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Final Technical report:

Low Cost Nanomaterials for Water Desalination and Purification

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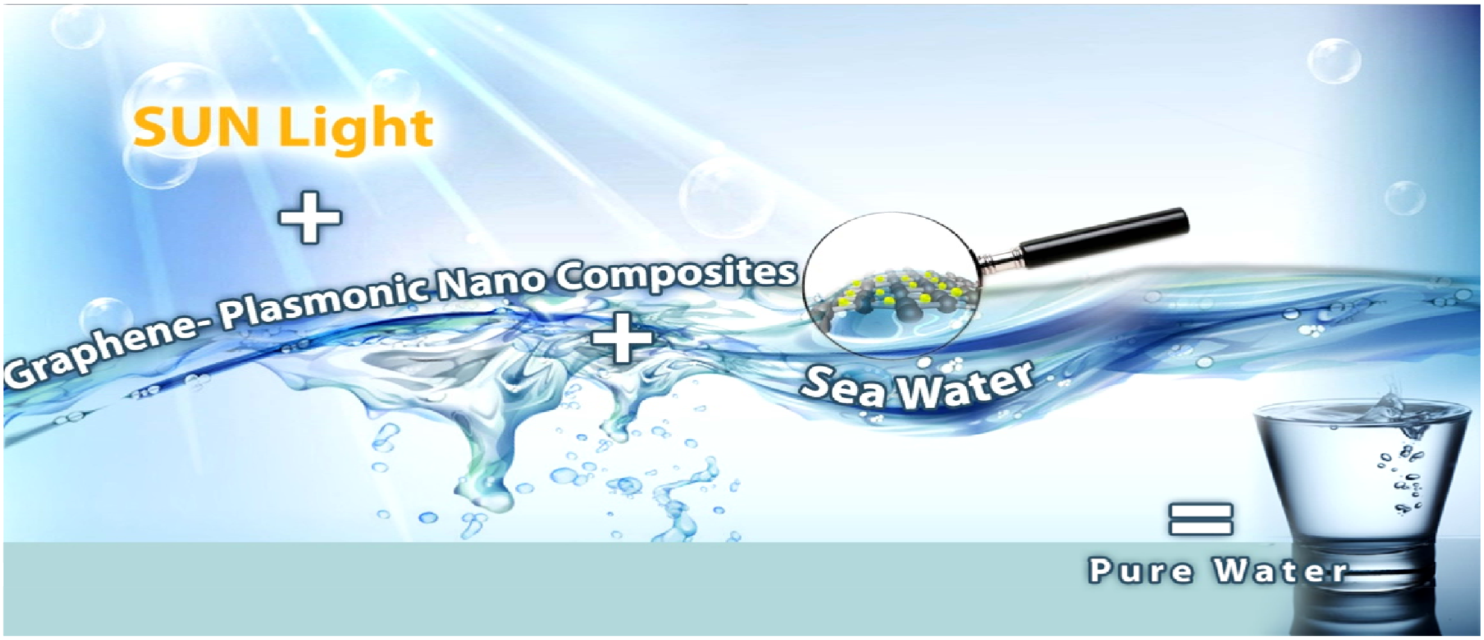

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Abstract:

While over 70 per cent of the Earth's surface is covered by water, most of it is unusable for human consumption. Freshwater lakes, rivers and underground aquifers represent only 2.5 per cent of the world's total freshwater supply. Unfortunately, in addition to being scarce, freshwater is also very unevenly distributed. The United Nations has compared water consumption with its availability and has predicted that by the middle of this century between 2 billion and 7 billion people will be faced with water scarcity.

Increased demand for water is a global problem. In many parts of the world local demand is exceeding conventional resources. More economical use of water, reducing distribution losses and increased use of recycled water can help alleviate this problem but if there is still a shortfall then ***desalination of seawater or brackish water is a must***.

Many areas suffering from water shortages are also short of conventional energy resources and cannot afford expensive fossil fuels. More recently, there is remarkable awareness that even if fossil fuels were much cheaper, the burning of these fuels will contribute to climate change and global warming. For these reasons, the use of renewable energy for desalination has to be encouraged. Renewable energy is not a firm source of power and energy is expensive to store in large quantities. Water on the other hand is easily and cheaply stored. Thus, there is compatibility between renewable energy and desalination.

This study aims to provide a review of the state of the art technologies of water desalination and discuss the benefits, disadvantage and economic impact of each. The key conclusion of this review is that desalination alone cannot deliver the promise of improved water supply unless that the desalination technology itself has evolved substantially. It has to be significantly cheaper, more reliable, less energy-intensive and more environmentally friendly. Nanotechnolgy would bring desalination technology to meet these requirements in the near future.

Recently, new methodologies have been developed recently based on using nanotechnology for water desalination such as Reverse osmosis, Ultra- and Nano-filtration. Also, new technologies based on using solar concentrators for solar desalination have been developed. This report will highlight all of these new methodologies in details.

New methodology which combines solar desalination and nanotechnology based on producing low cost nanocomposite to enhance the rate of solar thermal water desalination has been developed in our laboratory (patent pending). These new nanomaterials absorb light so strongly and convert it efficiently into heat energy. The basic idea of this new methodology is adding these new nanocomposite to salty sea water in simple solar still setup, which is directed always to the sun light. This would increase dramatically the rate of water evaporization, the

water vapour could be condensate, then collected and used as a pure water source. Simple solar still design has been developed in our laboratory to examine the concept of large enhancement of the rate of water desalination due to presence of efficient photothermal nanocomposite.

The new nanocomposite is a mixture of plasmonic nanomaterials and Graphene sheets. Plasmonic nanomaterials such as Silver and Gold nanoparticles has very strong light absorption in the visible region due to what is so called localized surface plasmon resonances. Graphene has very strong absorption all over the sun spectrum especially in the near IR region and also it is the most thermal conductive material ever been known. Understanding the coupling between the optical properties of metallic nanoparticles with different shapes (spheres, rods, prism) and graphene, and how this influences their absorption cross sections, ultrafast optical responses, as well as their photoelectrical and photothermal properties opens the door to fabricating novel composite for efficient photothermal energy conversion.

The main goal of this project was to fabricate and test a composite of different concentration of silver nanomaterials and Graphene to enhance the photothermal conversion which would enhance the rate of water vaporization. Also, modification of the Solar Still system using solar concentrator is one of our objectives. It is worth to mention that silver nanoparticles have super-antibacterial effect. This means that the obtained water is pure and clean not only from salt and impurities but also from all bacteria and microorganism. Water quality test such as turbidity, acidity & alkalinity, heavy metals, ions and salts and microorganism confirms that the obtained water using this method is ultrapure.

The environmental precautions of the developed methodology of water desalination using the joint application of nanotechnology and solar energy have been investigated. The toxicity of these nanomaterials which used for water desalination has been evaluated in vivo using animal model. The concentration used of the nanomaterials (Silver and gold nanoparticles and their composites with graphene) does not induce any sign of toxicity in rats. This methodology could be developed to be used for the use of sea water for cultivation. Moreover, the same nanocomposite could be used to produce steam from water using solar light and this could be developed to produce Solar heaters or even electricity.

Introduction:

Clean water is essential to human life and is a critical feedstock in a variety of key industries including electronics, pharmaceuticals and food. The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are decreasing due to (i) extended droughts, (ii) population growth, iii) more stringent health-based regulations, and (iv) competing demands from a variety of users. With only 3% of all available water on the planet being fresh water, seawater is the most abundant available source of drinking water and water for industrial use in many regions, and innovations in the development of novel technologies to desalinate water are among the most exciting and promising.

Tackling water shortage issues with desalting of seawater and salty water is common in the desert nations of the Middle East and the Mediterranean. More than 90% of Egypt is desert and most of the Egyptian population is concentrated in the Nile Valley. The fast growing development in Egypt has required big movements of investments and people from the Nile Valley towards the east, with the fantastic Red Sea and Sinai coastal zones, and also towards the Western Desert that has promising brackish groundwater potentialities. In both cases, fresh water supply is essential and desalination is a feasible option that can cover the wide gap between the available capacities and the accelerating demands. The cost of desalination, either thermal or membrane is extremely high. Advances in nanoscale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes.

Advances in nanotechnology suggest that many of the current problems involving water quality could be resolved or greatly ameliorated using nanocatalysts, nanosorbents, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticle enhanced filtration among other products and processes resulting from the development of nanotechnology. Additionally, nanotechnology-derived products that reduce the concentrations of toxic compounds to sub-ppb levels can assist in the attainment of water quality standards and health advisories. In this report, we developed novel nanomaterials and processes for treatment of surface water, groundwater and industrial wastewater contaminated by toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses. In addition, we discuss some of the risk and challenges associated with the development of cost effective and environmentally acceptable functional nanomaterials for water purification.

Background:

Over the last few decades desalination technologies have been used increasingly throughout the world to produce drinking water from brackish groundwater and seawater, to improve the quality of existing supplies of fresh-water for drinking and industrial purposes, and to treat industrial and municipal wastewater prior to discharge or reuse. In the early 1950s there were about 225 land-based desalination plants worldwide with a combined capacity of about 27 million gallons per day (mgd). There are now about 3,500 plants worldwide with a production capacity of about 3,000 mgd. As the demand for freshwater increases and the quality of existing supplies deteriorates, the use of desalination technologies will increase [2].

