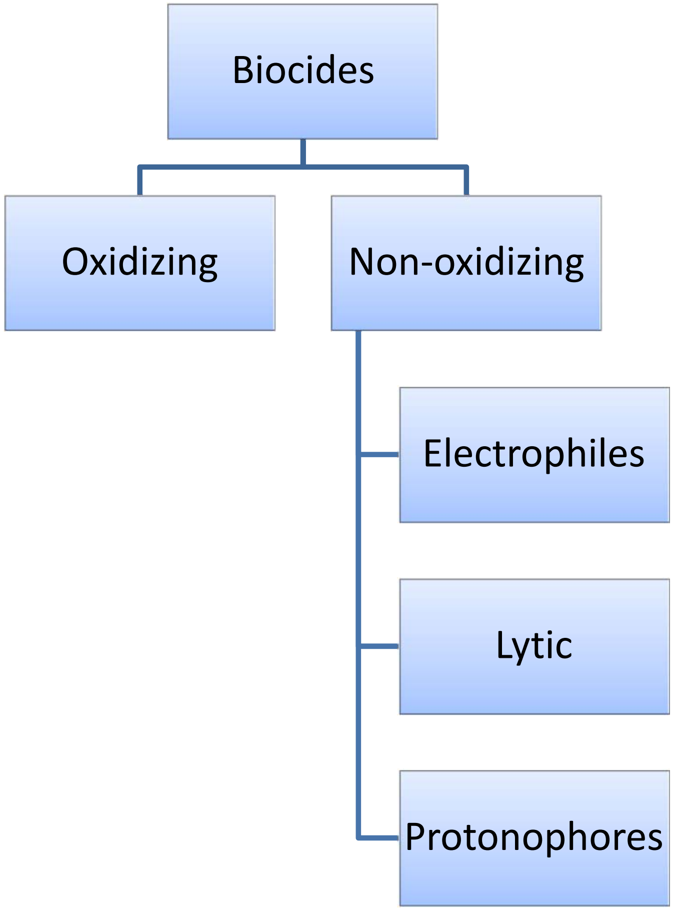
N_2 Gas bubbles

Clogging by Mineral Precipitation

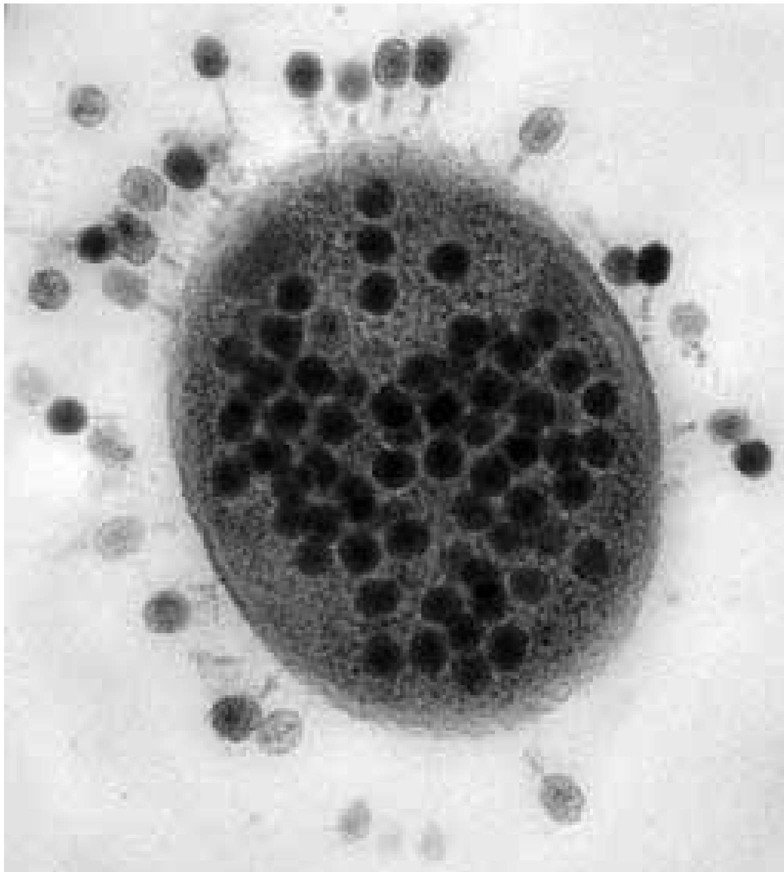
Biogenic minerals (e.g., FeS)

Microbial Control Strategies for Oil and Gas Reservoirs

- Biocides & bacteriostats
  - glutaraldehyde, nitrite
- Nutrient control
  - SO_4 removal (RO)
- Competitive inhibition
  - nitrate (NRB stimulation)



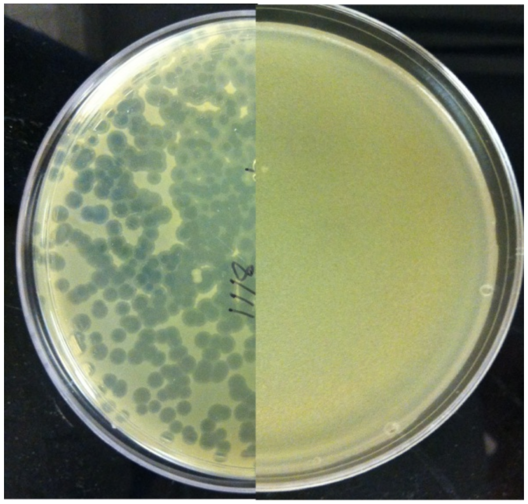
In Situ Control of Sulfidogens with Bacteriophages (Reservoirs & Pipelines)



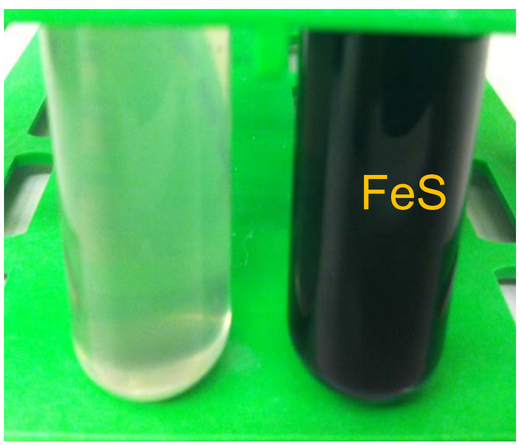
- Prevent souring by H_2S, corrosion, & clogging by FeS_2
- Advantages
  - o **Self-replicating** → low production costs, persistent protection
  - o **Penetrating** → degrade biofilms, can enhance transport properties
    - - encapsulation
    - - targeting through triggered release (increased local MOI)
  - o **Green** technology

Strategy: isolate and enrich **polyvalent** (broad-host-range) phages for "vaccination" inoculation of reservoirs.

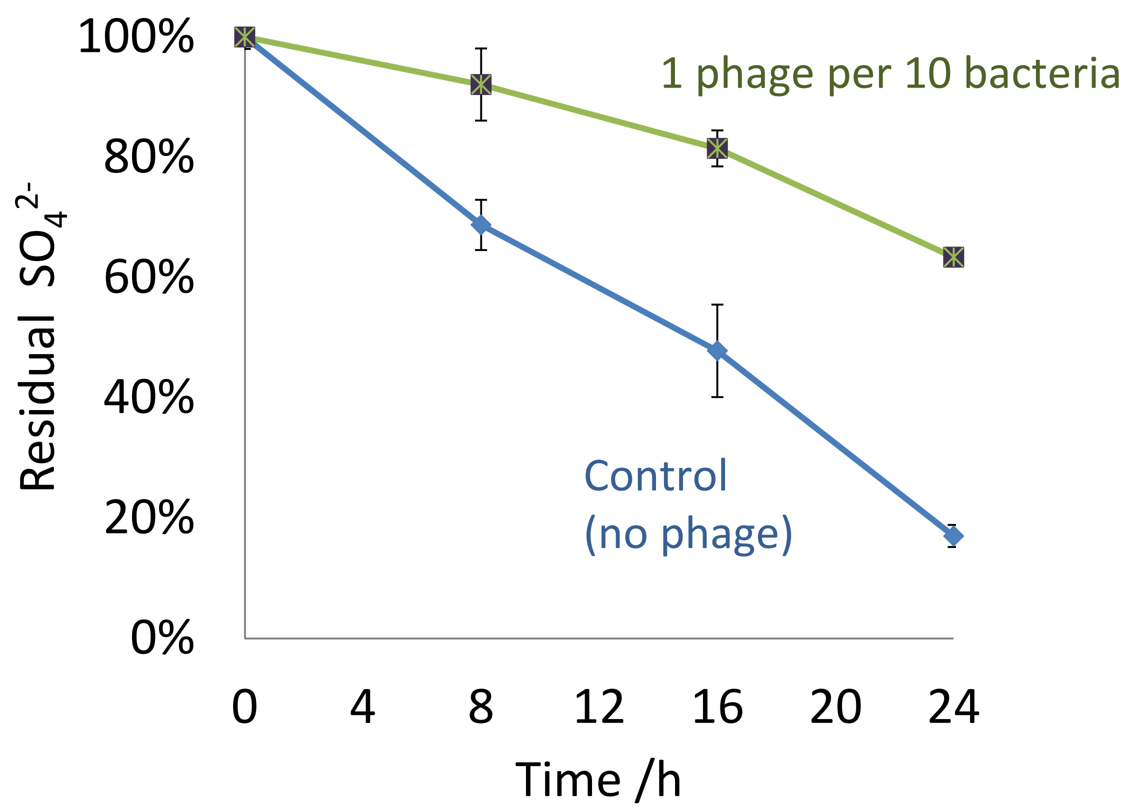
Inhibition of *Desulfovibro salexigens* ATCC 14944 by a phage from WWTP



With and without phage



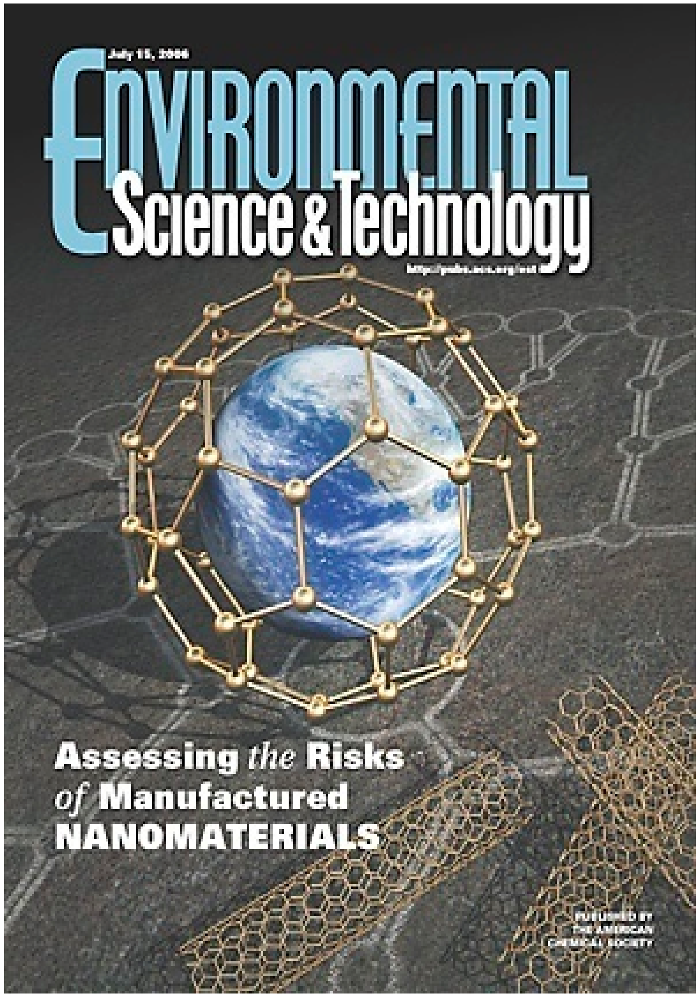
With and without phage



CONCLUSIONS

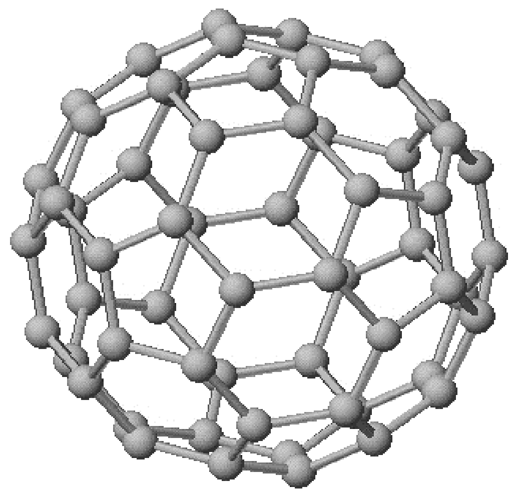
- Nanotechnology has a great potential for enabling exploitation of a broader range of water sources (e.g., sea water, flowback-water, wastewater)

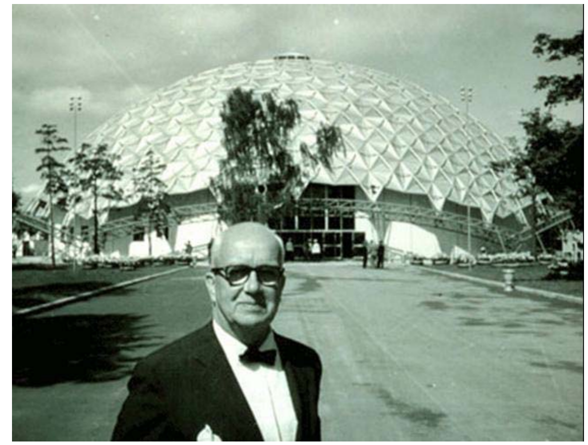
- Could help transform some infrastructure-, chemical- and energy-intensive treatment approaches towards catalytic & physical systems that obviate current tradeoffs between cost & performance, and between energy consumption & treatment rate



