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Chapter 18

Nanotechnology Solutions for Global Water Challenges

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The lack of clean and safe drinking water is responsible for more deaths than war, terrorism and weapons of mass destruction combined. This suggests contaminated water poses a significant threat to human health and welfare. In addition, standard water disinfection approaches such as sedimentation, filtration, and chemical or biological degradation are not fully capable of destroying emerging contaminants (e.g. pesticides, pharmaceutical waste products) or certain types of bacteria (e.g. *Cryptosporidium parvum*). Nanomaterials and nanotechnology based devices can potentially be employed to solve the challenges posed by various contaminants and

microorganisms. Nanomaterials of different shapes, namely nanoparticles, nanotubes, nanowires and fibers have the ability to function as adsorbents and catalysts. These possess an expansive array of physicochemical characteristics deeming them highly attractive for the production of reactive media for water membrane filtration, a vital step in the production of potable water. As a result of their exceptional adsorptive capacity for water contaminants, graphene based nanomaterials have emerged as an area of significant importance in the area of membrane filtration and water treatment. In addition, Advanced Oxidation Processes (AOPs) together with or without sources of light irradiation or ultrasound, have been found to be promising alternatives for water treatment at near ambient temperature and pressure. Furthermore, the uses of visible light active titanium dioxide photocatalysts and photo-Fenton processes have shown significant potential for water purification. A wide variety of nanomaterial based sensors, for the monitoring of water quality, have also been reviewed in detail. In conclusion, the rapid and continued growth in the area of nanomaterial based devices offers significant hope for addressing future water quality challenges.

Introduction

The availability and steady supply of drinking water is more and more difficult to achieve and this is becoming increasingly challenging, particularly in the developing world. It was estimated that in 2010 there were 748 million people throughout the world without access to improved water sources for drinking and many more rely on water that is not safe to drink due to contamination with pathogenic microorganisms (1). Polluted water constitutes a major threat to human health and welfare (2). According to the World Health Organization (WHO), 2 million people die every year from diarrheal diseases, attributed to unsafe water, sanitation and hygiene. Millions of people are exposed to unsafe levels of naturally occurring arsenic and fluoride in water, which can result in cancer and skeletal damage. Indeed, a report published in the medical journal *The Lancet* asserted that poor water sanitation and a lack of safe drinking water results in a greater number of deaths than war, terrorism and weapons of mass destruction combined (3). Furthermore, the reuse of wastewater is becoming increasingly important due to water scarcity throughout the globe, and it is vital to ensure that water for reuse is free from pathogenic microorganisms, especially for food-crop irrigation and recharge of aquifers. Solar energy is free and ubiquitous on the Earth's surface and the exposure of contaminated water to solar irradiation can make water safer to drink through the inactivation of pathogenic microorganisms by a combination of ultraviolet (UV) photolytic mechanisms (direct and indirect) and an increase in temperature. Many countries have started working on various

filtration systems to separate drinking water from dissolved ions, for example, sodium chloride from sea water, arsenic type carcinogenic chemical elements from ground water *etc.* Nanomaterial based composites are upcoming materials within the area of water filtration. For instance, the creation of nanopores in graphene and graphene oxide (GO) membranes makes them a very promising material for future water technologies, especially in the areas of desalination, water purification and arsenic removal. However, several challenges have to be met such as controlled creation of nanopores, maintaining the structural properties of nanomaterials, selective exclusion of ions from water *etc.* One of the major priorities of environmental monitoring today is the rapid and accurate detection of contaminants in water (4, 5). Therefore, it is of critical importance to develop robust, cost effective water cleaning devices and sensors that can accurately and rapidly detect and decontaminate the wide range of water contaminants, including heavy metal cations, organic pollutants and pathogenic bacteria and their toxins. In addition, the challenges posed in developing sensors include the extremely low concentrations of certain contaminants in water and the complexity of the water matrix. A number of nanotechnological solutions to address these challenges are described in the following sections.