Seawater distillation plants dominated the early desalination market, which was primarily overseas. However, due to lower energy requirements, desalination process called reverse osmosis (RO) now appears to have a slightly lower cost than distillation for seawater desalination (unless a dual purpose electric power/desalination plant is being built). For brackish water desalination, RO and another desalination process called electro-dialysis (ED) are both competitive. Other desalination technologies are used less widely due to their rudimentary development and/or higher cost. However, there is no single desalination technology that is considered ‘‘best’ for all uses [2].

The selection of the most appropriate technology depends on the composition of the feed water (prior to desalination), the desired quality of the product water, and many other site-specific factors. Desalination technologies cannot produce water where there is none. Brackish water can be most economically desalinated on a large scale (e. g., 1 mgd, or larger) at well-operated, centralized RO or ED plants at an overall cost (including both capital and operating costs) of about $1.50 to $2.50 per 1,000 gallons; for seawater, large scale distillation and RO both cost about $4 to $6 per 1,000 gallons.3 Although there are no developing desalination technologies that will generate major reductions (e. g., 50 percent) in water treatment costs, industry experts believe that the costs of RO and ED should continue to decrease as membranes, treatment equipment, and operational procedures are improved. Future cost reductions for distillation processes will probably be modest [3].

Water is desalinated in order to obtain fresh water suitable for animal consumption or irrigation, or, if almost all of the salt is removed, for human consumption. Sometimes the process produces table salt as a by-product. Most of the modern interest in desalination is focused on developing cost-effective ways of providing fresh water for human use in regions where the availability of water is limited. Large-scale desalination typically requires large amounts of energy as well as specialized, expensive infrastructure, making it very costly compared to the use of fresh water from rivers or groundwater. The large energy reserves of many Middle Eastern countries, along with their relative water scarcity, have led to extensive construction of desalination in this region. There are more than 7,500 desalting plants in operation worldwide producing several billion gallons of water per day. 57% are in the Middle East and 12% of the world capacity is produced in the Americas, with most of the plants located in the Caribbean and Florida. Saudi Arabia's desalination plants account for about 24% of total world capacity. However, as drought conditions continue and concerns over water availability increase, desalination projects are being proposed at numerous locations [1]. The following diagram outlines the key drivers in the development and investment in the water production in the forthcoming years.

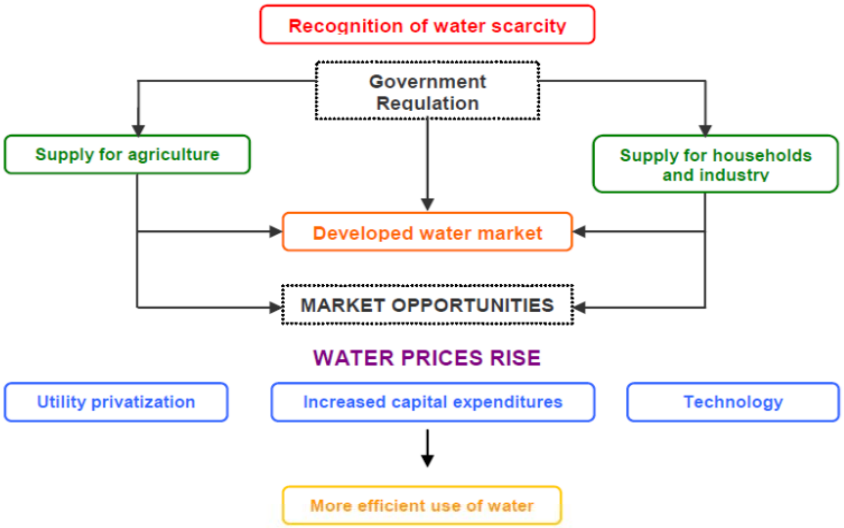


Figure (2): Investment in the water production

Key issues in Desalination:

- ***The pretreatment*** includes the entire necessary treatment step ahead of the reverse osmosis plant. It is determining for plant life time and to minimize chemical cleaning and membrane replacement. It has a direct impact on the plant performance [4].
- ***The reverse osmosis process*** can also be build with one or two passes, depending on the product water requirements and the seawater salinity and temperature. In most cases, 1 pass is sufficient to reach the EU drinking water standards, especially regarding the boron content (1 mg/L). To reach WHO boron guideline (0.5mg/L), a second pass might be necessary (Boron removal process) [4].
- ***The energy recovery*** device is the key factor that determines the plant electrical costs. It must be chosen carefully based on the local energy costs and environment policies [4].
- ***Post-treatment and/or polishing steps*** are required to condition the water after the reverse osmosis membrane process to make it suitable to your application [4].
- ***Brine disposal*** can be an environmental and economical issue in some areas where the fauna and flora are sensitive to local seawater salinity increase. Brine disposal should be studied and engineered case by case [4].

Overview of Sea water Desalination Process

Water desalination processes are divided into three main categories: (1) thermal energy, (2) mechanical energy, (3) electric energy, (4) chemical energy, as shown in figure (3).

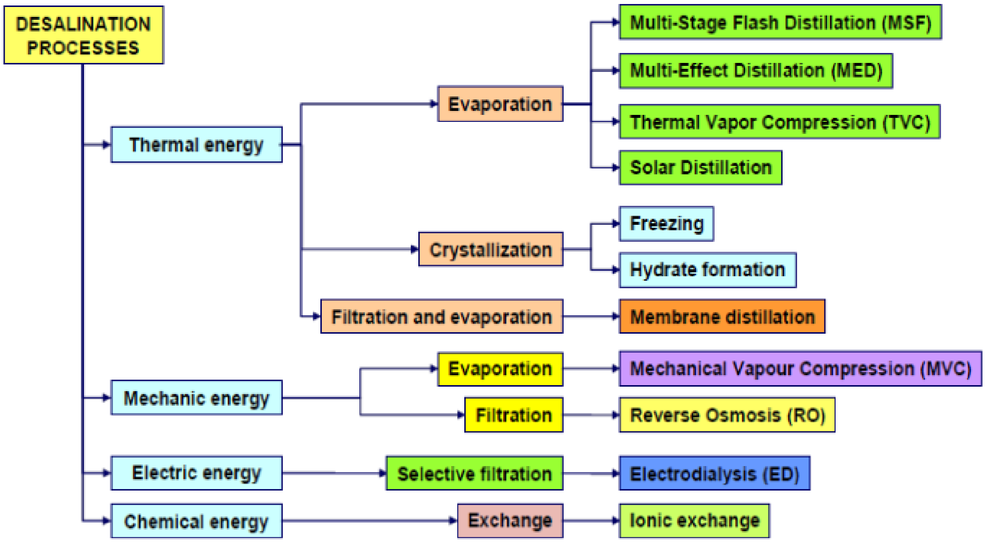


Figure (3): Classification of Water Desalination Processes

Membrane Technologies:

A membrane is a thin film of porous material that allows water molecules to pass through it, but simultaneously prevents the passage of larger and undesirable molecules such as viruses, bacteria, metals, and salts [5]. Membranes are made from a wide variety of materials such as polymeric materials that include cellulose, acetate, and nylon, and non-polymeric materials such as ceramics, metals and composites. Synthetic membranes are the most widely used membranes in the desalination process and their use is growing at a rate of 5-10% annually (Krukowski 2001). In general, membrane treatment processes use either pressure-driven or electrical-driven technologies. Pressure-driven membrane technologies include reverse osmosis (RO), nano-filtration (NF), ultra-filtration, and microfiltration [5].

Reverse Osmosis

Reverse Osmosis (RO) is a physical process that uses the osmosis phenomenon, i.e., the osmotic pressure difference between the saltwater and the pure water to remove salts from water (Figure 4). In this process, a pressure greater than the osmotic pressure is applied on saltwater to reverse the flow, which results in fresh water passing through the synthetic membrane pores separated from the salt. A concentrated salt solution is retained for disposal. The RO process is effective for removing total dissolved solids (TDS) concentrations of up to 45,000 mg/L, which can be applied to desalinate both brackish water and seawater. Reverse osmosis needs energy to operate the pumps that raise the pressure applied to salt water [5].Two common types of membranes used in RO process for desalination include Cellulose Acetate (CA) membranes and Non-CA membranes [5].