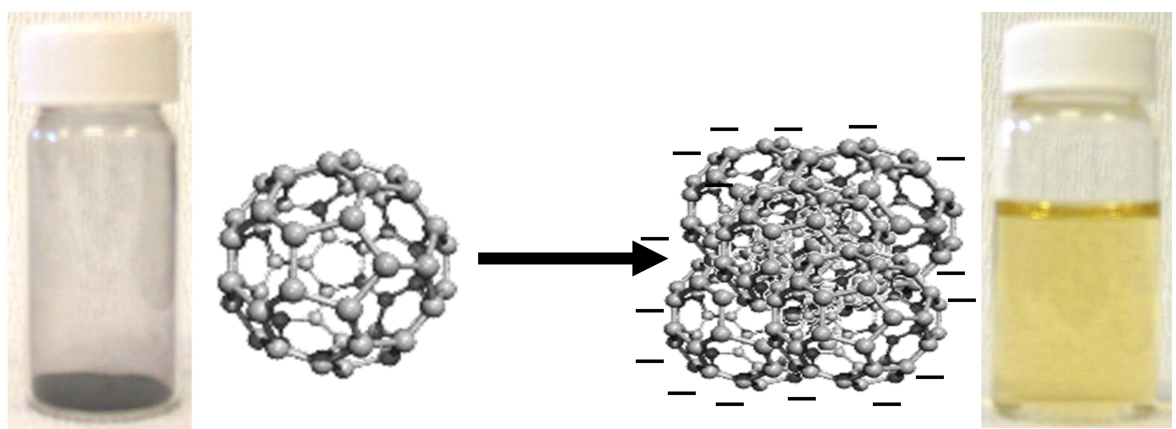
Example 1. C_{60}, nC_{60} and NOM

Photocatalyst
and Antioxidant
(sp2 hybridized)





R. Buckminster Fuller (Bucky)

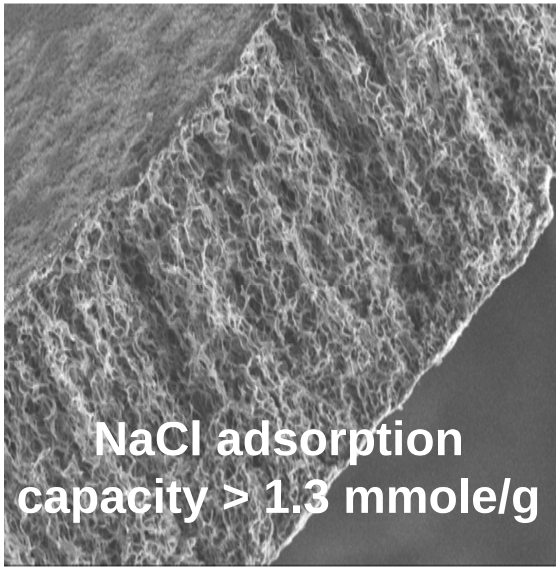


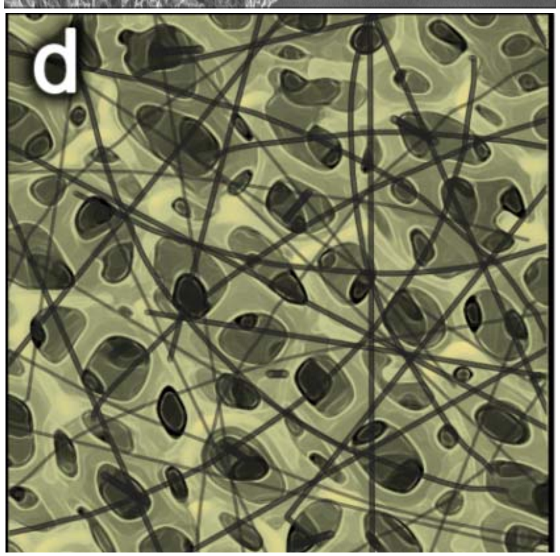
Solid or solution

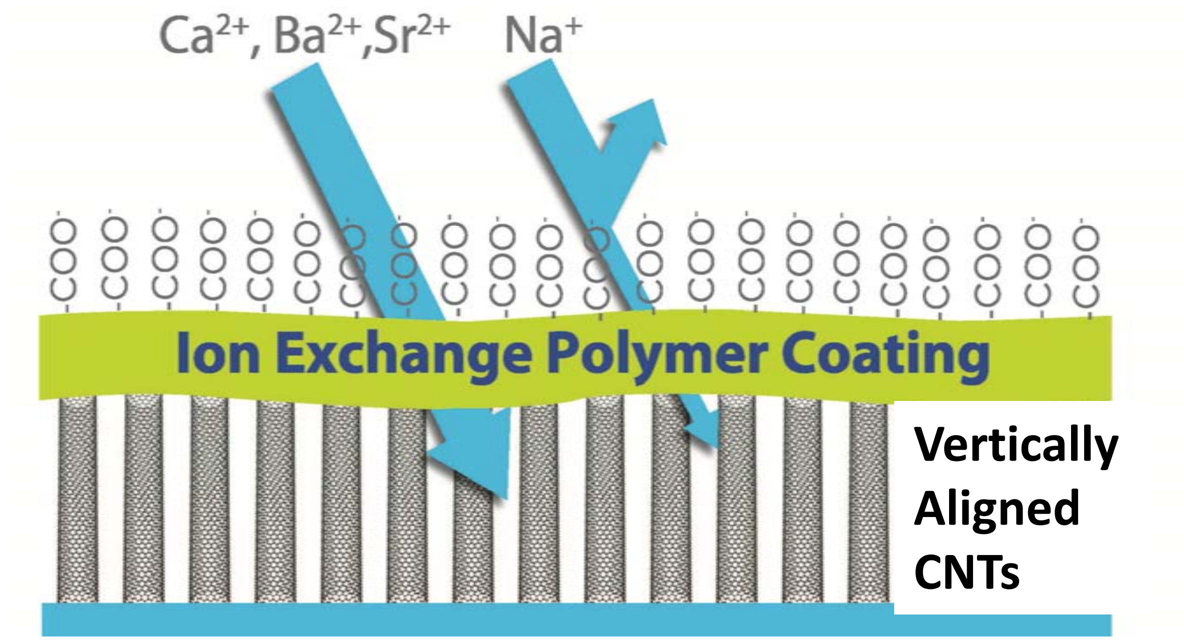
nC_{60} (20-200 nm)

Nano-Enabled CDI for Scaling Control

IX polymers enable preferential removal of divalent cations that cause scaling

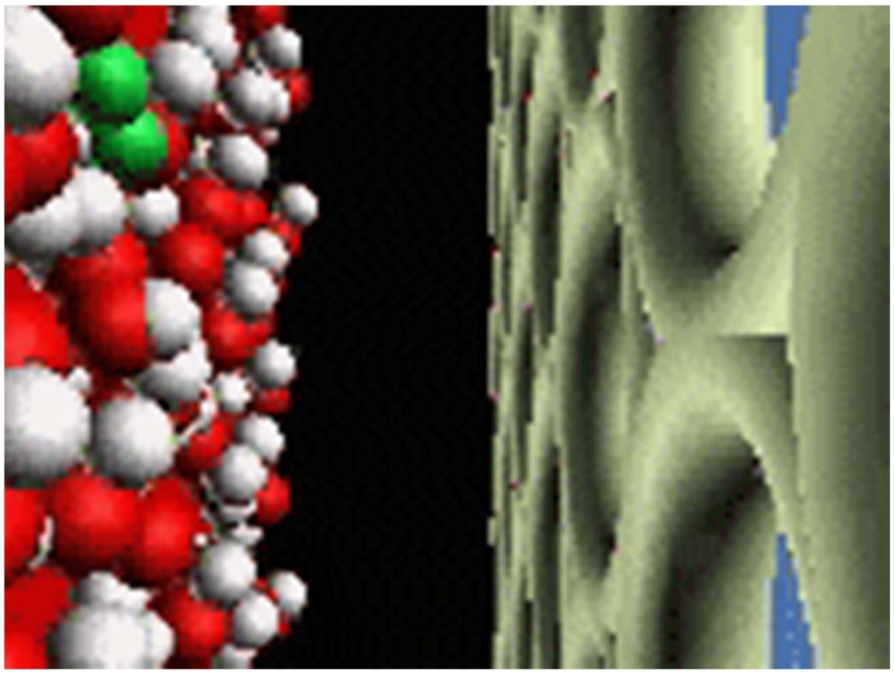


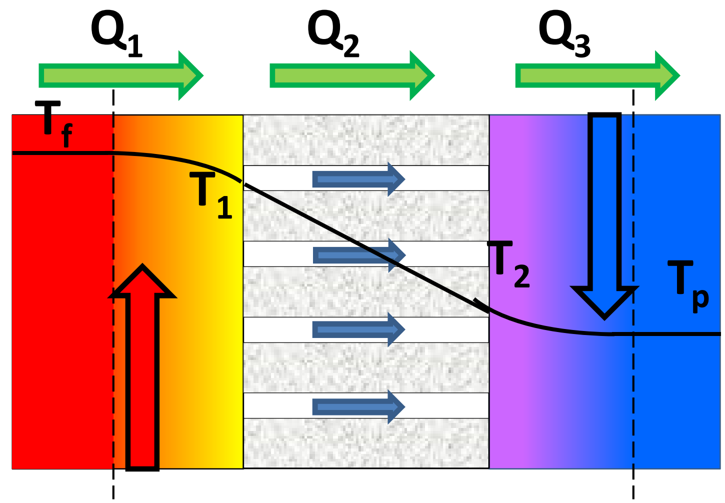




CNTs/graphene enhance sorption capacity, kinetics, mechanical strength and electrical conductivity.

Ex. 3. Low-Energy Desalination by Membrane Distillation





Temperature polarization:

$$\alpha = \frac{T_1 - T_2}{T_f - T_p}$$

Can reduce transmembrane temperature gradient by up to 70%

www.desalination.biz

Nanophotonics-Enhanced Membrane Distillation for Solar Desalination

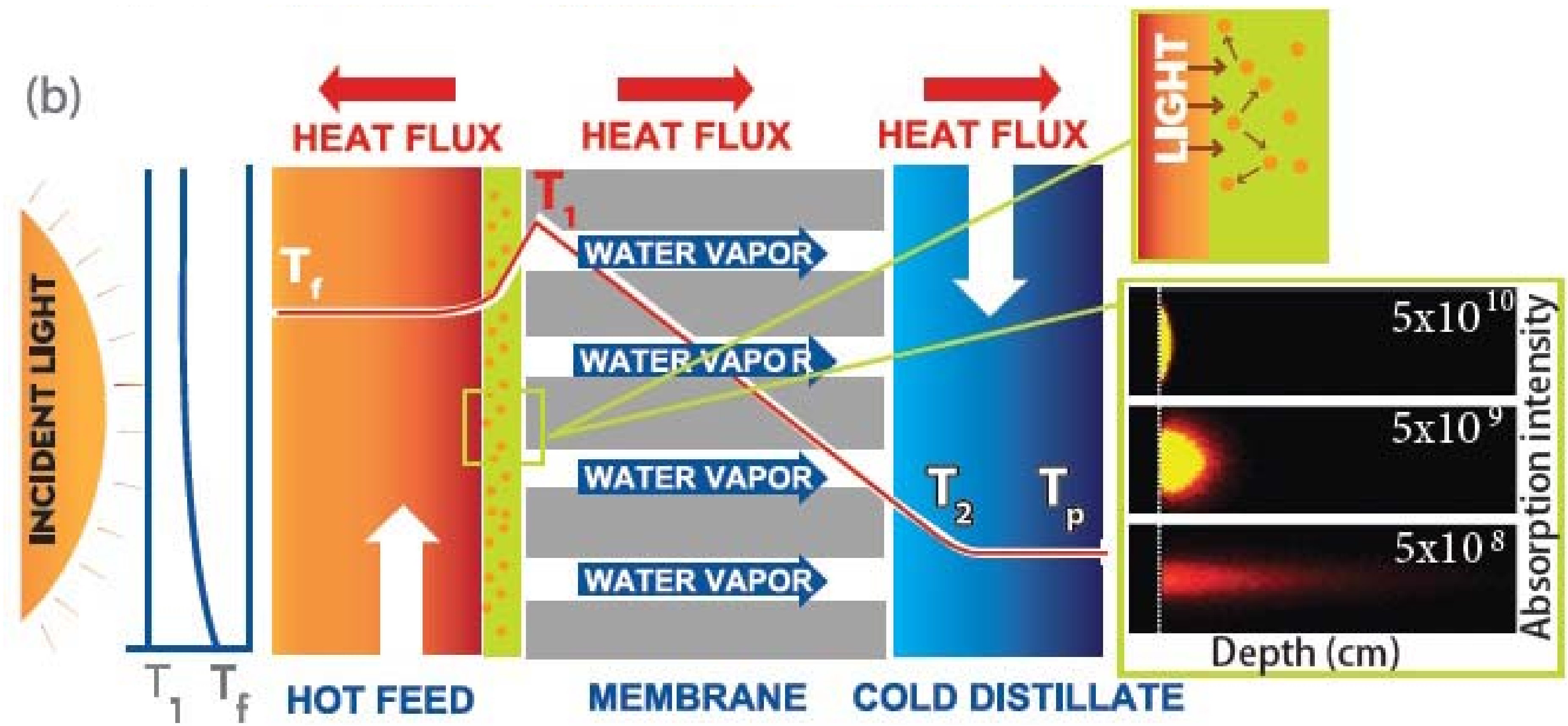


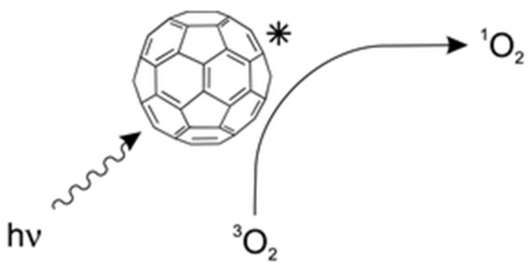
Plate-and-Frame Configuration

- Thin, patterned transparent poly(methyl methacrylate) sheet serves simultaneously as the top plate of the module, the optical window and the spacer that forms the feed flow channels.
- Mount it on a solar tracker to maximize sunlight collection.