Solar Disinfection of Water

The solar disinfection (SODIS) method is a protocol for the application of solar disinfection for drinking water (Figure 1). Clear 1-2 L polyethylene terephthalate (PET) bottles are filled with raw water and then exposed to the sun for 6-8 h (one day of sunshine) or two consecutive days in cloudy conditions. The SODIS water will possess a reduced load of pathogens and therefore be safer to drink. SODIS is recognized by the WHO as an appropriate Household Water Treatment intervention for the disinfection of water, particularly in regions where lack of access to safe water is an issue, including emergency situations. It is estimated that SODIS is currently being used by nearly more than 5.5 million people around the world, mainly in the developing regions of Asia, Africa and Latin America. SODIS has been compared with other household water treatment and storage methods and it was found that SODIS was slightly less cost-effective when compared to chlorination; however, the latter requires the distribution of sodium hypochlorite or chlorine tablets, whereas solar energy is widely and freely available (6).

Photocatalytic Enhancement of Solar Disinfection

Photocatalysis is the acceleration of a photoreaction by the presence of a catalyst. When a semiconductor (*e.g.* titanium dioxide (TiO_2)) is irradiated with electromagnetic radiation of wavelength equal to or greater than its band gap, the absorption of photons gives rise to the formation of electron-hole pairs (e^- and h^+) in the semiconductor. These charge carriers can recombine with the energy being

re-emitted as light or heat, or they may migrate to the catalyst surface. If the charge carriers reach the semiconductor particle surface they may participate in redox reactions. In the presence of water and oxygen (O_2), the redox reactions at the surface of the photocatalyst will result in the production of reactive oxygen species (ROS). The ROS can not only destroy a large variety of chemical contaminants in water but also cause fatal damage to microorganisms (Figure 2).

Figure 1. SODIS process. (Reproduced with permission from reference (6). Copyright 2014 Royal Society of Chemistry.)

In 1985, Matsunaga *et al.* first reported the inactivation of bacteria using semiconductor photocatalysis (7). Since then, there have been a large number of research studies reporting the use of photocatalysis to inactivate microorganisms including bacteria (cells (8, 9), spores and biofilms (10), viruses (11), protozoa (12), fungi (13) and algae) (14). Photocatalytic disinfection has been reviewed by several researchers including Byrne *et al.* (15), McCullagh *et al.* (16), Malato *et al.* (17) and Robertson *et al.* (18). The majority of published research papers have focused on the assessment of novel materials, new reactor systems or the effect of experimental parameters on the rate of inactivation. A number of studies have investigated the mechanism involving ROS and their interaction with the biological structures on or within the microorganisms, and the resulting

inactivation. Dalrymple *et al.* conducted a review of the mechanisms involved but concluded that the exact sequence of events leading to loss of viability is not completely clear (19). The hydroxyl radical ($\cdot\text{OH}$) has been suggested to be the primary radical species responsible for microorganism inactivation, however superoxide radical anion ($\text{O}_2^{\cdot-}$), hydroperoxyl radical ($\text{HO}_2^{\cdot}$) and hydrogen peroxide (H_2O_2) have also been shown to contribute (20). Unlike antibiotics, ROS attack is not specific to one site or an individual pathway and the development of bacterial resistance to photocatalysis is considered to be almost impossible.

Figure 2. Schematic representation of photocatalysis mechanism on a titanium dioxide (doped and undoped). (Reproduced with permission from reference (6). Copyright 2014 Royal Society of Chemistry.)

In photocatalysis, ROS attack the microorganism from the outside initially, and then inside, destroying the sensitive metabolic processes and genetic material. The resistance of the outer layers of the organism to ROS attack determines the ability of the organism to resist. The thick protein, carbohydrate and lipid structures surrounding protozoa and bacterial spores yield greater resistance to ROS attack, when compared to viruses, fungi and bacteria, with resistance to photocatalytic inactivation observed in that order respectively (18). Given the complexity in the structure of microorganisms it is clear why the complete mechanism of photocatalytic inactivation is still not fully understood. The accepted sequence of events, taking place during photocatalytic inactivation of microorganisms, is that prolonged ROS attack results in damage of the cell wall, followed by compromise of the cytoplasmic membrane and direct attack of intracellular components.