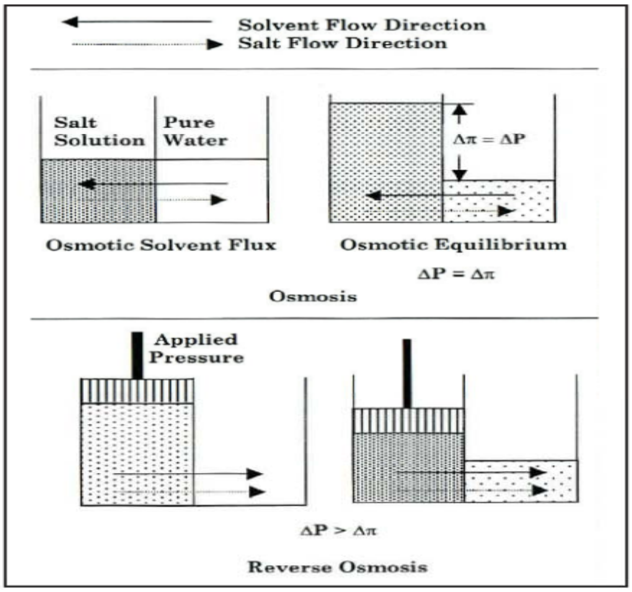


Figure (4): Reverse Osmosis Process

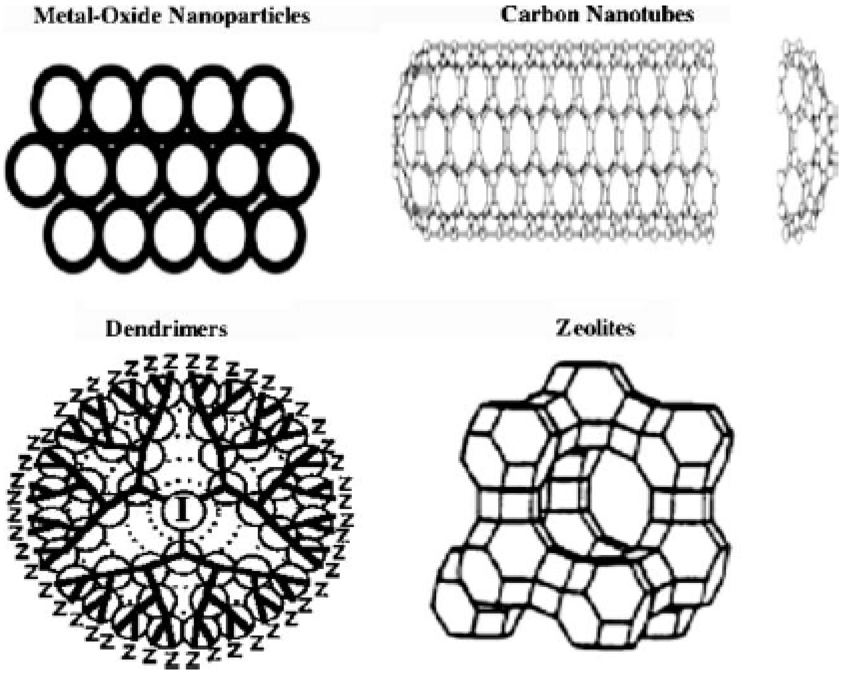
Nano-filtration:

A nanofiltration (NF) membrane works similar to reverse osmosis except that with NF, less pressure is needed (70 and 140 psi) because of larger membrane pore size (0.05 µm to 0.005 µm). Nanofiltration can remove some total dissolved solids, but is often used to partially soften water and is successful at removing solids, as well as dissolved organic carbon. Membrane processes such ultrafiltration as (UF), nanofiltration (NF) and reverse osmosis (RO) are emerging as key components of advanced water purification and desalination technologies. Van der Bruggen & Vandercasteele (2003) have reviewed the use of nanofiltration to remove cations, natural organic matter, biological contaminants, organic pollutants, nitrates and arsenic from groundwater and surface water. Favre-Reguillon et al. (2003) showed that nanofiltration can be used to remove minute quantities of U(VI) from seawater. Mohsen et al. (2003) have evaluated the use of nanofiltration to desalinate water. They found that nanofiltration in combination with reverse osmosis could effectively render brackish water potable. Peltier et al. (2003) demonstrated an improvement in water quality for a large water distribution system using nanofiltration. Substantial reductions in the quantities of both organic and biological contaminants (e.g., bacteria and viruses) were achieved using this process.

Nanomaterials have a number of key physicochemical properties that make them particularly attractive as separation media for water purification. On a mass basis, they have much large surface areas than bulk particles. Nanomaterials can also be functionalized with various chemical groups to increase their affinity toward a given compound. They can also serve as high capacity/ selectivity and recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/ anions in aqueous solutions. Nanomaterials also provide unprecedented opportunities to develop more efficient water-purification catalysts and redox active media due their large surface areas and their size and shape-dependent optical, electronic and catalytic properties. Nanomaterials are also being used to develop chlorine-free biocides through functionalization

with chemical groups that selectively target key biochemical constituents of waterborne bacteria and viruses.
Srivastava et al. (2004) recently reported the successful fabrication of carbon nanotube filters. These new filtration membranes consist of hollow cylinders with radially aligned carbon nanotube walls. Srivastava et al. (2004) showed that the filters were effective at removing bacteria (Escherichia coli and Staphylococus aureus) and Poliovirus sabin 1 from contaminated water. The carbon nanotube filters are readily cleaned by ultrasonication and autoclaving. DeFriend et al. (2003) reported the successful fabrication of alumina UF membranes using alumina (A-alumoxanes) nanoparticles (7–25 nm). The pore-size, and molecular weight cut-off (MWCO) of the membranes depend to a large extent on the 'uniformity' of the alumina nanoparticles. The new UF membranes, which have MWCO between 1000– 10,000 Da and average pore diameter of 4 nm, showed selectivity toward a number of synthetic dyes (e.g., Direct Red 81, Direct Blue 71 and Direct Yellow 71). DeFriend et al. (2003) also showed that the selectivity and permeate flux through the UF membranes can be increased by doping the alumina nanoparticles with Fe, Mn and La. Stanton et al. (2003) have fabricated novel NF membranes by deposition of 4.5–5.0 layer pairs of poly(styrene sulfonate)/poly(allylamine hydrochloride) onto porous alumina. The new NF membranes exhibit high water flux, high retention of divalent cations [Ca(II) and Mg(II)] and anions such as chlorides and sulphate) selectivity ratios up to 80. Note that Hollman & Bhattacharaya (2004) have also prepared novel membranes with enhanced metal ion retention and permeate flux by deposition of multilayers of charged polypeptides [poly(9Lglutamic acid) or poly(L-lysine)] inside the pores of functionalized polycarbonate track-etched membranes (thickness = 10 lm and pore diameter = 200 nm).

Nanotechnology would also provide novel opportunities to develop more efficient and cost effective nanostructured and reactive membranes for water purification and desalination. Nanomaterials which could be used in water purification and desalinations includes the following:



Solar thermal desalination systems

Solar energy can be used in two forms. Either as thermal energy by heating a fluid or by converting it into electricity using photovoltaic arrays (PV). Solar energy is a relatively diffuse source of energy. It is also available almost everywhere, unlike wind, geothermal or even conventional fuels. Depending on the energy demand of the application, it may require large areas. Yet, most solar energy conversion systems are modular and can be installed almost everywhere (e.g. house roofs) which relieves the space availability problem. Cost effectiveness is strongly influenced by the amount of solar radiation available at the site.

Solar thermal desalination: The basic principles of solar water distillation are so simple, as distillation replicates the way nature makes rain [4]. The sun's energy heats water to the point of evaporation. As the water evaporates, water vapor rises, condensing on the glass surface for collection. This process removes impurities such as salts and heavy metals as well as eliminates microbiological organisms. The end result is water cleaner than the purest rainwater [5].

Two types of systems could be included in this category: (1) Simple solar operated devices such as solar stills; (2) solar assisted distillation systems such as multi-effect humidification systems. These devices have low efficiency and low water productivity due to the ineffectiveness of solar collectors to convert most of the energy they capture, and to the intermittent availability of solar radiation [5].

For this reason, solar thermal desalination has so far been limited to small-capacity units, which are appropriate in serving small communities in remote areas, exposed to water scarcity and at the same time, are characterized by high levels of solar radiation [5].

Solar still

Solar-still designs can generally be grouped into four categories: (1) basin still, (2) tilted-wick solar still, (3) multiple-tray tilted still, and (4) concentrating mirror still. The basin still consists of a basin, support structure, transparent glazing, and distillate trough. Thermal insulation is usually provided underneath the basin to minimize heat loss. Other ancillary components include sealants, piping and valves, storage, external cover, and a reflector (mirror) to concentrate light. Single basin stills have low efficiency, generally below 45%, due to high top losses. Double glazing can potentially reduce heat losses, but it also reduces the transmitted portion of the solar radiation [6]. A tilted-wick solar still uses capillary action of fibers to distribute feed water over the entire surface of the wick in a thin layer. This allows a higher temperature to form on this thin layer. Insulation in the back of wick is essential. A cloth wick needs frequent cleaning to remove sediment built-up and regular replacement of wick material due to weathering and ultraviolet degradation. Uneven wetting of the wick can result in dry spots that reduce efficiency [6].