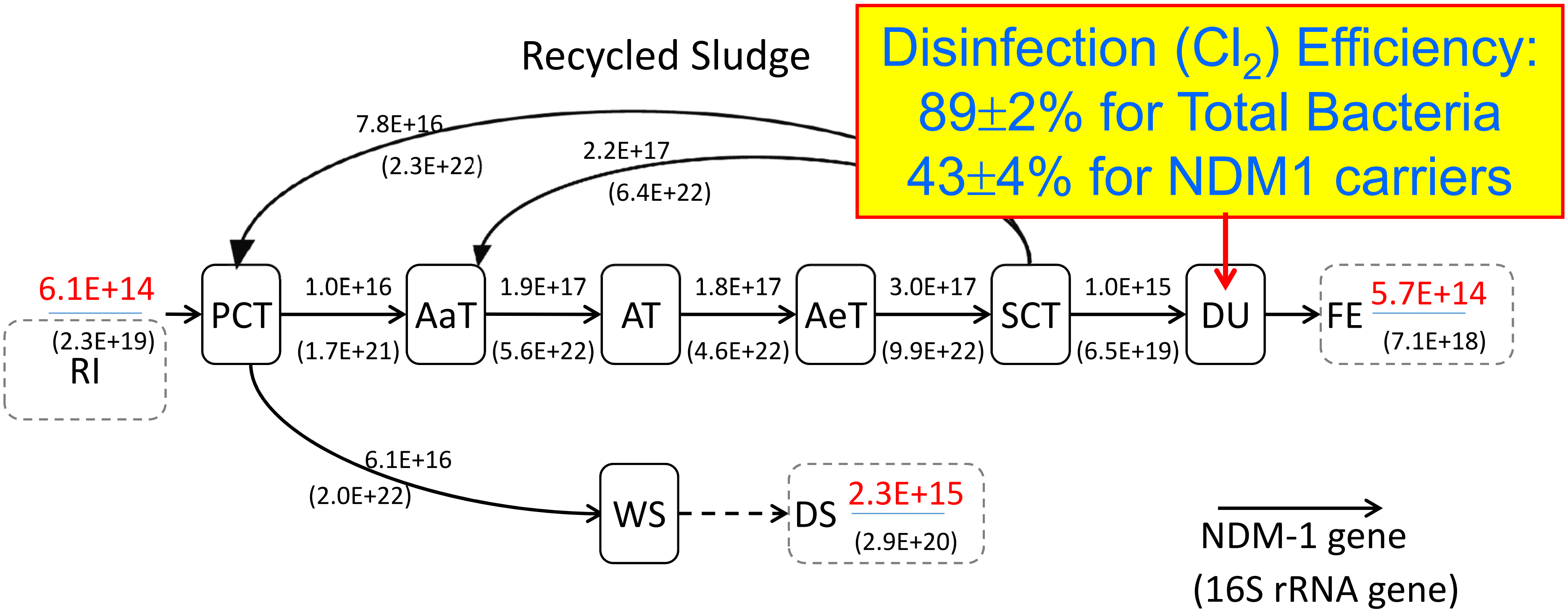
http://www.wassertech.net/content/view/34/29/lang,thai/

Nano-Enabled Water Treatment @ Rice

- Sand filter coated with nano-magnetite to remove As (pilot in Guanajuato, Mexico, reported by BBC, NY Times, Forbes and CBC).
- Fouling-resistant membranes that also inactivate virus (nAg, nano-TiO_2)
- Pd/Au hypercatalysts to treat TCE (Pilot at Dupont site)
- Novel amino-fullerene photocatalysts to enhance UV and solar disinfection and advanced oxidation processes



Proliferation of Multi-drug Resistant "Superbugs" (NDM-1 positive) from Sewage Treatment Plants



NDM-1 flow output (genes/day) was
4.6-fold greater than influent values

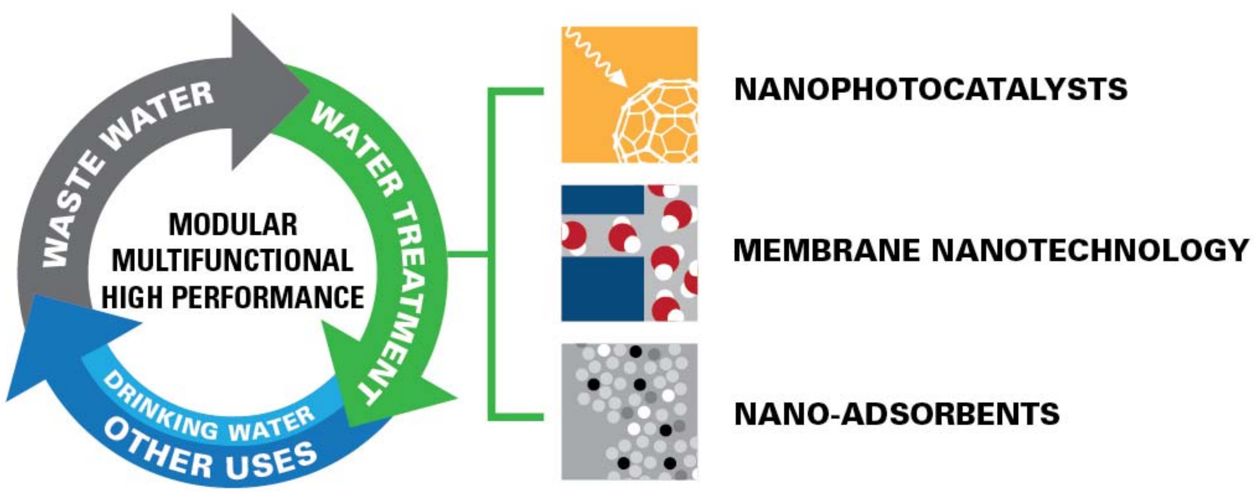
Yi L., F. Yang, J. Mathieu, D. Mao, W. Qing, and P.J.J Alvarez (2014). ES&T Letters. (1), 26−30

Why Nano?

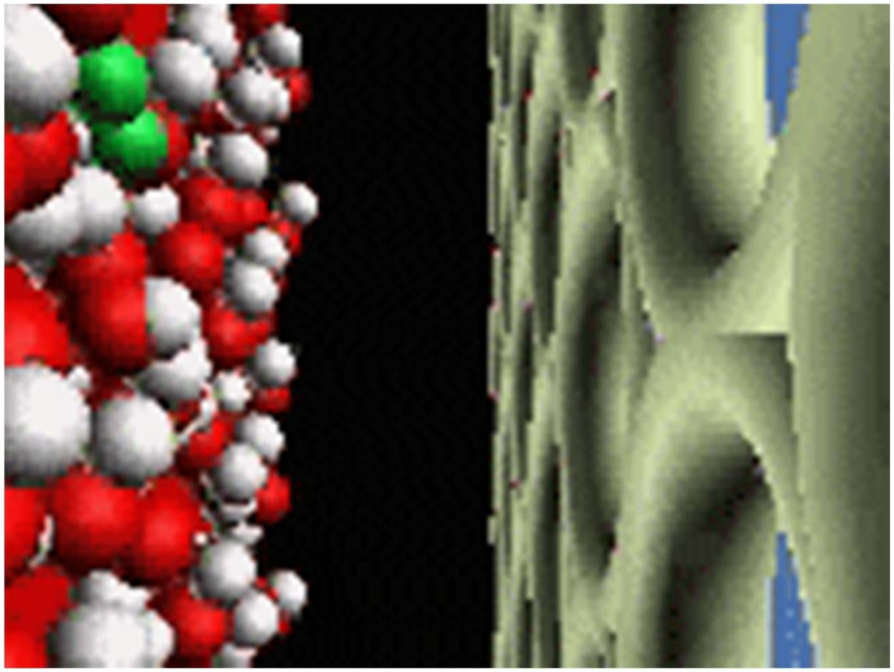
Leap-frogging opportunities to:

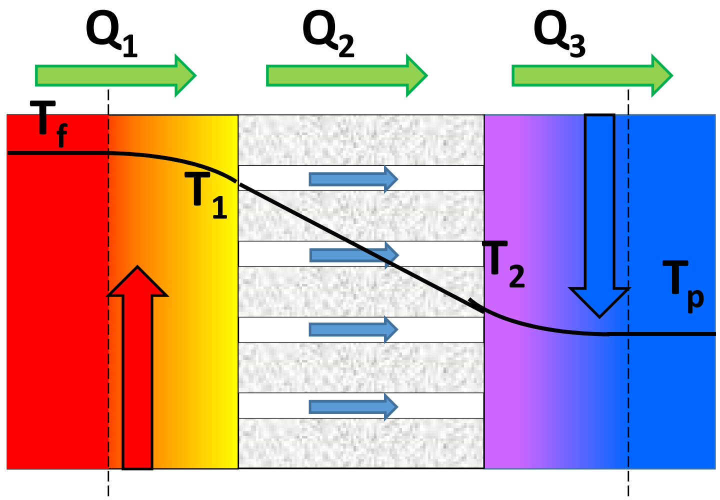
- Develop high-performance multifunctional materials and systems that are easy to deploy, can tap unconventional water sources, and reduce the cost of remote water treatment

- Transform predominantly chemical treatment processes into modular and more efficient catalytic and physical processes that exploit the solar spectrum and generate less waste



Example 3. Low-Energy Desalination (and Disinfection) by Membrane Distillation





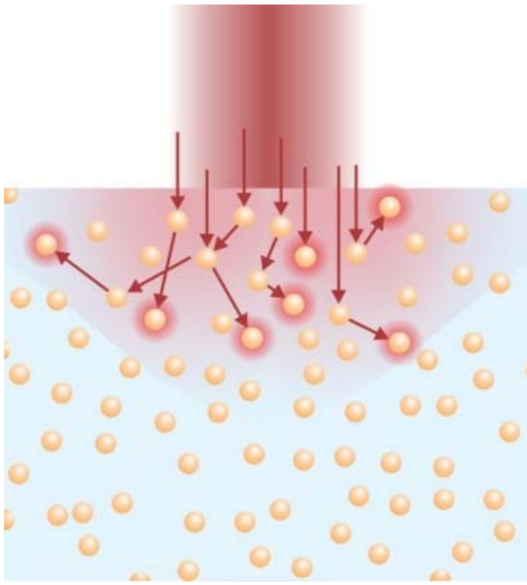
Temperature polarization:

$$\alpha = \frac{T_1 - T_2}{T_f - T_p}$$

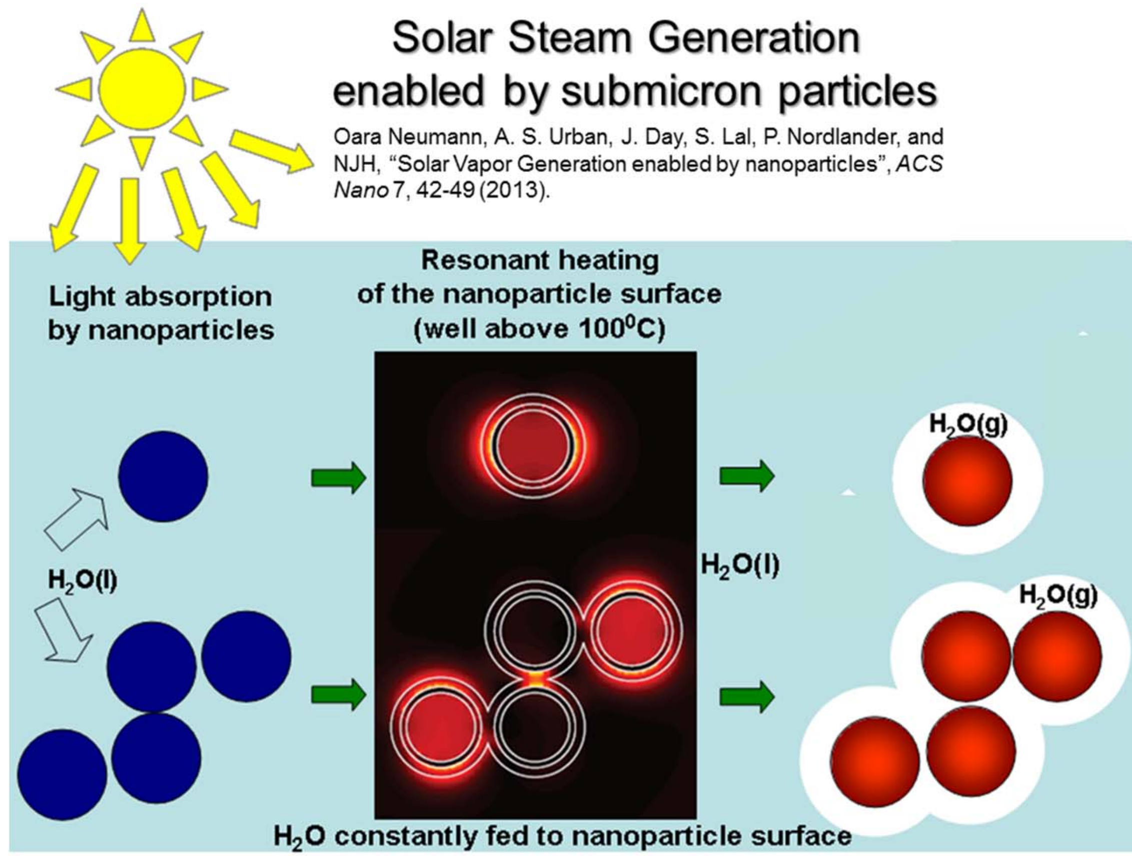
Can reduce transmembrane temperature gradient by up to 70%