Nanocatalyst for Heterogeneous Advanced Oxidation Processes in Water Decontamination

In recent decades, AOPs, which use oxidants (ozone (O_3), O_2 , and/or H_2O_2) and/or catalysts (transition metals, iron, and semiconductor) together with or without sources of light irradiation or ultrasound, have been found to be promising alternatives for environmental remediation, especially for water treatment at near ambient temperature and pressure (21–24). Typical AOPs include $\text{H}_2\text{O}_2/\text{UV}$,

TiO₂/UV, ozone based processes (O₃/UV, O₃/H₂O₂, and catalytic ozonation), and those based on the Fenton or Fenton-like reactions. These technologies can produce highly reactive free radicals, such as the hydroxyl radical ($\cdot\text{OH}$) (25). The hydroxyl radical is the second strongest oxidant with an oxidation potential at 2.80 V. It is effective at destroying organic pollutants rapidly with second-order rate constants, usually in the range of 10^9 – 10^{10} M⁻¹ s⁻¹, and non-selectively with nearly all electron-rich organic compounds (26), such as hydrocarbons (23, 27), organic dyes (28, 29), antibiotics (30, 31), pesticides (32, 33), landfill leachates (34, 35), explosives (36–38), phenols (39, 40), and microbial contaminants (17, 41). Meanwhile, nanocatalysis is one of many practical applications of nanotechnology. Nanocatalysis involves the synthesis and function of catalytic materials at the nanoscale range (<100 nm) in the form of nanoparticles (NPs) or nanosize porous supports with controlled shapes and sizes (42). The introduction of nanocatalysts in heterogeneous AOPs has led to appreciable improvements in decontamination efficiency for water treatment due to their large specific surface area, where catalytic active sites are exposed (43). In this section, we discuss some important research studies and the application of nanocatalysts in heterogeneous AOPs for water decontamination in recent years.

Advances in Ozonation Applications while Employing Nanomaterials

Ozonation has been widely applied in water treatment throughout the world, especially for the treatment of various organic compounds (44–46). Through direct oxidation, ozone can react with organic pollutants, although it is relatively slow and selective; through indirect reaction, reactive radicals (mainly $\cdot\text{OH}$) can be generated *via* ozone decomposition in the presence of nanomaterials as catalysts for the degradation of different organics contaminants. However, the generation of $\cdot\text{OH}$ is pH dependent, which largely limits its application (47).

Catalytic ozonation, which includes homogeneous and heterogeneous catalytic ozonation, has been widely investigated in order to improve the treatment efficiency of organic pollutants. Currently, more efforts have been focused on heterogeneous catalytic ozonation. During heterogeneous catalytic ozonation, ozone can be activated using transition metal oxide catalysts to enhance the production of hydroxyl radicals. Moreover, nanomaterial based catalysts have shown a distinctive and significant potential for the enhancement of reaction kinetics and many nanomaterials have been investigated, including metal oxides, metals or metal oxides on supports (48, 49).

Catalytic ozonation with TiO₂ NPs was proven to provide significant improvement for nitrobenzene removal when compared with ozone alone which follows a hydroxyl radical based mechanism (50). ZnO NPs catalyzed ozonation was investigated by Tabatabaei *et al.* for the degradation of 4-nitrochlorobenzene (51). They found that a pH of 3 was the optimum pH for greatest removal efficiency. The effect of ZnO catalyst particle size on ozonation was examined in another study for the degradation of 2,4,6-trichlorophenol. This showed that the degradation efficiency follows the

order of nanometer>submicrometer>micrometer (52). Co_3O_4 NPs were also employed for catalytic ozonation during phenol degradation which showed higher catalyst activity in contrast to bulk Co_3O_4 material (53). Besides, the same study found that the reaction performed at 298 K was faster than that at 283 K or 313 K. Magnetic NiFe_2O_4 NPs synthesized by Zhao *et al.* was also employed for catalyzing ozonation during phenol degradation which can be recovered *via* calcination and ozonation (54). Another study investigated the role of magnetic spinel ferrites (MnFe_2O_4 and NiFe_2O_4) in catalytic ozonation during phenacetin removal, which demonstrated the magnetic properties and excellent catalytic activity of the new catalyst (55). Activated carbon coated with Fe_3O_4 NPs was also used as an ozonation catalyst for the degradation of phenol and was demonstrated to promote removal efficiency. The removal efficiency was highest at neutral pH (56). Moreover, nano- Fe_3O_4 -impregnated alumina particles was demonstrated to be effective and stable for catalyzing the ozonation of *para*-chlorobenzoic acid (57).