In a multiple-tray tilted still, a series of shallow horizontal black trays are enclosed in an insulated container with a transparent glazing on top. The feed-water supply tank is located above the still, and the vapor condenses and flows down to the collection channel and finally to the storage. The construction of this still is fairly complicated and involves many components that are more expensive than simple basin stills. Therefore, the slightly better efficiency it delivers may not justify its adoption [7]. The concentrating mirror solar still uses a parabolic mirror for focusing sunlight onto an evaporator vessel. The water is evaporated in this vessel exposed to extremely high temperature. This type of still entails high construction and maintenance costs. Solar stills are characterized by low production rates of about 4–6 L/(m^2 day) [6,7]. Three types of solar stills are shown in Figure (4):

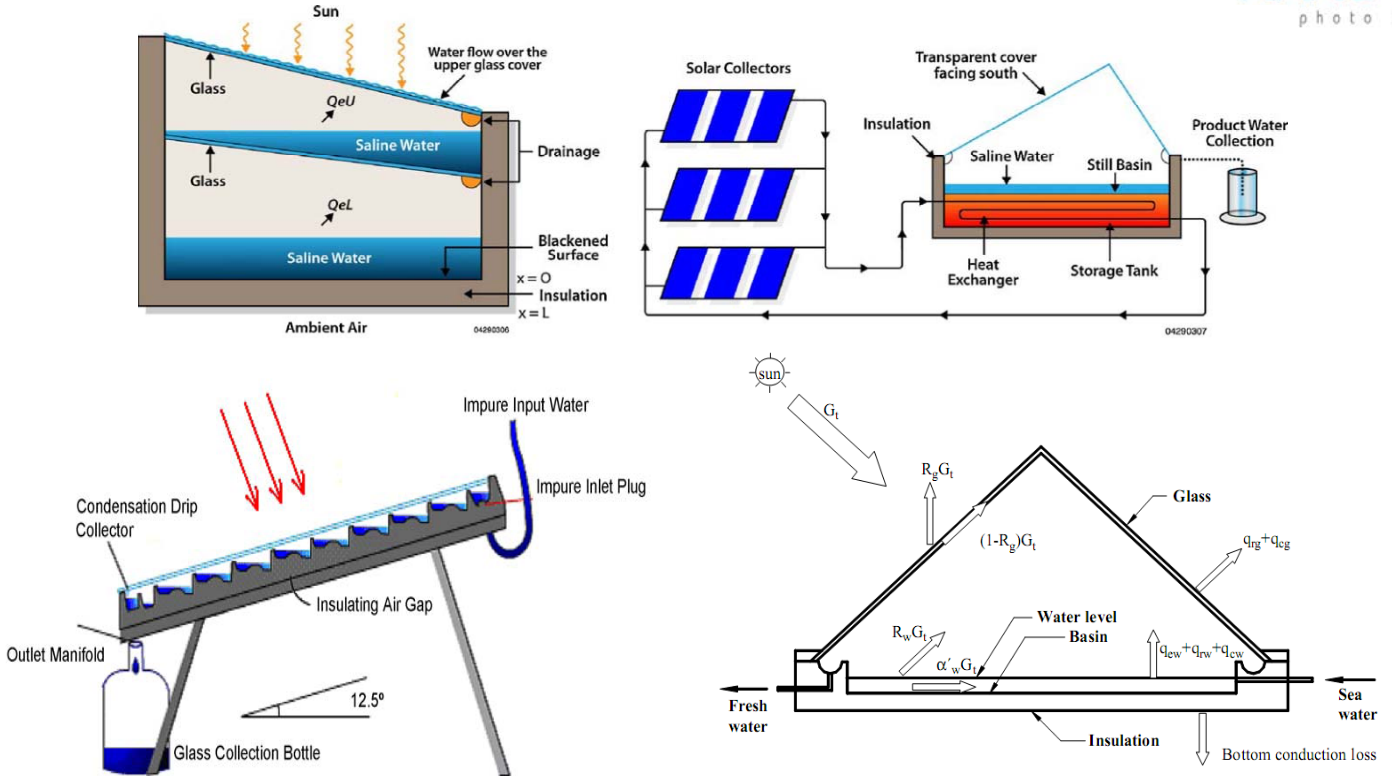


Figure (3): Schematic diagrams of a simple solar still.

- *The promise of nanotechnologies for water treatment*

The use of nanotechnologies in Water could be in monitoring, desalinization, purification and waste water treatment. This, in theory, plays a large role in averting future water shortages. But hoping that the 'magic' of nanotechnology will solve all water problems is still far away to be true, because of the basic problems of accessibility to technologies, affordability, and nanotechnology-based applications are still in R&D stage. None of them has been scaled up to industrial levels yet [8,9].

Nanomaterials have a number of key physicochemical properties that make them particularly attractive as separation media for water purification. On a mass basis, they have much large surface areas than bulk particles. Nanomaterials can also be functionalized with various chemical groups to increase their affinity toward a given compound. They can also serve as high capacity/selectivity and recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/anions in aqueous solutions. Nanomaterials also provide unprecedented opportunities to develop more efficient water-purification catalysts and redox active media due their large surface areas and their size and shape-dependent optical, electronic and catalytic properties [10,11]. Nanomaterials are also being used to develop chlorine-free biocides through functionalization with chemical groups that selectively target key biochemical constituents of waterborne bacteria and viruses [10].

Nanotechnology would provide novel opportunities to develop more efficient and cost effective nanostructured and reactive membranes for water purification and desalination. Nanomaterials which could be used in water purification and desalinations includes metal, metal oxides nanoparticles, Graphene and carbon nanotubes. For combined water desalination, solar energy and nanotechnology, nanotechnology could enhance the performance of solar concentrator which collect the solar energy and focus the light into the target. Also, nanomaterials could absorb light efficiently and transfer it into solar heat.

• *Plasmonic Nanomaterials*

Studying metallic nanoparticles attracts great interest because of their unusual chemical and physical properties which make them suitable for many technological applications such as catalysis, electronics, optics, and biotechnology. From the technological point of view, the capability of tuning their optical and the electronic properties gradually by controlling the particle size and shape make them unique systems.

Metallic nanoparticles exhibit a very strong UV-VIS absorption band that is not present in the spectrum of the bulk metal. This absorption band is due to the collective excitation of the conduction electrons when the size of the particles is less than the mean free path of the electron in the metal. This is known as the *localized surface plasmon resonance* (LSPR).

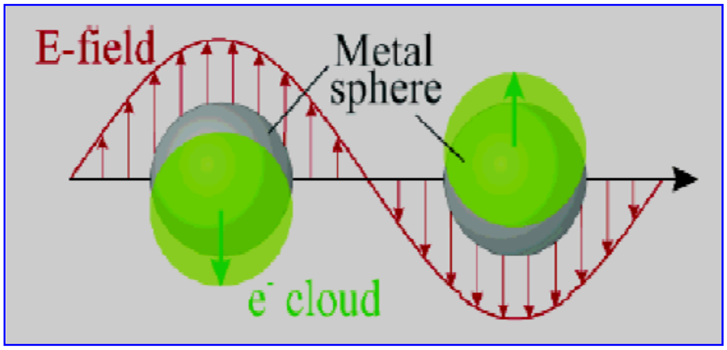


Figure (4): Sketch explains simply the surface plasmon absorption. The electric field of the incident light induces a polarization of the free surface electrons with respect to the heavier ionic core. The dipolar coherent oscillation of the free surface electrons is called plasmon band.

Localized surface plasmon resonances can be supported by a wide variety of structures. Individual particles can take shapes ranging from the simple sphere to ellipsoids, rods, stars, and crescents. Particle size and shape are even more important in determining the position of the resonance [12]. As the size of the particle increases there is an increase in the amount of absorption and scattering, both of which contribute to the optical extinction of a metallic nanoparticle. Also, as the size increases scattering takes over from absorption as the dominant contribution to the extinction, and there is a change in the position and width of the LSPR. The rod shaped gold nanoparticles have two absorption bands. The first one, which appears at 520 nm, corresponds to the oscillation of the electrons perpendicular to the long rod axis and so called transverse plasmon absorption. This band is insensitive to the nanorod length, and coincides with the surface plasmon absorption band of the gold nanospheres. The other absorption band appears at a lower energy and is caused by the oscillation of the free electrons along the long rod axis and is known as longitudinal surface plasmon absorption [13]. **Figure 5** shows the absorption spectra of the spherical and rod shape gold nanoparticles and their TEM images. This longitudinal plasmon band is very sensitive to the aspect ratio of the rods. By increasing the aspect ratio, the band shifted to a lower energy.

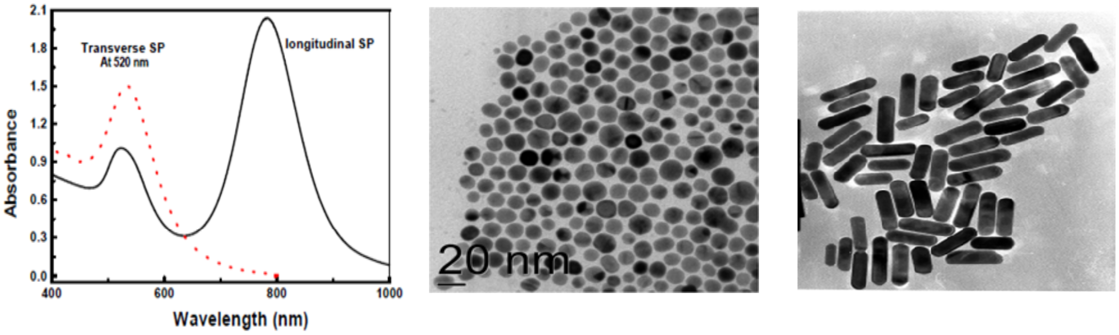


Figure (5): Dependence of the surface plasmonic resonance on the particle shape

- ***Graphene:***

Graphene sheet is an infinite two-dimensional layer consisting of sp^2 hybridized carbon atoms (Figure 6), which belongs to one of the five 2D Bravais lattices called the hexagonal (triangular) lattice. It is noteworthy that by piling up graphene layers, in an ordered way, one can form 3D graphite. Graphene was initially considered as a theoretical building block used to describe the graphite crystal, and to study the formation of carbon nanotubes (rolled graphene sheets), and predict their fascinating electronic properties. This 2D atomic (one atom thick) crystal of carbon has as fingerprint a unique electronic structure with linear dispersion close to the Fermi level [14].