www.desalination.biz

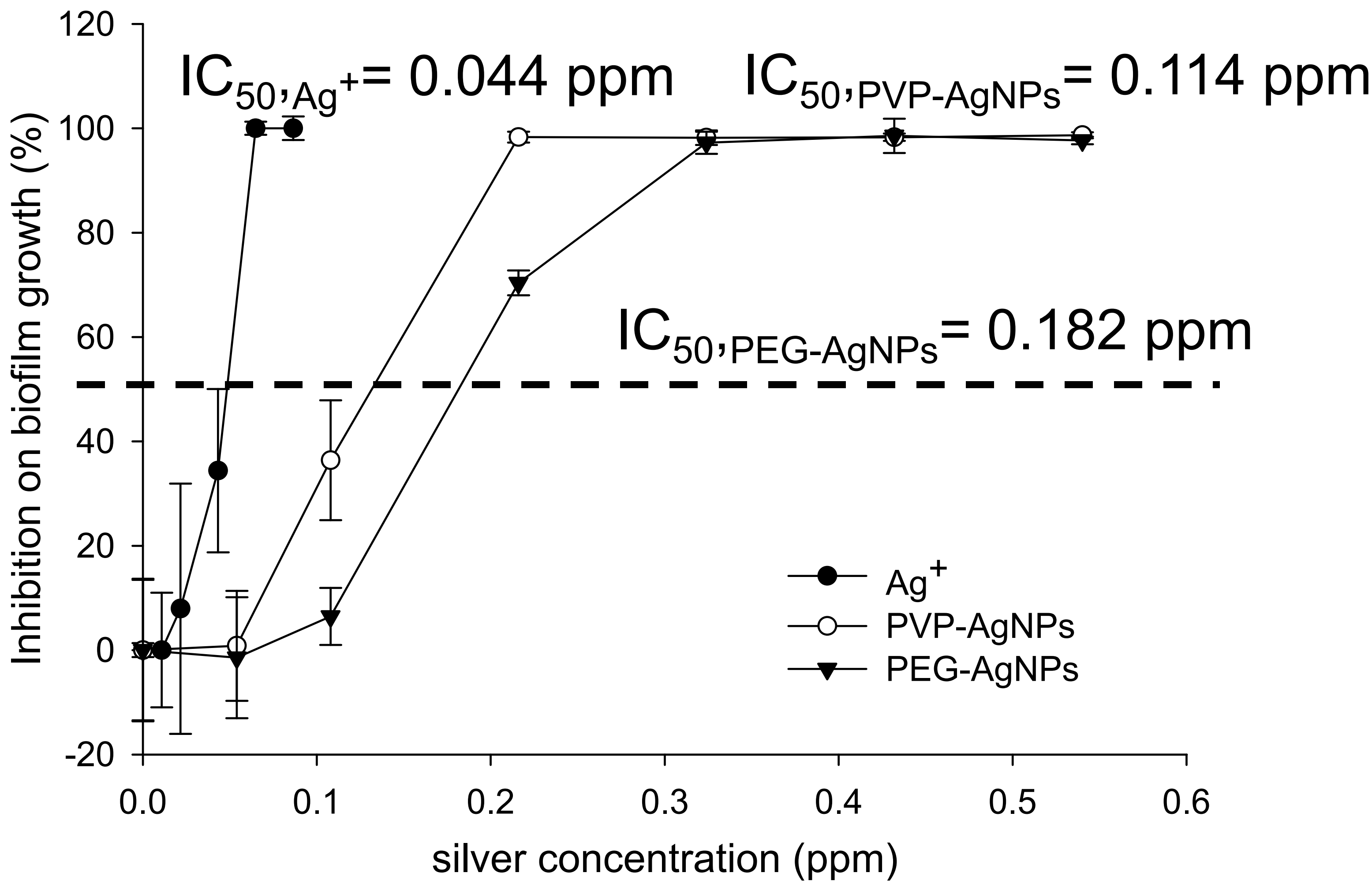
Photonics of Nanoparticles for Solar-Thermal Applications



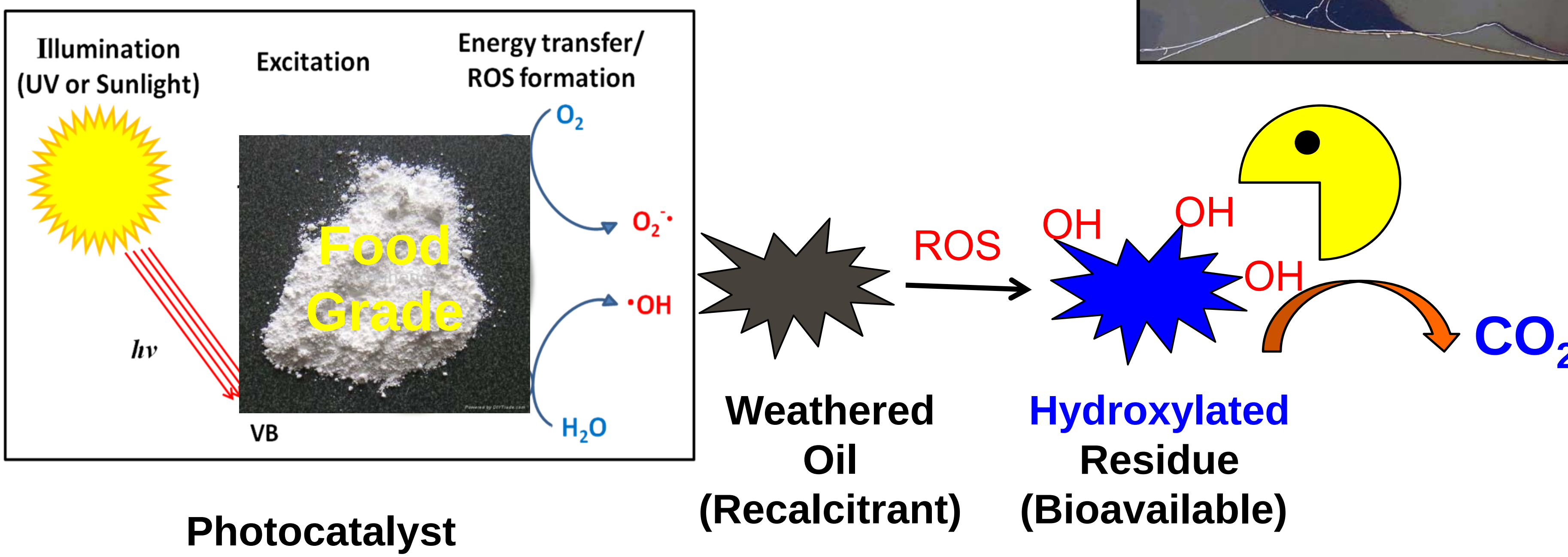
Light localization by multiple scattering confines solar energy, enabling high efficiency heat transfer (N. Hogan et al., TBP)



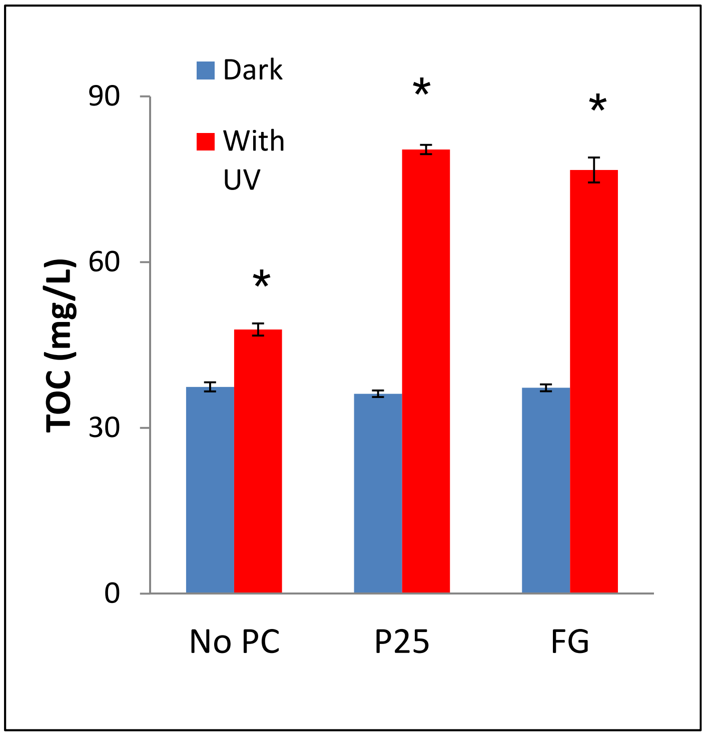
Inhibition on biofilm development increased from PEG-AgNPs to PVP-AgNPs to Ag^+

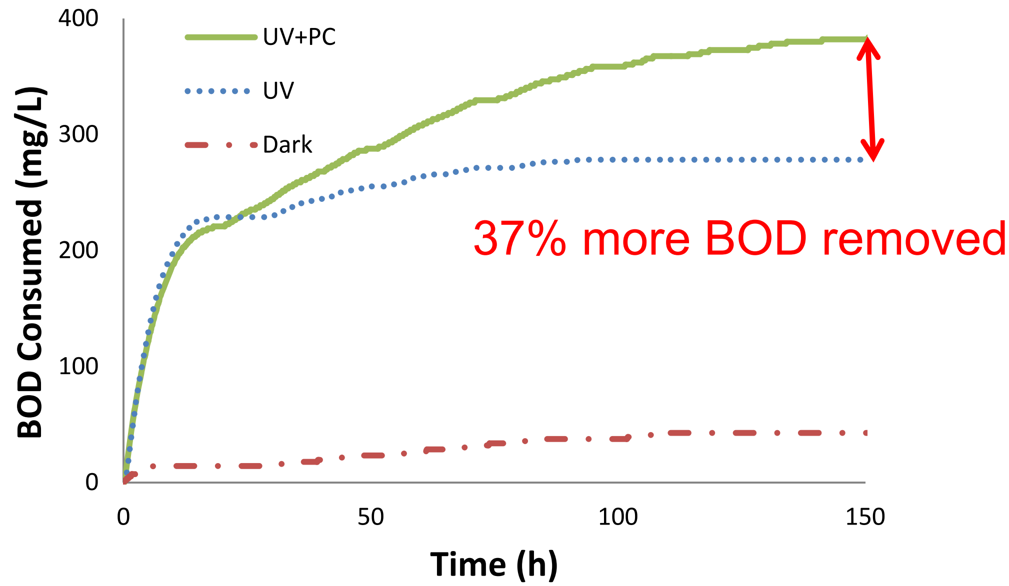


Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation



Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil

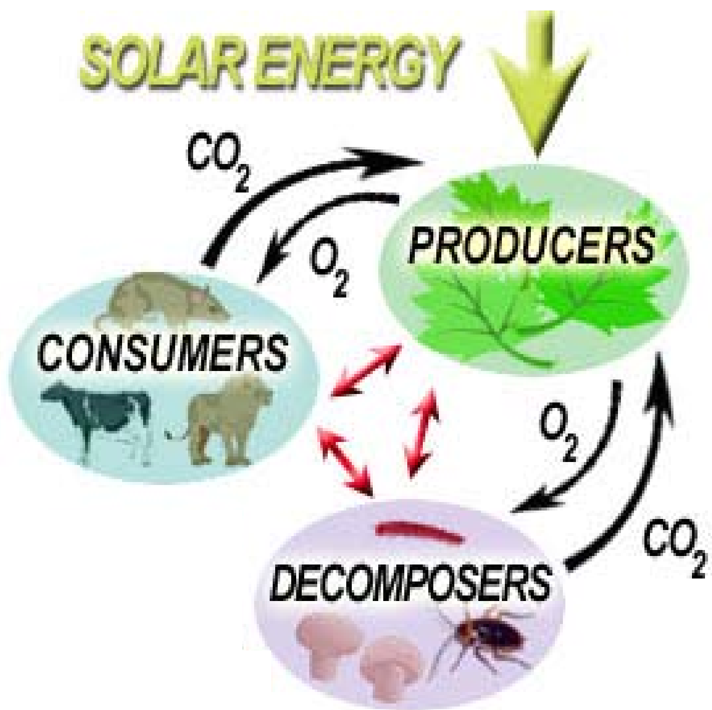




* statistically significant (*p* <0.05)
after 1-day exposure

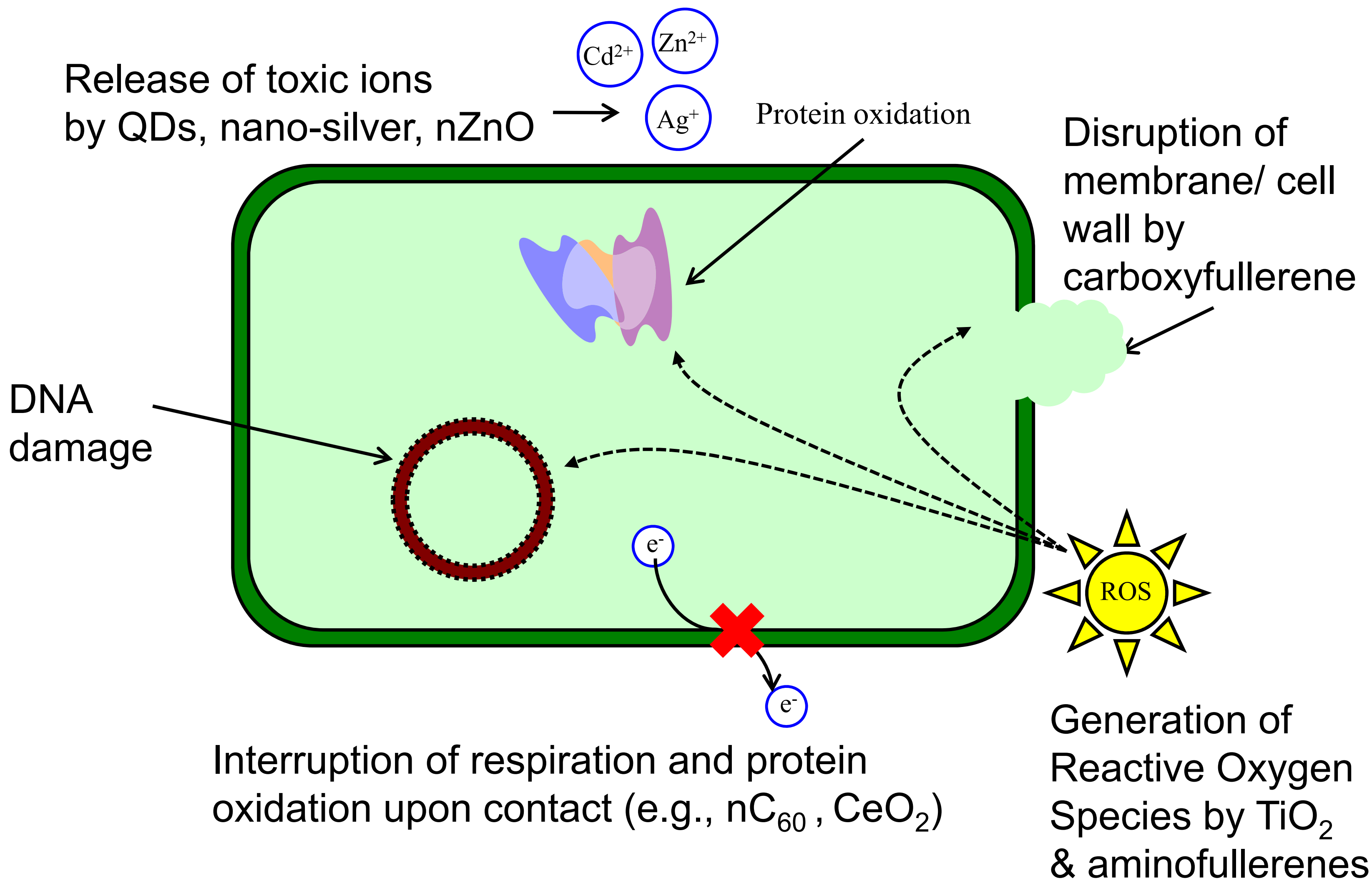
Brame J., S.W. Hong, J. Lee and P.J.J. Alvarez (2013). *Chemosphere* 90: 2315–2319.