When using catalytic ozonation for the degradation of different organic compounds, catalysts would accelerate the generation of reactive radical species (*e.g.* $\cdot\text{OH}$) in the system which can eventually lower the selectivity of ozonation and improve the reaction efficiency for pollutant removal. Currently, the degradation efficiency and effectiveness of catalytic ozonation against some emerging contaminants, such as cyanotoxins, still requires further research.

Advances in Heterogeneous Fenton Processes Applied in Conjunction with Nanomaterials

The Fenton reaction, which was initially discovered by Fenton (1894) when using peroxides with iron ions for the oxidation of tartaric acid, has been developed into a variety of processes, including homogeneous Fenton process, heterogeneous catalysis, photo-Fenton process, electro-oxidation, photo-electro-oxidation process, sono-Fenton, sono-photo-Fenton, and sono-electro-Fenton (21–23). The principal Fenton reaction is shown in Eq. (1). At first, a mixture of ferrous iron and hydrogen peroxide in acidic solution produces the $\cdot\text{OH}$ (Eq. (1)). The generated ferric ions can be reduced by excess hydrogen peroxide to produce ferrous ion again and more radicals (Eq. (2)).

However, the homogeneous Fenton process is impractical to apply to *in situ* environmental remediation. In order to maintain a pH of approx. 2.8, a large amount of acid must be added to the reaction solution to avoid iron precipitation and production of a large amount of ferric hydroxide sludge. On the other hand, heterogeneous Fenton processes can mediate over a wide range of pH values in the presence of catalyst to prevent iron hydroxide precipitation (21). A wide range of solid catalysts have been investigated using the heterogeneous Fenton processes,

such as nano-zero valent iron (58), iron-containing zeolite (59), resin-supported Fe(II) or Fe(III) (60, 61), activated carbon loaded iron (62) or copper oxide metals (63), and iron-coated pumice particles (64). Among these catalysts, nanocatalysts have certain advantages since they have high specific surface area and therefore a greater number of active sites per unit mass accompanied by a low diffusional resistance, and also are easily accessible to target molecules (23). In the next two sub-sections, we summarize recent advances in the development of nanocatalysts in heterogeneous photo-Fenton and Fenton-like processes for water treatment.

Photo-Fenton Processes

A combination of ferrous or ferric iron with hydrogen peroxide under light irradiation can produce more $\cdot\text{OH}$ and increases the rate of decontamination in water treatment due to the photochemical regeneration of ferrous ions by photo-reduction (Eq. (3)) (65). However, the operating cost of photo-Fenton process is much higher in terms of energy and UV-lamp consumption. Besides, the photo-Fenton process requires all of the catalyst be accessible to light irradiation. Thus, several strategies have been investigated to minimize cost and improve efficiency by the application of nanocatalysts or solar energy.

The photo-Fenton reaction, employing zero valent iron NPs as a source of iron, demonstrated an improvement for 2-chlorophenol removal compared with goethite (66). Nanoscale iron(III) catalyst, bound onto the surface of carbon binder, was investigated by Vinita *et al.* for the degradation of 2,4,6-trichlorophenol under solar radiation (67). They found that a pH of 3 and a concentration of H_2O_2 at 800 mg L^{-1} was the optimum conditions for degradation efficiency. Nanosized Fe_3O_4 particles were also applied to UV-Fenton oxidation during catechol degradation using a wide initial pH range (2.0-8.0), which followed a mechanism based on the generation of $\cdot\text{OH}$ (68). Moreover, a pillared laponite clay-based Fe particle nanocomposite was proven to be effective and stable for the photo-Fenton mineralization of azo-dye with negligible Fe leaching (69). GO-amorphous FePO_4 was also applied during the photo-Fenton degradation of Rhodamine B as an effective and stable heterogeneous catalyst (70). The results showed that the introduction of GO could promote the reaction by offering more active sites, increasing adsorption capacity and accelerating the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle by enhancing the utilization of solar light and its electron transfer capabilities.