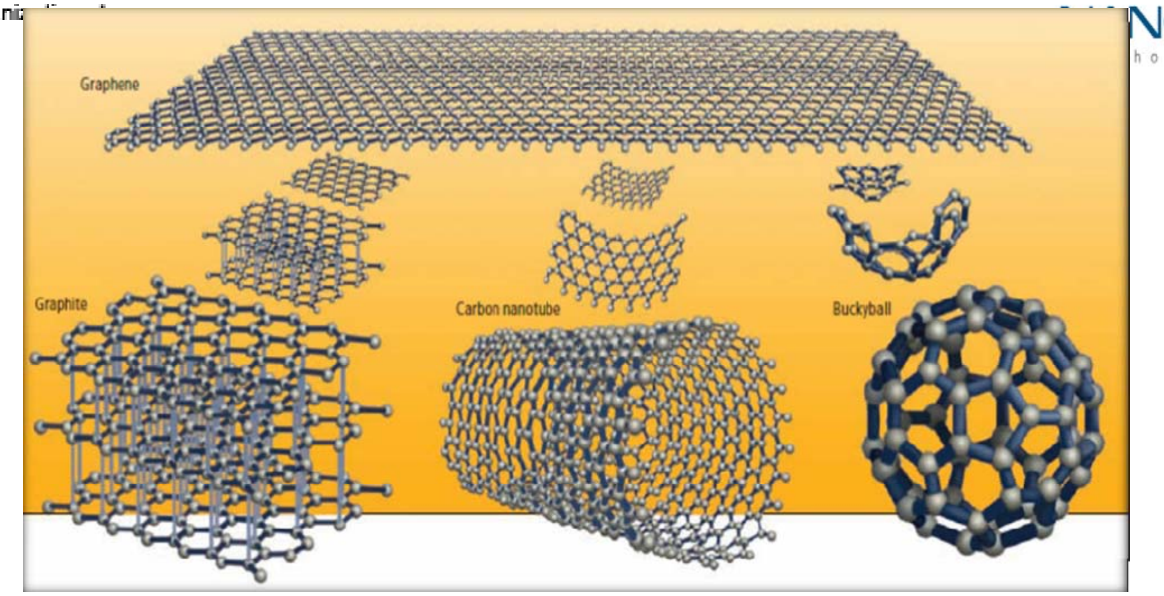


Figure (6): Graphene (top), a plane of carbon atoms that resembles of honeycomb, is the basic building block of all the “graphitic” materials depicted below. Graphite (bottom row at left), the main component of pencil “lead,” is a crumbly substance that resembles a layer cake of weakly bonded graphene sheets. When graphene is wrapped into rounded forms, fullerenes result. They include honeycombed cylinders known as carbon Nanotubes (bottom row at center) and spherical soccer ball– shaped molecules called buckyballs (bottom row at right).

Charge carriers in graphene are better described as massless Dirac fermions, which result in new phenomena. There are other pseudo-2D sp^2 hybridized carbon structures, such as bilayer- and few-layer-graphene, which exhibit particular properties that are different from both graphene and graphite (Figure 7). Whenever these structures exhibit AB stacking they will be referred as graphitic stacks. This distinction is made because it has been demonstrated that the properties of graphene can be recovered in systems with several sp2 hybridized carbon layers when stacking disorder is introduced. However, the physicochemical properties of graphene appear to be very different from bilayer graphene and few-layer graphene. Therefore, it is also important to include these two graphene categories in this review (see below and Figure 7) [14].

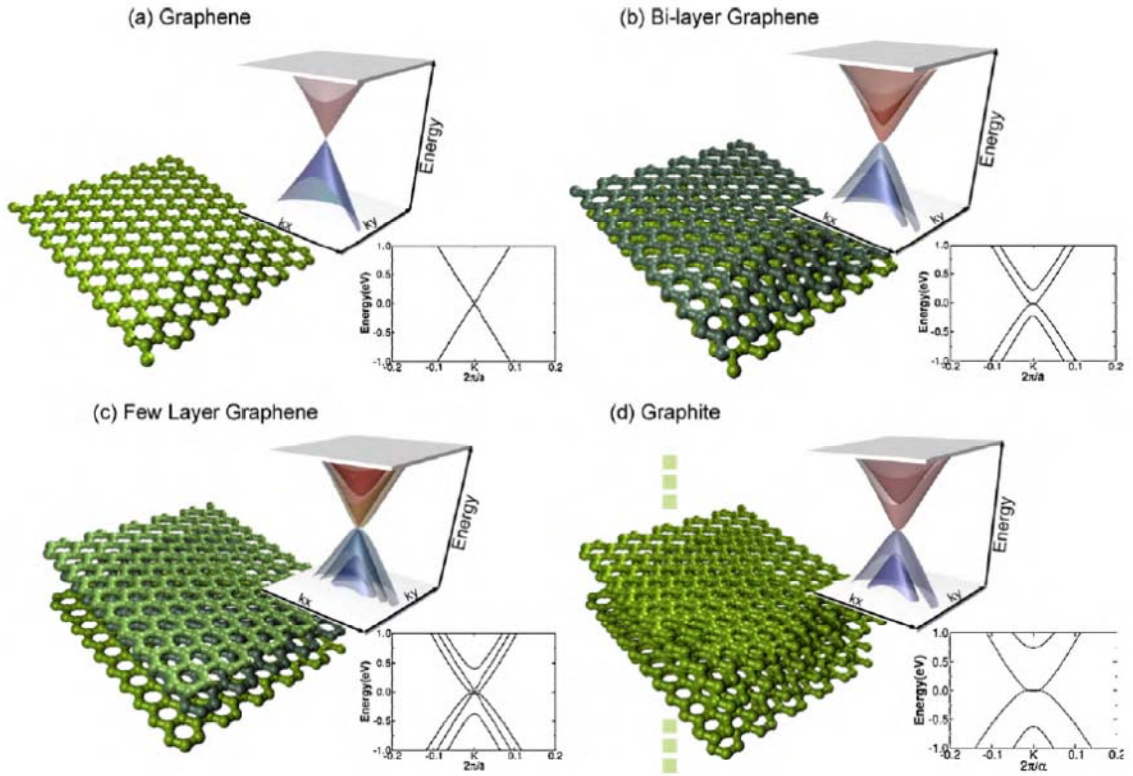

(a) Graphene
(b) Bi-layer Graphene
(c) Few Layer Graphene
(d) Graphite

Figure (7): Low energy DFT 3D band structure and its projection on kx close to *k* point K (π/a*[2/3, 0.0 0.0]) for (a) graphene, (b) bilayer graphene, (c) trilayer graphene and (d) graphite.

Theoretical work has been proposed regarding the possibility of stable flat sp^2 hybridized carbon sheets containing pentagons, heptagons and hexagons, termed Pentaheptite (2D sheets possessing heptagons and pentagons only) [15] or Haeckelites (2D crystals containing pentagons, heptagons and/or hexagons: Figure 7) [16]. These flat structures are intrinsically metallic and could exist in damaged or irradiated graphene. However, further experiments are needed in order to produce them and identify them successfully. Some synthesis routes to graphene started to be reported in 2001, using heat treatments, at 1600 ◦C of diamond nanoparticles over HOPG [17]. However, extensive studies on graphene started only after Novoselov et al. [18] were able to isolate graphene sheets using a simple micromechanical exfoliation method placing scotch-tape over commercial HOPG.

- ***Properties of graphene and few-layered graphene***

The electronic properties of graphene change with the number of layers and by the relative position of atoms in adjacent layers (stacking order). For bilayer graphene, the stacking order can be either AA, with each atom on top of another atom; or AB, where a set of atoms in the second layer sits on top of the empty center of a hexagon in the first layer. As the number of layers increase, the stacking order can become more complicated. For graphite, there are three common types of stacking: (i) AB or Bernal stacking, (ii) ABC or rhombohedral stacking, and (iii) no discernible stacking order or turbostratic stacking. The most stable stacking is AB, thus it has been studied more than other graphene-based stacks. However, the other stacking orders are certainly possible, especially in few-layer graphenes, and remain to be studied in detail. In fact, it has been recently found that bilayer graphene often exhibits AA stacking [19].

The thermal properties of graphene have been recently measured by Balandin, et al. [20], who found that a suspended graphene sheet obtained by mechanical exfoliation could exhibit extremely high thermal conductivity values ranging from $(4.84\pm0.44)\times10^3$ to $(5.30\pm0.48)\times10^3$ W/mK; higher than experimental values for carbon nanotubes and diamond. However, more recent experimental results on CVD grown suspended graphene indicate lower values (~2500W/mK) [21]. Nevertheless, these outstanding thermal properties could be exploited in the fabrication of heat dissipaters and polymer composites with high thermal conduction.