Microbial-nanoparticle Interactions to Inform Risk Assessment



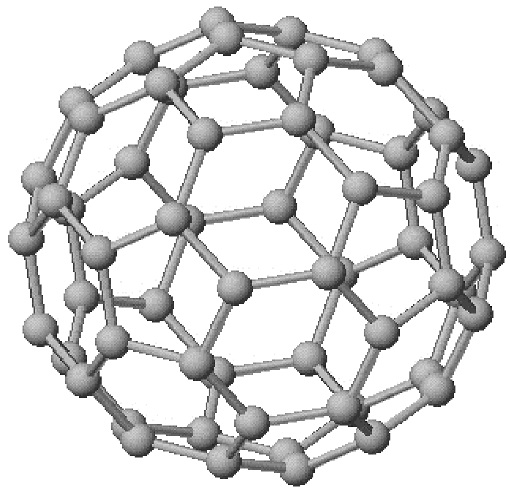
- Bacteria are at the foundation of all ecosystems, and carry out many ecosystem services
- Disposal/discharge can disrupt primary productivity, nutrient cycles, biodegradation, agriculture, etc.
- Antibacterial activity may be fast-screening indicator of toxicity to higher level organisms (*microbial sentinels*?)

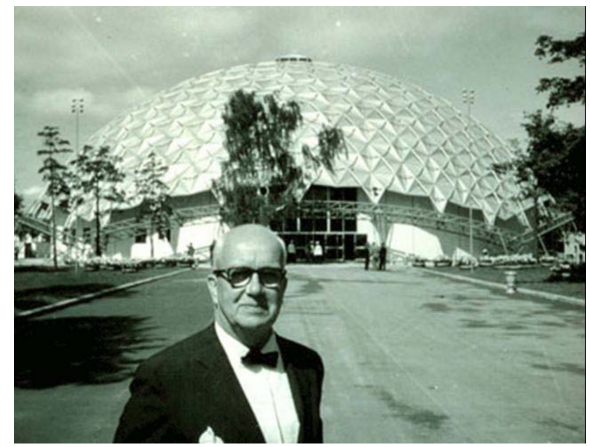
Selected Antimicrobial Mechanisms



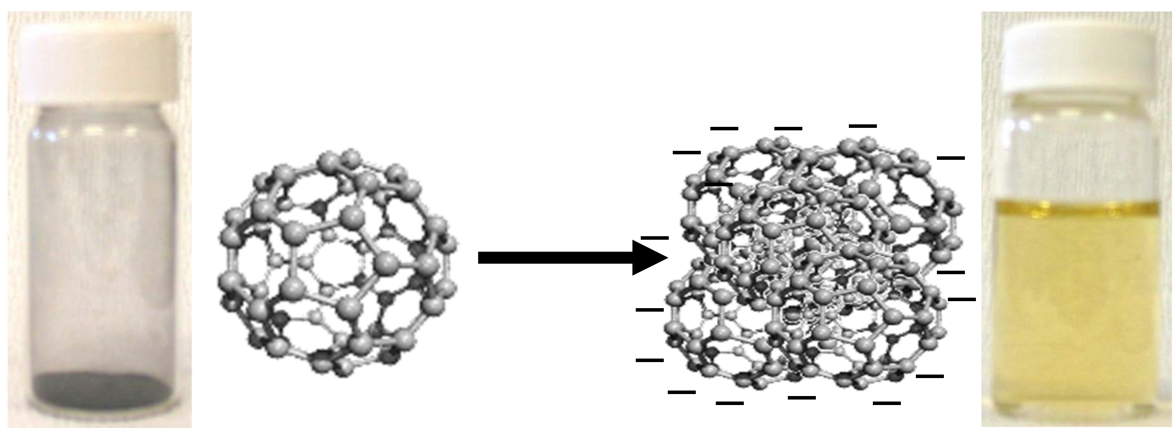
Example 1. C_{60}, nC_{60} and NOM

Photocatalyst
and Antioxidant
(sp2 hybridized)





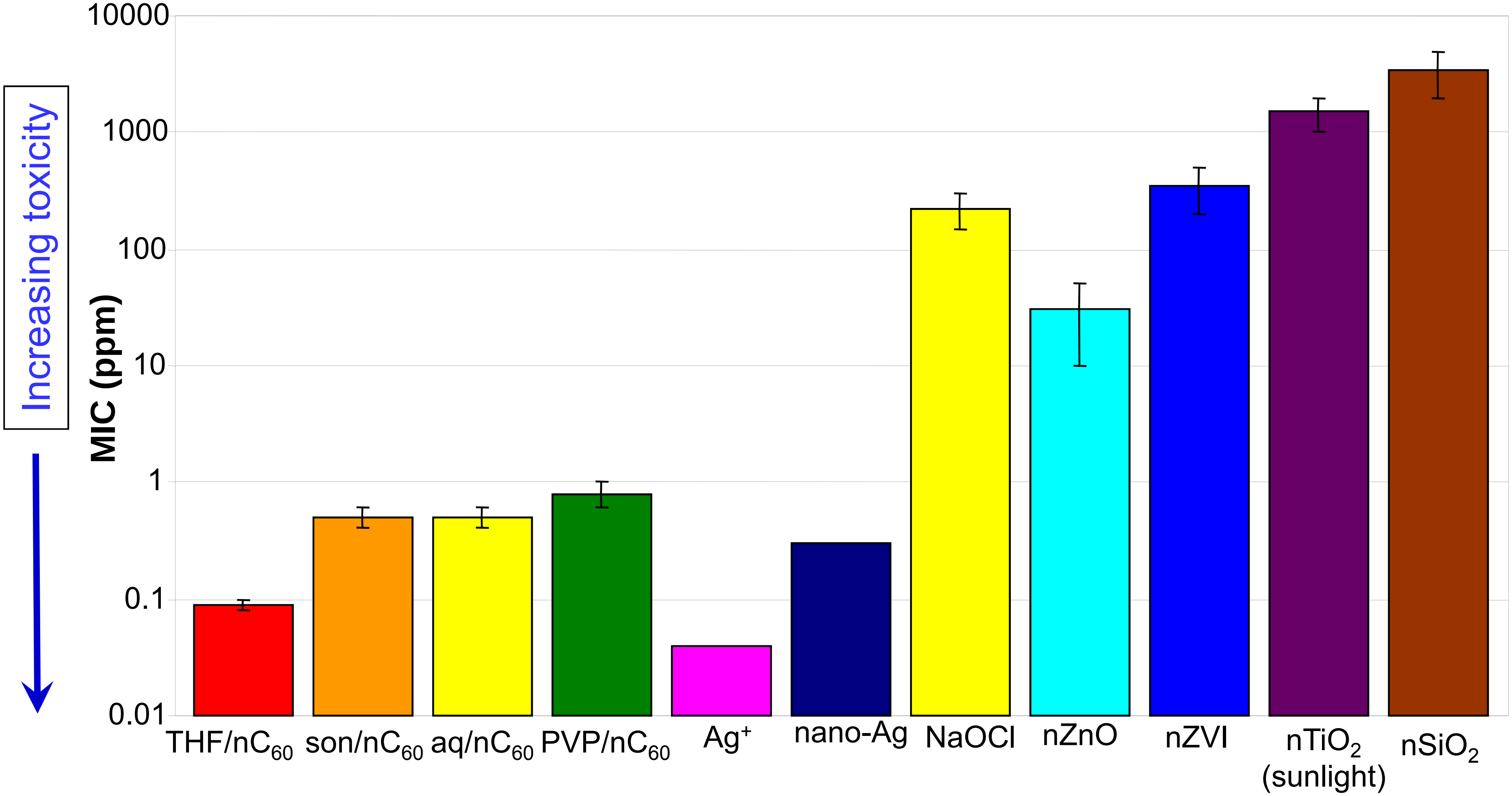
R. Buckminster Fuller (Bucky)



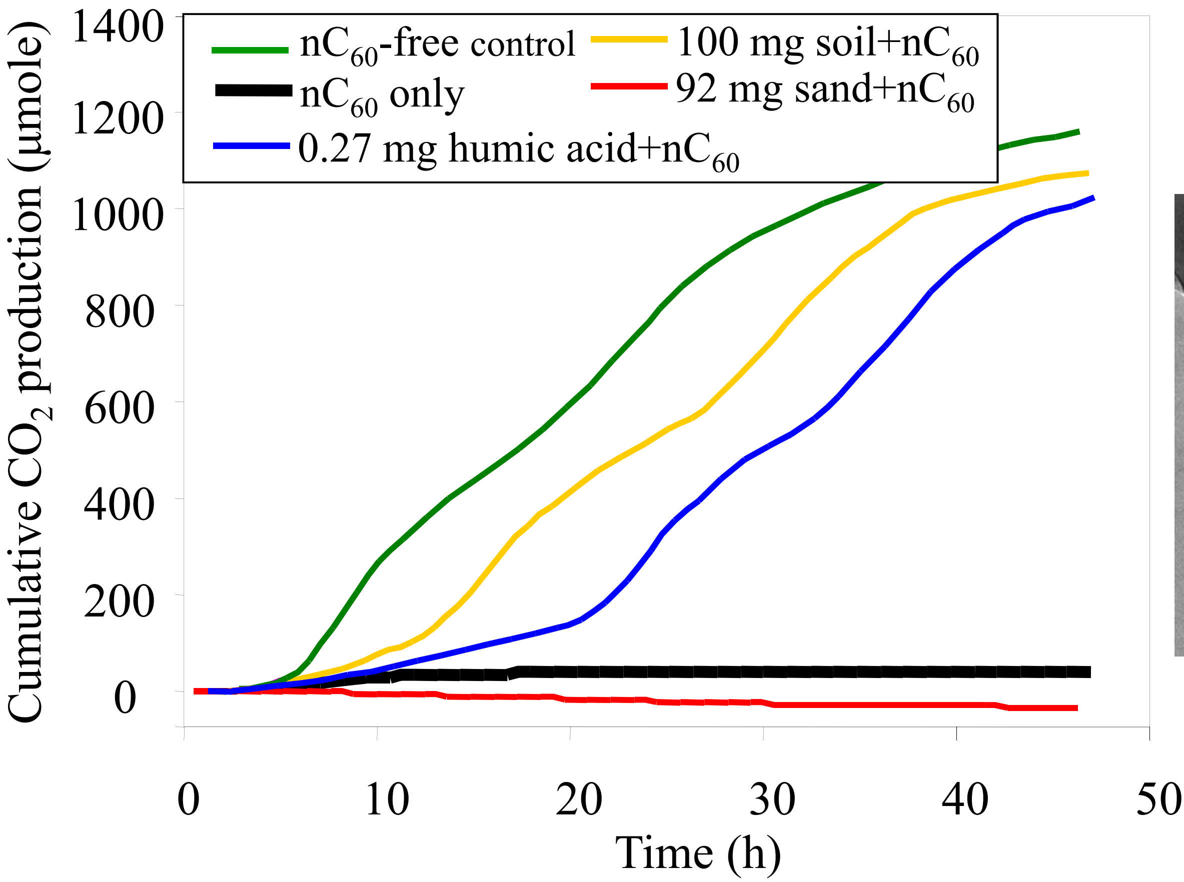
Solid or solution

nC_{60} (20-200 nm)

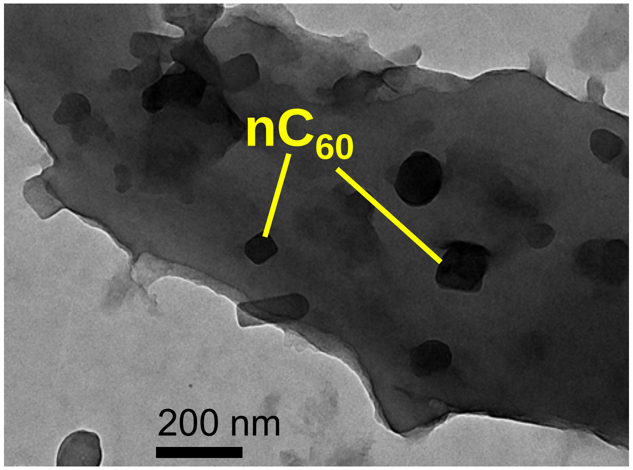
nC_{60} may be more toxic to bacteria than many other common nanomaterials



NOM reduces bioavailability & toxicity of nC_{60}



nC_{60} trapped by humic colloids



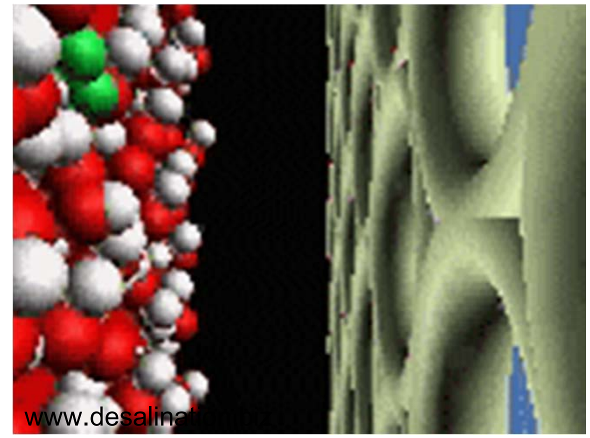
Humic acid concentrations as low as 0.1 mg/L eliminated toxicity