Fenton-like Processes

The ideal Fenton-like process will only consume H_2O_2 to generate $\cdot\text{OH}$ with a recyclable catalyst at neutral pH, without the drawbacks of Fenton reaction such as iron waste and acid pH values. During the Fenton-like processes, important parameters are the catalytic activity and stability of the material. The application of NPs as catalysts of Fenton-like reactions has been described by many investigators.

Zhao *et al.* fabricated a perovskite-based composite BiFeO₃/carbon aerogel (BFO/CA) as a heterogeneous Fenton-like catalyst, with three-dimensional (3D) structure, nano-scaled size and high surface area, for the oxidation of ketoprofen as the target pollutant. The results showed that nano-BFO/CA retained almost all of its high catalytic activity in the pH range of 3-7, and exhibited very low iron leaching, even in acidic condition (71). Zeng *et al.* also used nano-magnetite (Fe₃O₄) as the iron source and cathodic Fenton generation of H₂O₂ for the degradation of 4,6-dinitro-*o*-cresol. The magnetite was proven to be more stable, reusable and easy to separate compared to ferrous salt (72). Moreover, the presence of nitrilotriacetic acid (NTA), a biodegradable agent, was demonstrated to accelerate the degradation of carbamazepine by eighty times when using the nano-Fe₃O₄/H₂O₂ system over a range of pH (5.0-9.0) (73). The nano nickel-zinc ferrite catalyst was also applied to the Wet Peroxide Oxidation process during the degradation of 4-chlorophenol under neutral condition, exhibiting the excellent stability of the catalyst with little iron leaching after five consecutive cycles (74).

Novel Photocatalytic Materials for Visible Light Activity

Most research investigating photocatalytic disinfection is carried out using TiO₂, a wide band gap semiconductor ($E_{bg} = 3.2$ eV for anatase) requiring UV excitation. Only approx. 4% of the solar spectrum is in the UV domain. For solar applications, visible light active materials are desirable (Figure 3) to increase the number of photons which can be utilized.

Figure 3. Visible light activation enabled by narrowing the band-gap.
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While more photons can be utilized, narrower band gap materials have a smaller voltage window to drive the redox reactions at the interface (75). The number of publications concerning the photocatalytic disinfection of water using novel visible light active materials is increasing and there are several good reviews concerning visible light active photocatalytic materials (8, 15, 75).

Matsunaga *et al.* provided one of the earliest accounts of doping TiO₂ for the photocatalytic inactivation of microorganisms (we use the term doped loosely to include surface loading) (7). Pt loaded TiO₂ powders were demonstrated to inactivate *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli* within 2 hours (7). The doping of ZnO nanostructures has been reported to enhance the inactivation of microorganisms, either by providing a red shift in the band gap or by the dopant acting as a co-catalyst. A number of dopants including Pd (76), Ce (77), Cu (78), and Ag (79) have been reported to enhance the inactivation of microorganisms. Karunakaran *et al.* investigated the use of ZnO and Ag doped ZnO materials for the inactivation of *E. coli*. The materials were synthesized by three methods, *i.e.* sol-gel (79), combustion (80) and microwave synthesis (81), out of which sol-gel synthesized materials have demonstrated the highest photocatalytic disinfection efficiency. Metal ion dopants are the most studied for visible light activity, although there is some disagreement over reported improvements in efficiency (82). TiO₂ doped with a variety of elements have been investigated for photocatalytic disinfection. Vohra *et al.* have explored Ag⁺ doped TiO₂ P25 for the disinfection of indoor air. *Bacillus cereus*, *Staphylococcus aureus*, *E. coli*, *Aspergillus niger*, and MS2 bacteriophage have been successfully inactivated (83). Ag-TiO₂ has also been effective for the disinfection of water (84). Cu and S doped TiO₂ NPs have been effectively utilized for the inactivation of *E. coli* and *Micrococcus lylae*, respectively (85, 86). Nonmetal doping of TiO₂ and ZnO with C, N, S, B, and halogens has been reviewed by Rehman *et al.* (87) and by Im *et al.* (88) Co-doped materials are often reported to be more effective than the single dopant materials. For example, Li *et al.* compared N and C,N co-doping for their inactivation rate of *E. coli* (89). Other photocatalysts, such as WO₃ (90), have been doped to improve visible light activity, and present a further approach to developing new materials for disinfection (91). Rengifo-Herrera and Pulgarin reported on the photocatalytic activity of N,S co-doped and N-doped commercial anatase (Tayca TKP 102) TiO₂ powders towards phenol oxidation and *E. coli* inactivation. The doped materials did not present any enhancement as compared to undoped TiO₂ (Evonik Aeroxide P25) under simulated solar irradiation. They concluded that, while the N or N,S co-doped TiO₂ are colored materials, the localized states responsible for the visible light absorption do not play an important role in the photocatalytic activity (92).