Carbon is a versatile adsorbent that is heavily used in the removal of various pollutants including heavy metals from aqueous solutions [22,23-27]. Various forms of carbon and their composites have been investigated to improve the adsorption efficacy [9-12]. Carbon nanotubes (CNTs) have shown exceptional adsorption capability and high adsorption efficiency for various organic pollutants such as benzene [14], 1,2-dichlorobenzene [28], trihalomethanes [29] and polycyclic aromatic hydrocarbons (PAHs) [30]. CNTs were found to be superior sorbents for inorganic pollutants such as fluoride [31], and several divalent metal ions [32–38]. Li et al. [37] reported that CNTs with more defects and poor quality possess higher surface area and exhibit better lead sorption capacity compared to aligned CNTs. Activation of CNTs plays an important role in enhancing the maximum sorption capacity. Activation causes modification in the surface morphology and surface functional groups and causes removal of amorphous carbon. Activation of CNTs under oxidizing conditions with chemicals such as HNO_3, $KMnO_4$, H_2O_2, NaOCl, H_2SO_4, KOH, and NaOH have been widely reported [30,39,40,41]. During activation, the metallic impurities and catalyst support materials are dissolved and the surface characteristics are altered due to the introduction of new functional groups [37,39-42].

Graphene can be considered as an ideal membrane since its thickness is only one carbon diameter. In this study, using molecular dynamics simulations, we investigate water transport through a porous graphene membrane and compare the results with water transport through thin (less than 10 nm in thickness/ length) carbon nanotube (CNT) membranes. For smaller diameter pores, where a single-file water structure is obtained, CNT membranes provide higher water flux compared to graphene membranes. For larger diameter pores, where the water structure is not single-file, graphene membranes provide higher water flux compared to CNT membranes [44].

Graphene sheets is also strong absorber, because of its balck color, it absorbs at the whole sun spectrum. The advantage of graphene is its low price and chemical stability.

Methods and procedures

1. *Fabrication of plasmonic nanomaterials of different shape*

Recently, Mohamed et al [45] optimized the microwave method to produce gold particles with desired shape and size distribution. Microwave irradiation (MWI) is one of the most promising techniques for the preparation of nanomaterials with controlled size and shape since neither high temperature nor high pressure are needed [45] The main advantage of MWI over other conventional heating methods is heating the reaction mixture uniformly and rapidly. Due to the difference in the solvent and reactant dielectric constants, selective dielectric heating can provide significant enhancement in the transfer of energy directly to the reactants which causes an instantaneous internal temperature rise. By using metal precursors that have large microwave absorption cross-sections relative to the solvent, very high effective reaction temperatures can be achieved. This allows the rapid decomposition of the precursors thus creating highly supersaturated solutions where nucleation and growth can take place to produce the desired nanocrystalline products. Since in MWI it is possible to quench the reaction very early on (~10 s), this provides the opportunity of controlling the nanostructures from small spherical nuclei to short rods to extended assemblies of nanowires by varying the MWI reaction time and the relative concentrations of different organic surfactants with variable binding strengths to the initial precursors and to the nanocrystals.

Using Mohamed's method [45] the size, shape and morphology of the nanocrystals could be tailored by varying the ratio of capping agent oleylamine to oleic acid, the microwave time, and the concentration of the gold ions (**Figure 8**). They were able to obtain, spheres, rods, prism, and stars.

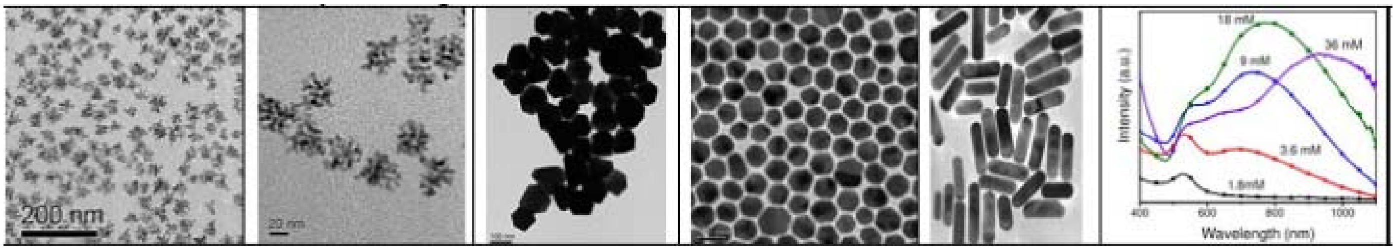


Figure (8): TEM images of different shapes of gold including; flowers, pyramids, hexagons, and rods by using Mohamed et al., and their absorption spectra.

The photothermal properties of these plasmonic materials will be investigated using femtosecond laser spectroscopic technique. The best photothermal material will be chosen in order to be used for water desalination.

2. *Fabrication of Graphene sheets*

Graphene will be made by two different methods:

- ***Chemical reduction method***

The most powerful method for production of graphene is using colloidal suspensions of graphite oxide. This approach is both scalable, affording the possibility of high-volume production, and versatile in terms of being well suited to chemical functionalization. These advantages mean that the colloidal suspension method for producing graphene could be used for a wide range of applications. In this method powdered flake graphite is oxidized using strong oxidizing agents such as potassium permanganate and hydrogen peroxide in presence of sodium nitrate and by carful treatment yellow-brown cake was finally collected indicated of formation of grapheme oxide [46]. Several reducing agents could be used to reduce graphene oxide into graphene such as hydrazine hydrated [47].

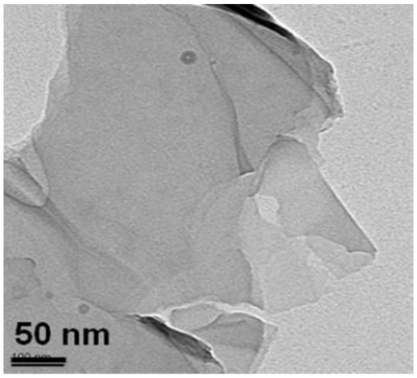


Figure (10): TEM images of prepared Graphene by the reduction of Graphene oxide

Plasmonic Graphene nanocomposites:

Gold nanoparticles have been prepared via reduction of gold ions using sodium citrate as reducing and capping material**.** Figure 8 shows the absorption spectra and the TEM images of the prepared sample. The histogram indicates that the average size of the prepared particles is about 13 nm.

Figure 11: A) TEM images of the gold nanoparticles, b) histogram indicate the average particle size and C) the absorption spectra of the gold nanoparticles

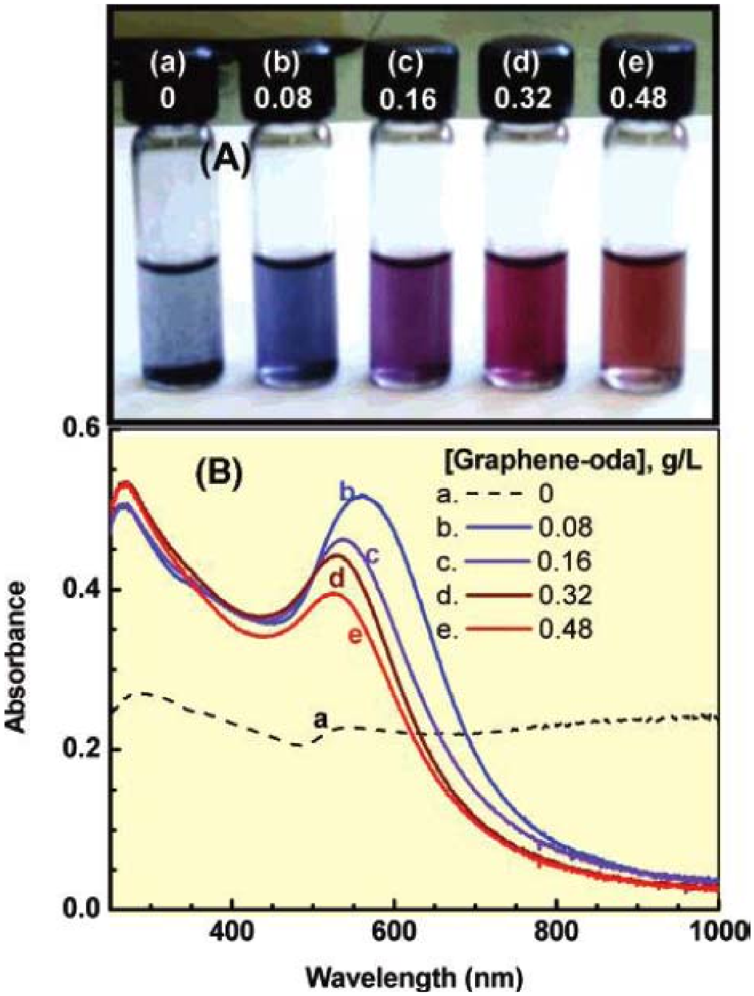


Figure 12: Photograph (top) and absorption spectra (bottom) of 1 microgram of gold nanoparticles in THF containing different concentrations of Graphene