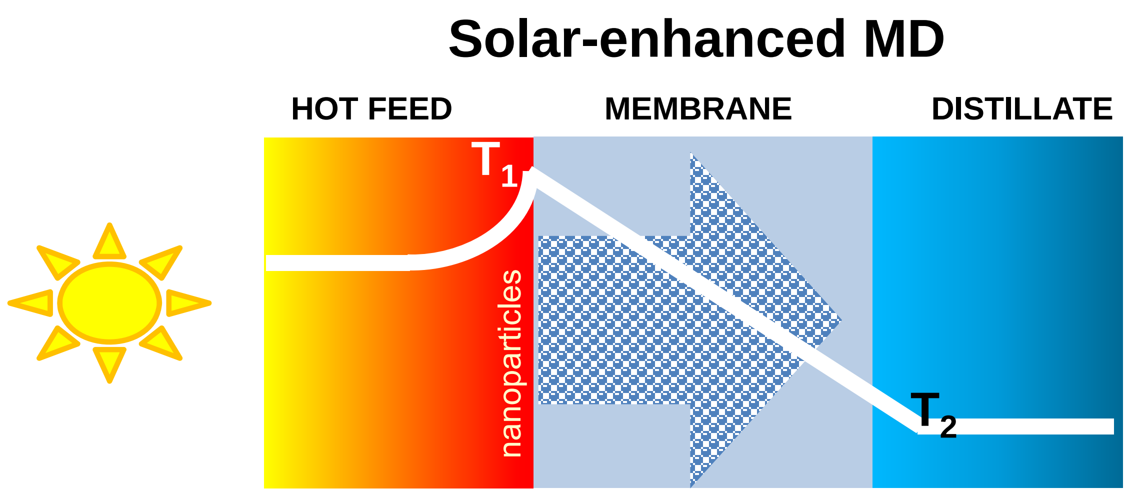
Li, D., Lyon D.Y., Q. Li, and P.J.J. Alvarez (2008). Environ. Toxicol. Chem. 27(9):1888-1894

Example 3. Direct Solar Desalination by Membrane Distillation

Direct solar (membrane) distillation

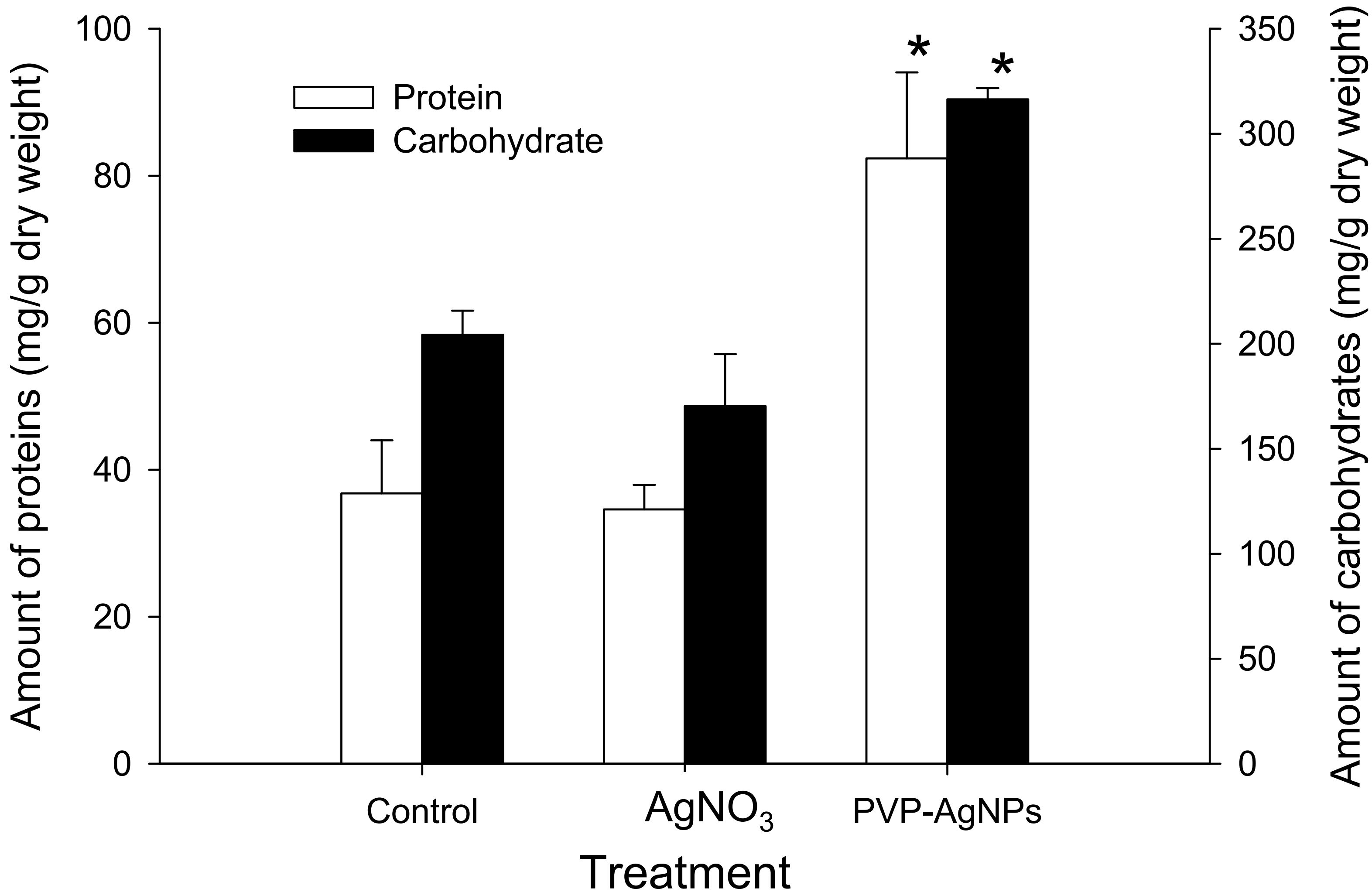
- Uses nanophotonics to convert sunlight to heat efficiently
- NPs create plasmon resonance to generate vapor on membrane surface





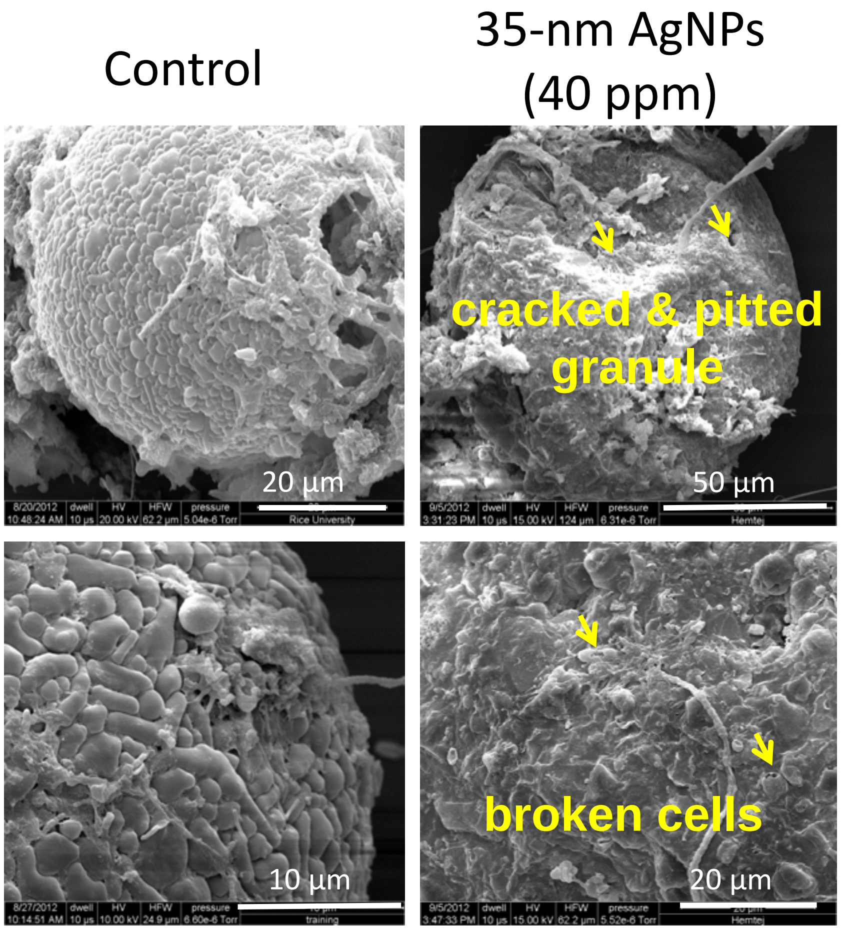
Higher T gradient = higher flux

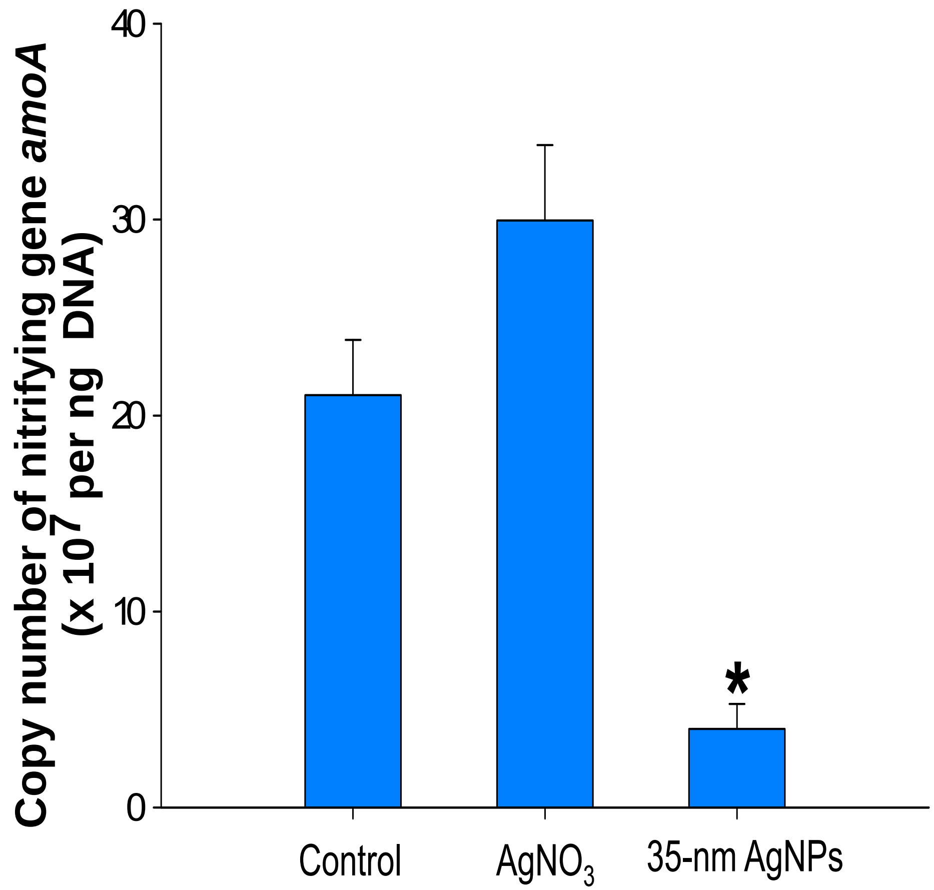
Sub-lethal Exposure of *P. aeruginosa* PAO1 to AgNPs Stimulates Production of Biofilm Proteins & Carbohydrates



The exposure concentration was 0.0216 ppm for all the silver treatments.

AgNPs also had higher impact than Ag^+ on activated sludge!



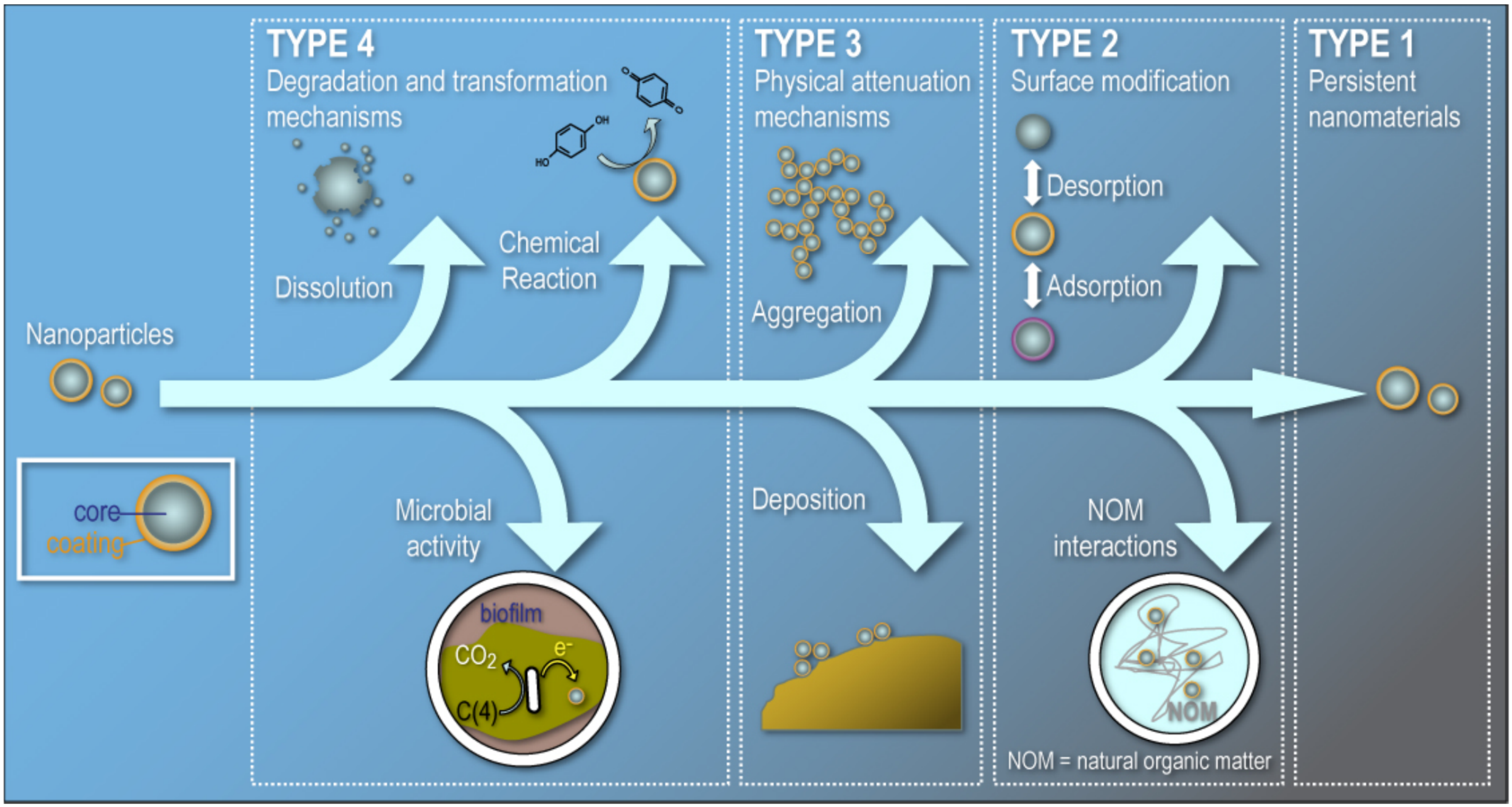


AgNPs damaged AS floc, which can affect clarification and recycling

AgNPs decreased abundance of nitrifiers, hinders N removal

Yang Y., J. Quensen, J. Mathieu, Q. Wang, J. Wang, M. Li, J. Tiedje, and P. Alvarez (2014). Wat. Res. 48:317-325.