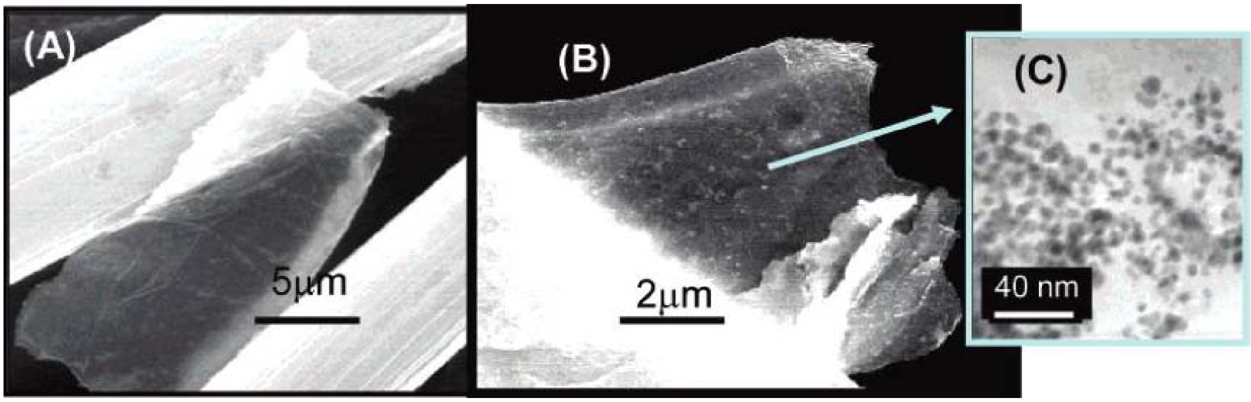


Figure 13: SEM and TEM images of the Gold-Graphene nanocomposite at different magnifications

Lab-scale testing of the concept of using Graphene –gold or graphene silver nanocomposites as an efficient photothermal material for water desalination has been carried out in simple destilation sytem as shown in Figure 11. In this method, a mixture contains 0.1 g of Graphen contain 50 Microgram of gold particles have been added to one liter of Sea water, and exposed to sun light in the following simple water distillation system as shown in Figure 14.

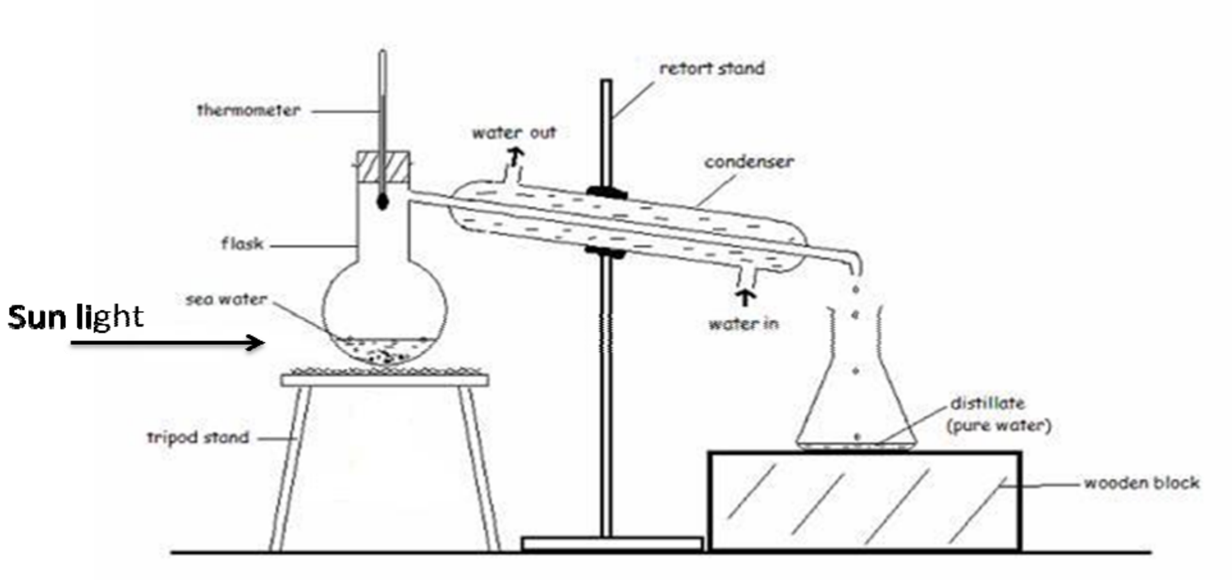


Figure 14: Schematic diagram for simple water distillation system

Upon testing these materials as a photoabsorber and photothermal materials, our measurements indicate that the temperature rise up till 104 ^{0}C upon adding our nanocomposite and exposure to halogen lamp for 40 minutes. Using sun light, it rises up to 64 C. Figure 15 shows the rate of temperature rise upon exposure into light from halogen lamp after adding different nanomaterials. It is clear that mixture of gold and graphene is much more efficient than plasmonic nanomaterials alone.

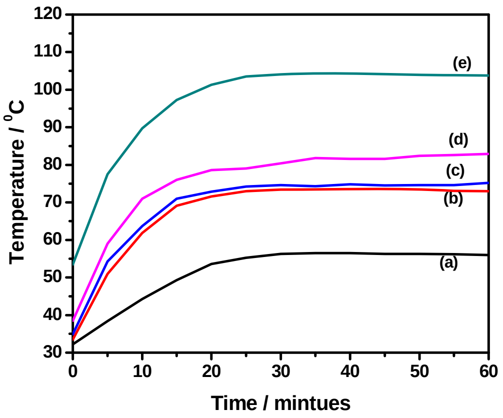


Figure 15: Sea Water as control, b) Sea water + silver nanoparticles, c) Sea water + gold nanoparticles, d) Sea Water +Graphene, e)Sea water + mixture of Graphene and gold particles

Water Quality insurance:

The obtained water via desalination using graphene nanocomposite has been tested chemically and biologically. All chemical testing has been carried out according to the standard international protocols in order to determine water quality such as: Salinity, pH, dissolved oxygen test, hardness, heavy metal content, and the total amount of phosphate, sulphate and carbonate ions. Our result indicates that our obtained water is totally pure and free from all salts, metal ions and heavy metals.

Water quality	Our obtained desalinated Water	Drinking water
PH	7	6.8
Calcium content	Zero	50 ppm
Chlorine content	zero	100 ppm
Oxygen	1.5%	2.2%
Sulphate ions	Zero	20 ppm
Mg ions	Zero content	30 ppm
Salinity	Zero	0.03 %
Hardness	zero	2%

Many protozoa, bacteria, viruses, algae and fungi are found in natural water systems. Some are pathagenic (typhoid, cholera and amoebic dysentry can result from water-borne pathogens). The excessive growth of algae (called 'algal bloom') can degrade water quality because it lowers dissolved oxygen levels thereby killing other living things. The level of bacterial contamination of water due to animal waste is measured by determining the number of coliform organisms such as E. coli. The obtained distillated water using our methodology was examined under optical microscopy and using Cell count reader in order to determine if there is any type of micro-organism or bacteria exsit in our water sample. This biological testing indicate that the water is totally clean and it does not have any micro-organism. That might be because of the photothermal effect of the nanocomposites which raise the temperature and cause bacteria death. Or because of the presence of silver nanoparticles which has super antiseptic and anti-bacterial activity.

1.d Environmental precautions of Nanomaterials used for water desalination

The development of nanomaterials not only provides many benefits to diverse scientific fields but also poses potential risks to humans and the environment. For the successful application of nanomaterials in water desalination, it is essential to understand the biological fate and potential toxicity of these nanoparticles. The aim of this study was to evaluate in vivo potential toxicity of biocompatible magnetic nanoparticles to enable their diverse applications in life science, such as drug development, protein detection, and gene delivery. Biocompatible silver nanocomposites with graphene synthesized by chemical method.

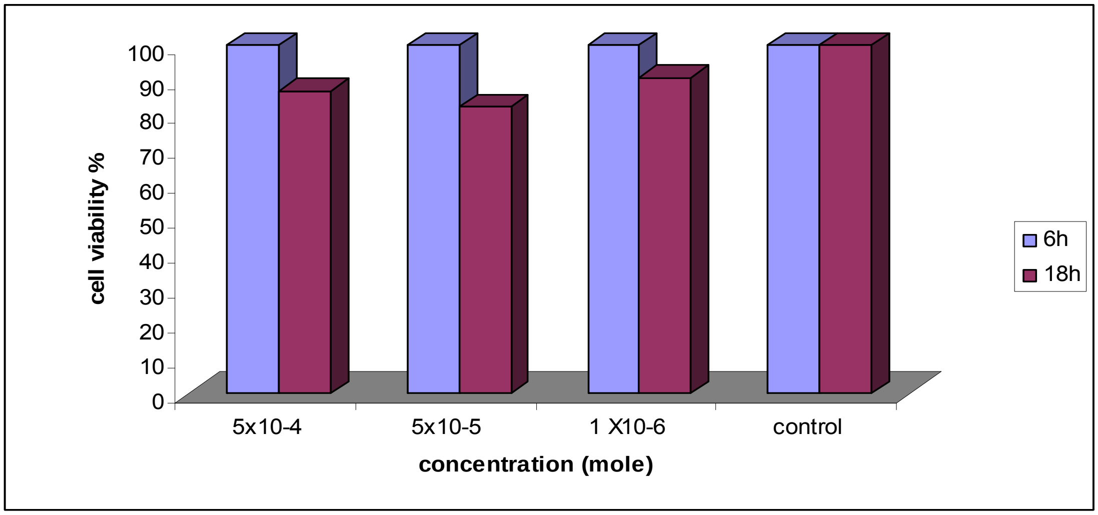


Figure 16: Cytotoxicity of Graphene silver nanocomposites

These data clearly indicates that our nanocomposites did not showed any cells toxicity for 6 hours incubation period even at relatively high concentrations (0.05 mM). However, at 18 hours incubation period, low toxicity (cells death) was detected at different concentration range from 5% to 15%.