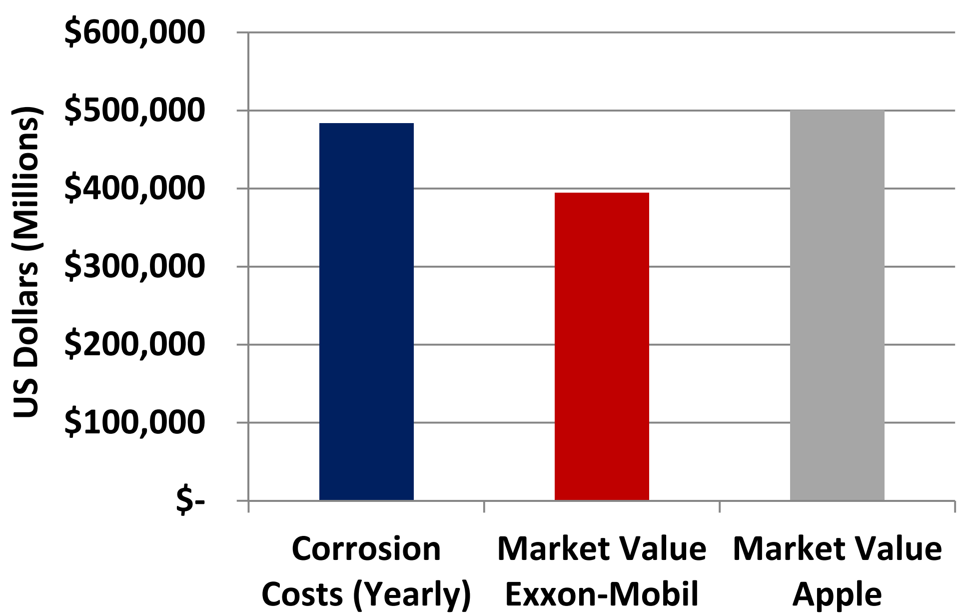
Nanoparticle Modifications in the Environment



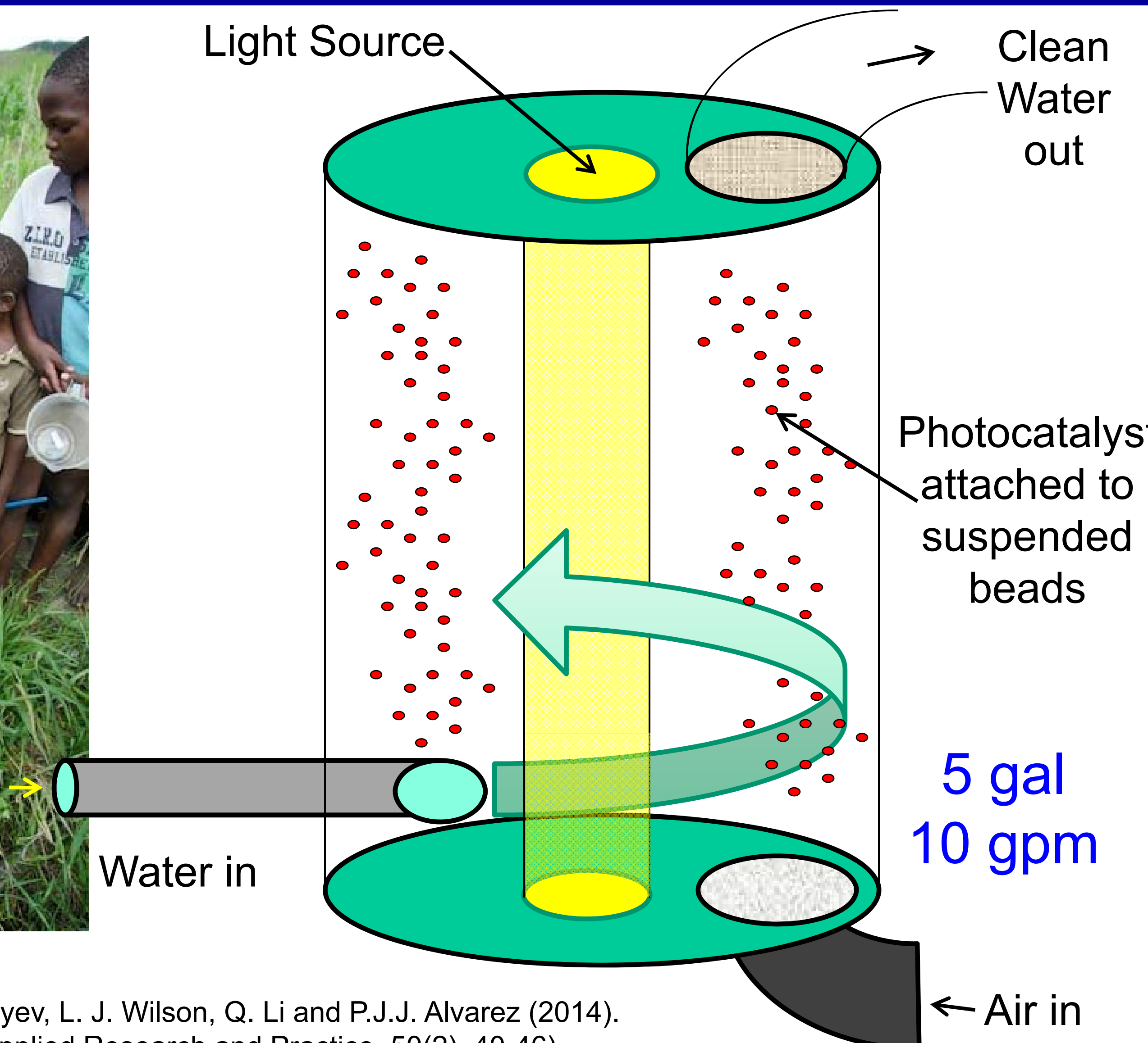
Alvarez P.J.J., V. Colvin, J. Lead and V. Stone (2009). Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano 3(7): 1616-1619.

Background on Biofouling

- Biofouling impairs membranes, water distribution and storage systems cooling towers, heat exchangers., etc.
- Biofouling and microbial-induced corrosion costs 3.1% of US GDP* (~$500 billion/year), which is close to the value of the two most valuable companies in the world



Fluidized Bed Photocatalytic Reactor for Point-of-Use Disinfection and Pesticide Removal



Brame J., V. Fattori, R. Clarke, Y. Mackeyev, L. J. Wilson, Q. Li and P.J.J. Alvarez (2014). Environmental Engineer and Scientist: Applied Research and Practice. 50(2), 40-46.

nAg-PSf Membranes Enhance Virus Removal

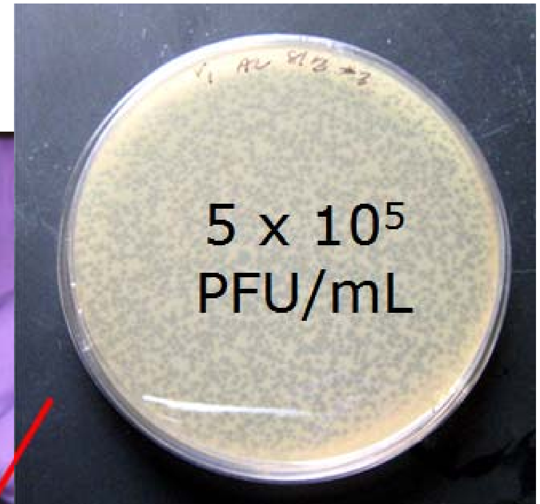
Removal of MS2:

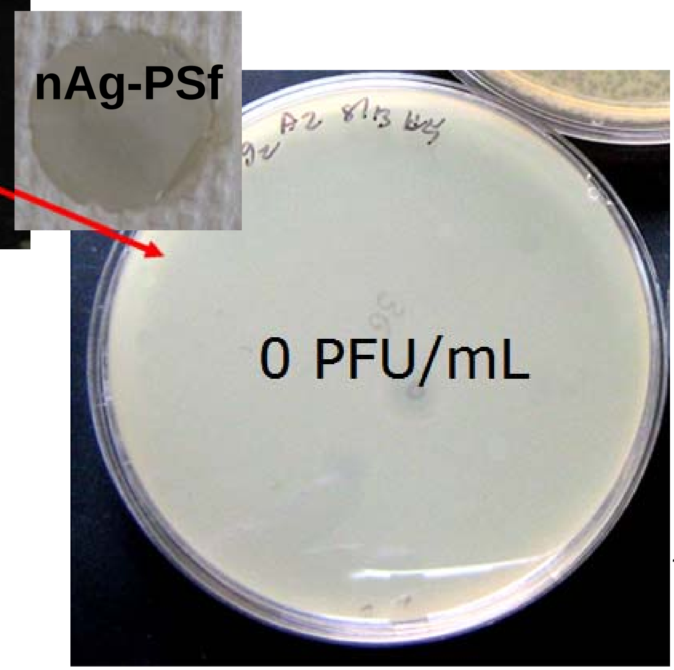
PSf: 99.9%

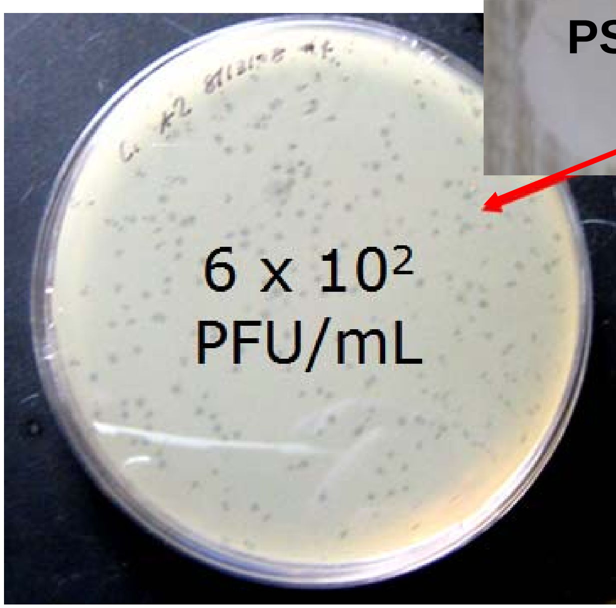
nAg-PSf: > 99.999%

Surface Water Treatment Rule:

99.99% Virus Removal





Vision: Nano-Enabled Water Treatment & Reuse

"Nano" particles:

- High surface areas
- Hyper-catalytic functions
- Tunable physical properties
- Multifunctional membranes
- Faster kinetics

Transformative Technologies to

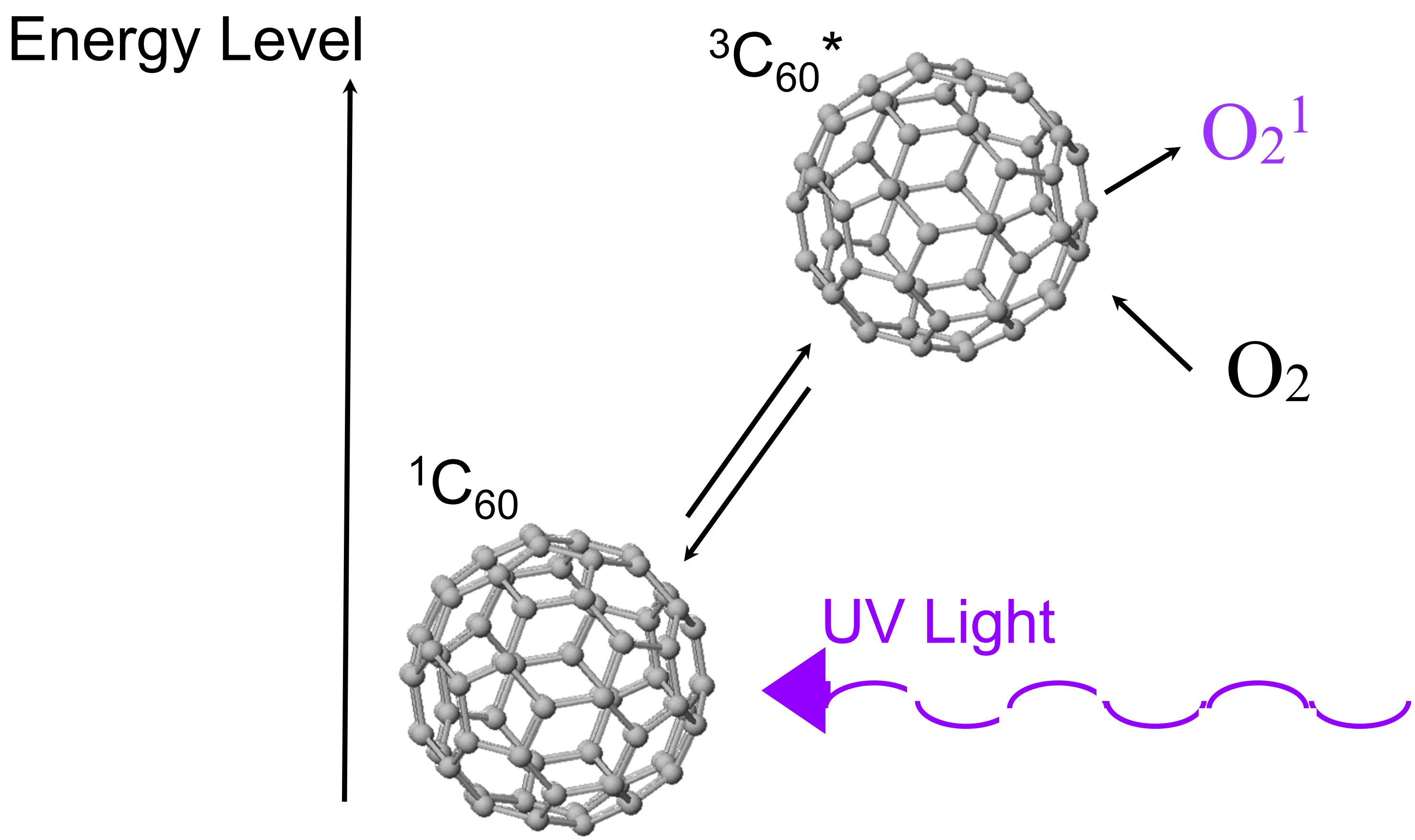
**clean water,
enhance water infrastructure, &
enable integrated water management & reuse**