The results suggest that these silver Graphene nanocomposites do not have any cytotoxcity in the dark. More research work need to be done to study the effect of light on the cell viability.

For *in vivo* study, experimental animals rats were used. Where intraperitoneal administration of different doses of nanoparticles ranged from 1pp up to 2000 ppm into rats, the acute, subacute and subchronic toxicity were evaluated. It was observed that, during these intervals, metallic nanocomposites did not induce any abnormal clinical signs in the laboratory animals and the LD_{50} cannot be established within the administered doses. In addition, the Biochemical, hematological and histopathological investigations indicated that, there was a slight inflammatory response during the acute stage in the treated groups especially those administered high doses compared to the control group. This observation was decline through the subacute stage and completely recovered at the end of the subchronic stages. Also it is observed that, silver nanocomposites have no significant adverse effects on the normal animal growth as was reflected by normal body weight increase. Bone marrow of the treated rats was examined for any abnormality, there was no abnormity observed in the morphology and count of bone marrow cell under the histopathological and hematological examination. Taken together all of these finding, we could conclude that silver-graphene nanocomposites did not cause apparent in vivo toxicity in rats within this concentration range.

References:

1. G. M. Rios, Nanotechnologies and membrane engineering at the core of water and related questions in the Mediterranean and Middle-East countries, Options Méditerranéennes, A n° 88, 2009 - Technological Perspectives for Rational Use of Water Resources in the Mediterranean Region.
2. Using Desalination Technologies for Water Treatment, Background paper, March 1988, NTIS order #PB88-193354
3. L. Wagner, "Water desalination – Tap into the liquid Gold", Research report, MORA ASSOCIATES, December 2007.
4. http://www.solaqua.com/solstilbas.html
5. A. Al-Karaghouli, D. Renne, L.L. Kazmerski, Solar and wind opportunities for water desalination in the Arab regions, Renewable and Sustainable Energy Reviews 13 (2009) 2397–2407.
6. Al-Hayek I, Badran OO. The effect of using different designs of solar stills on water distillation. Desalination 2004;169:121–7.
7. J Gordes, Understanding Solar Stills, Technologies for development, Volunteers in Technical Assistance (VITA) (1985) [Technical Paper].
8. J. Theron, J. A. Walker and T. E. Cloete, Nanotechnology and Water Treatment: Applications and Emerging Opportunities, Critical Reviews in Microbiology, 34 (2008) 43-69.
9. Thembela Hillie & Mbhuti Hlophe, Nanotechnology and the challenge of clean water, Nature Nanotechnology 2, 663 - 664 (2007)
10. Amira A. El-Adly, Waled M. El-Senousy, Farag A. Samhan and Mona B. Mohamed, Photothermal Efficiency of Gold Nanorods in Controlling Microorganisms in Water, Journal of Applied Sciences Research, 4(12): 1811-1816, 2008
11. Rehab M. Amin, Mona B. Mohamed, Marwa A. Ramadan, Thomas Verwanger, and Barbara Krammer, Rapid and sensitive microplate assay for screening the effect of silver and gold nanoparticles on bacteria, Nanomedicine (2009) 4(6), 637 – 643
12. A. J. Morfa, T. H. Reilly, J. C. Johnson, and J. v. de Lagemaat, "Plasmons in solar energy conversion", SPIE 10.1117/2.1200906.1651 (2009).
13. Mie, G. Ann. Phys, 1908, 25, 329.
14. Mauricio Terrones et al., Graphene and graphite nanoribbons: Morphology, properties, synthesis, defects and applications (Review), Nano Today (2010) 5, 351—372.
15. V.H. Crespi, L.X. Benedict, M.L. Cohen, S.G. Louie, Phys. Rev. B 53 (1996) R13303.
16. H. Terrones, M. Terrones, E. Hernandez, N. Grobert, J.C. Charlier, P.M. Ajayan, Phys. Rev. Lett. 84 (2000) 1716.
17. A.M. Affoune, B.L.V. Prasad, H. Sato, T. Enoki, Y. Kaburagi, Y. Hishiyama, Chem. Phys. Lett. 348 (2001) 17.
18. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.
19. Z. Liu, K. Suenaga, P.J.F. Harris, S. Iijima, Phys. Rev. Lett. 102 (2009) 015501.
20. A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Nano Lett. 8 (2008) 902.

21. W. Cai, A.L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, R.S. Ruoff, Nano Lett. 10 (2010) 16451.
22. M. Zabihi, A. Ahmadpour, A. Haghighi Asl, Removal of mercury from water by carbonaceous sorbents derived from walnut shell, J. Hazard. Mater. 167 (2009) 230-236.
23. S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219-243.
24. M. Goyal, M. Bhagat, R. Dhawan, Removal of mercury from water by fixed bed activated carbon columns, J. Hazard. Mater. 171 (2009) 1009-1015.
25. A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review, J. Hazard. Mater. 167 (2009) 1-9.
26. J.M. Nabais, J.A. Gomes, Suhas, P.J. Carrott, C. Laginhas, S. Roman, Phenol removal onto novel activated carbons made from lignocellulosic precursors: Influence of surface properties, J. Hazard. Mater. 167 (2009) 904-910.
27. M. Imamoglu, O. Tekir, Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks, Desalination 228 (2008) 108-113.
28. X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian and Z. Jia, Chem. Phys. Lett., 376(1–2) (2003) 154–158.
29. C. Lu, Y. Chung and K. Chang, Wat. Res., 39(6) (2005) 1183–1189.
30. K. Yang, X. Wang, L. Zhu and B. Xing, Environ. Sci. Technol., 40(18) (2006) 5804–5810.
31. Y. Li, S. Wang, X. Zhang, J. Wei, C. Xu, Z. Luan and D. Wu, Mater. Res. Bull., 38(3) (2003) 469– 476.
32. C. Lu and C. Liu, J. Chem. Technol. Biotechnol., 81 (2006) 1932–1940.
33. Y. Li, S. Wang, J. Wei, X. Zhang, C. Xu, Z. Luan, D. Wu and B. Wei, Chem. Phys. Lett., 357(3–4) (2002) 263–266.
34. Y. Li, S. Wang, Z. Luan, J. Ding, C. Xu and D. Wu, Carbon, 41(5) (2003) 1057–1062.
35. Y. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu and B. Wei, Carbon, 41(4) (2003) 2787–2792.
36. Y. Li, Z. Di, J. Ding, D. Wu, Z. Luan and Y. Zhu, Wat. Res., 39(4) (2005) 605–609.
37. Y.H. Li, Y. Zhu, Y. Zhao, D. Wu and Z. Luan, Diamond Relat. Mater., 15 (2006) 90–94.
38. C. Chen and X. Wang, Ind. Eng. Chem. Res., 45(26) (2006) 9144–9149.
39. E. Raymundo-Pinero, T. Cacciaguerra, A. Simon and F. Beguin, Chem. Phys. Lett., 412(1–3) (2005) 184–189.
40. E. Raymundo-Pinero, P. Azaïs, T. Cacciaguerra, D. Cazorla-Amoros, A. Linares-Solano and F. Beguin, Carbon, 43(4) (2005) 786–795.
41. T.S. Sreeprasad, Shihabudheen M. Maliyekkal, K.P. Lisha, T. Pradeep, Journal of Hazardous Materials, Accepted 23-11-2010.
42. Venkata K.K. Upadhyayula, Shuguang Deng, Martha C. Mitchell, Geoffrey B. Smith, Science of the Total Environment 408 (2009) 1–13
43. K.L.Kelly,E.Coronado,L.L.Zhao,andG.C.Schatz,"The optical Properties of metal nanoparticles: The influence of size, shape,and dielectric environment,"J.Phys.Chem.B 107,668–677(2003).
44. Myung E. Suk and N. R. Aluru, J. Phys. Chem. Lett. 2010, 1, 1590–1594

45. Mona B. Mohamed, Khaled M. AbouZeid, Victor Abdelsayed, Ahlam A. Aljarash, and M. Samy El-Shall, ACS Nano 4 (5), (2010) pp. 2766
46. HummersJr, W. S.; Offeman, R. E., Preparation of Graphitic Oxide. Journal of the American Chemical Society 1957, 80, 1339.
47. Gao, X. F.; Jang, J.; Nagase, S., Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design. Journal of Physical Chemistry C 2010, 114 (2), 832-842.
48. H. M. A. Hassan, V. Abdelsayed, A. S. Khder, K. M. AbouZeid, J. Terner and M. S. El-Shall, J. Mater. Chem., **19**, 3832-3837 (2009).