Enable high-performance water treatment and remediation systems with

(1) Less infrastructure,
(2) Less materials/reagents (selective targeting)
(3) Lower costs & energy

Example 1:
Enhancing UV/Solar Disinfection

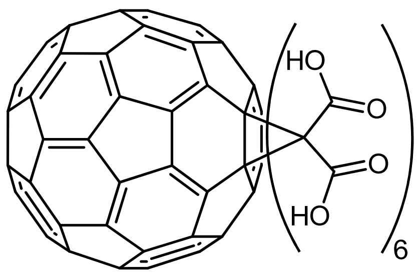
- UV disinfection of DW is increasingly used to inactivate cyst-forming protozoa such as *Giardia* and *Cryptosporidium* without harmful DBPs.
- However, UV is relatively ineffective to treat virus unless the contact time and energy output are significantly increa$ed



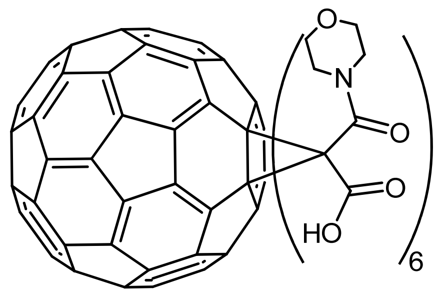
Light excites C_{60} to triplet state. Energy transfer between $^3C_{60}^*$ and molecular oxygen gives rise to singlet oxygen ($^1O_2$)

Hotze M., J. Labille, P.J.J. Alvarez and M. Wiesner (2008). Environ. Sci. Technol. 42, 4175–4180

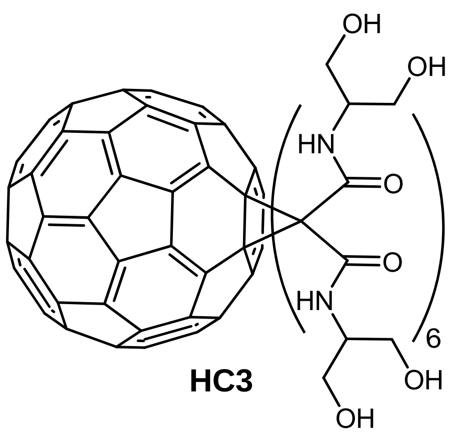
"Water Soluble" Derivatized Fullerenes



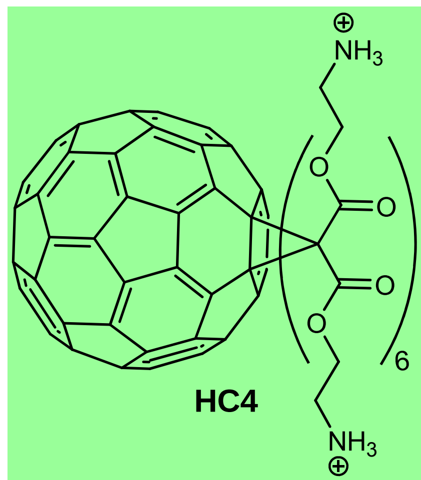
HC1



HC2

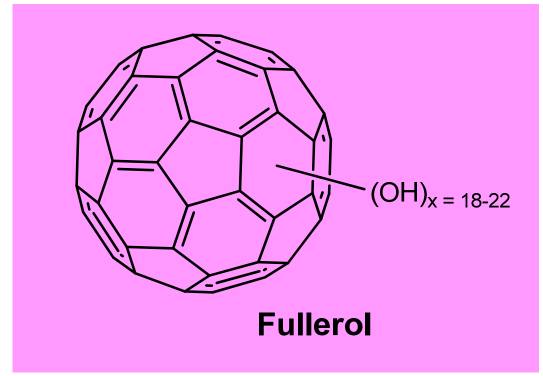


HC3



HC4

vs



Fullerol

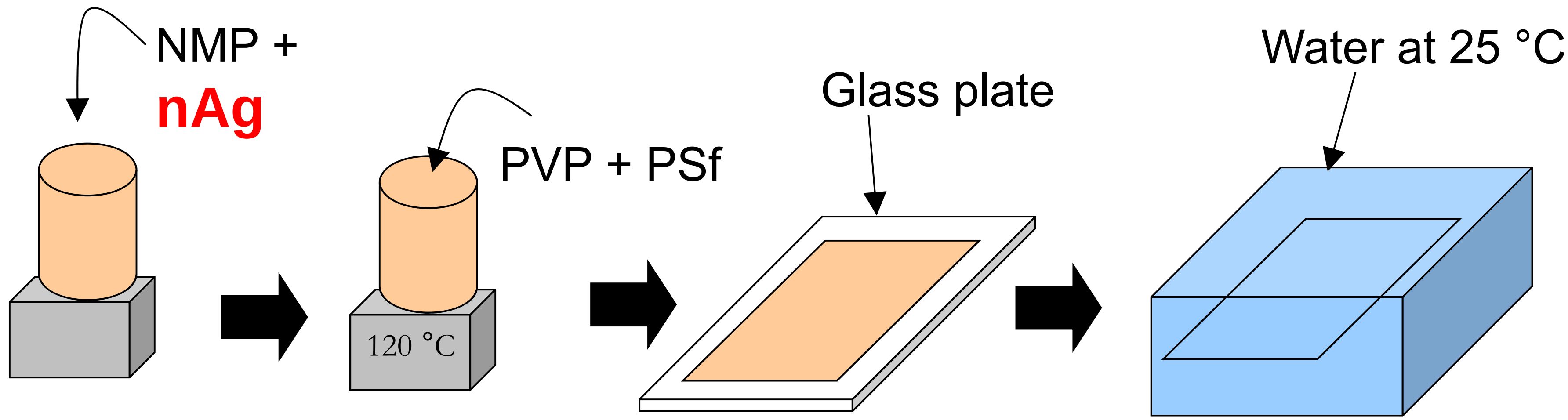
* Commercially Available, MER Corp.

* Synthesized in Lon Wilson's lab, Dept of Chemistry, Rice University (Bingel reaction)

Superior $^{1}O_2$ Production confirmed by EPR & Laser Flash Photolysis

Example 2: Biofouling of Water Treatment Membranes

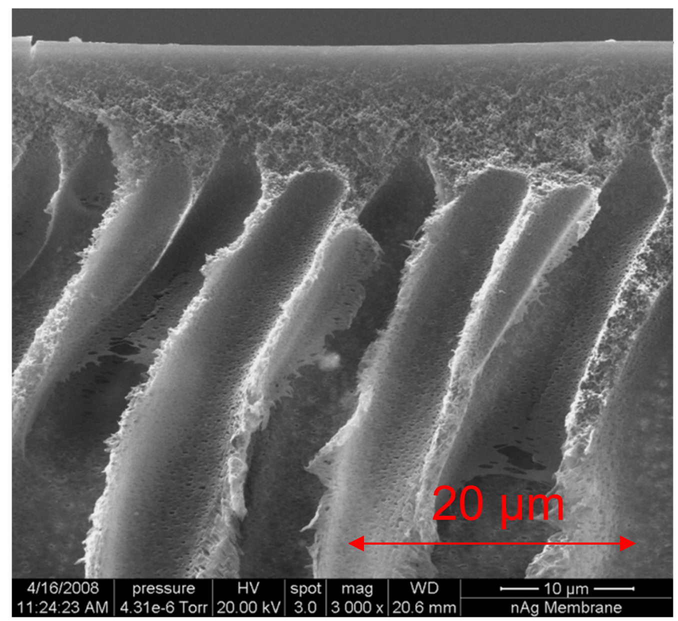
Fouling-Resistant UF Membrane Fabrication (Wet Phase Inversion)



1. Collodion preparation :

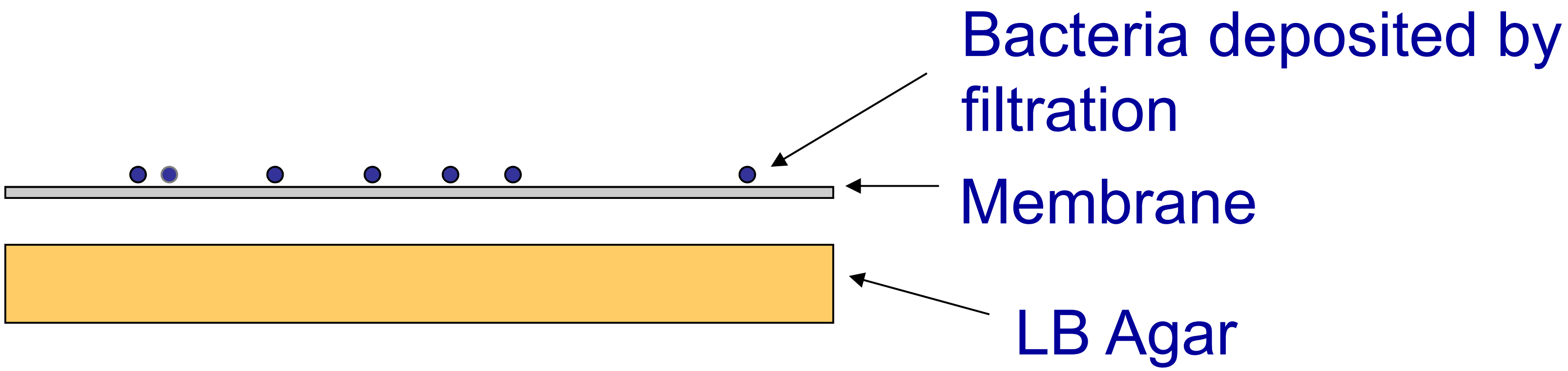
2. Film casting at room temperature

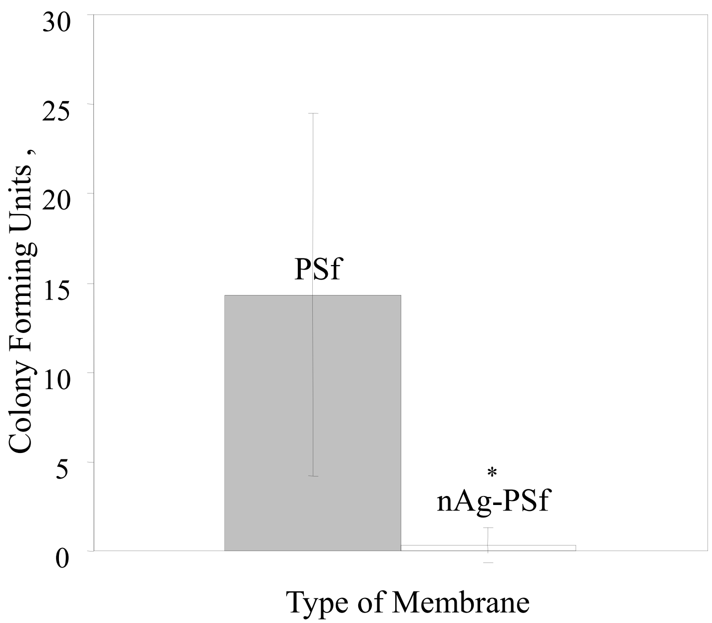
- Nanoparticle solubilisation in NMP. Ultrasonication (100 W, 4 min)
- Addition of PVP at 70 °C
- Slow addition of PSF while stirring at 120 °C



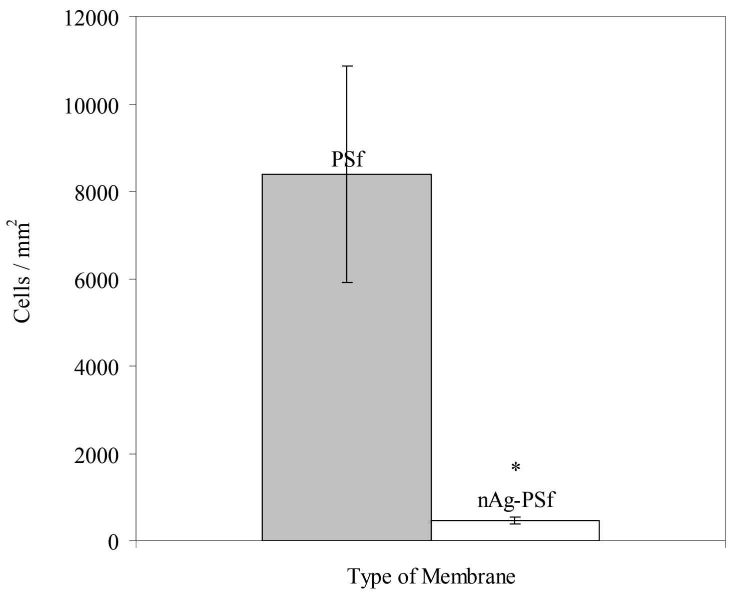
NMP = N-methylpyrrolidone ; PSf = Polysulfone ; PVP=Poly(vinylpyrrolidone)

Bacterial growth inhibition test





Inhibition of growth of *E. coli*



Inhibition of *E. coli* attachment onto membrane surface

Zodrow K., L. Brunet, S. Mahendra, Q. Li, and P.J.J. Alvarez (2009). *Wat. Res* doi:10.1016/j.watres.2008.11.014