Metal carbide, nitride and sulfide materials generally have narrower band gaps than oxide materials but they tend to undergo photoanodic corrosion in aqueous media. Some nonmetal oxide materials have been reported for the inactivation of microorganisms *e.g.* ZnIn₂S₄ was reported to show visible light photocatalytic activity for the inactivation of *E. coli* (under electrochemical bias) (93). Binary metal oxides *e.g.* bismuth vanadate photocatalysts have also been reported for their disinfection properties (94, 95), with further enhancements in rates of disinfection reported with Ag loading as a co-catalyst (96). Titanium oxynitrides (TiON) and

niobium oxynitrides have been reported to show activity for the disinfection of water with PdO NP modified TiON nanofibers reported for *E. coli* inactivation under visible light (97). Also, perovskite materials such as $K_4Nb_6O_{17}$ and Ag/Cu modified $K_4Nb_6O_{17}$ have been investigated for the photocatalytic inactivation of *E. coli* under visible light irradiation (98, 99).

Graphene, Carbon Nanotubes, and their Composites Used in Water Technologies

Graphene is the thinnest and strongest material known, having many fascinating properties such as a large surface to volume ratio, extraordinary high electron mobility, electrical and thermal conductivity, very high stiffness, high hydrophobicity *etc.* It is an array of single layer carbon atoms which are arranged in hexagonal rings (100, 101). Among all the properties of graphene, the hydrophobic nature of graphene can be utilized in water treatment. As we know, a hydrophobic material will naturally repel water. But when nanopores are generated on the graphene sheet, it allows water permeation. Recently, many research groups are studying the filtration capabilities of graphene sheets possessing nanopores and it is reported that graphene can remove ions like calcium, sodium and magnesium. In March 2012, Lockheed Martin Corp. patented graphene filters operating through size exclusion principle in which nanopores of graphene permit the passage of water molecules but prevent the flow of calcium (9.9 nm), magnesium (8.2 nm) and sodium (9.7 nm) (102). Before this work, in October 2010, researchers from Australia and Shanghai developed a new technique called capacitive deionization (CDI) which uses graphene-like nanoflakes as electrodes to purify water. In 2012, scientists from Massachusetts Institute of Technology (MIT) simulated the filtration of salts from salt water using nanoporous graphene. They have claimed that the filtration rate through this membrane is 2-3 orders higher in magnitude than current commercial desalination technologies.

Fernandez-Ibanez *et al.* evaluated TiO_2 -reduced graphene oxide (RGO) composites for the disinfection of water contaminated with *E. coli* cells and *Fusarium solani* spores, under natural sunlight (Figure 4) (103). Rapid water disinfection was observed with both *E. coli* and *F. solani*. An enhanced rate in the *E. coli* inactivation efficiency was observed when the TiO_2 -RGO composite was compared to TiO_2 (Evonik Aeroxide P25). The disinfection efficiency was also evaluated using filtered sunlight, where the major part of the solar UVA was cut-off ($\lambda > 380$ nm) using a Plexiglass screen. In this case, a much greater time was required for the inactivation of *E. coli* using TiO_2 P25, but the same inactivation rate was observed for TiO_2 -RGO. This indicated that visible light activity could be attributed to singlet oxygen production by the TiO_2 -RGO composites which would lead to *E. coli* inactivation.

Figure 4. **a)** TiO_2 -GO aggregate before photo-reduction, **b)** TiO_2 -RGO after UV assisted photo-reduction and **c)** $E. coli$ inactivation at several TiO_2 -RGO concentrations. Figure inserts shows the efficiency of TiO_2 -RGO and TiO_2 -P25 for $E. coli$ inactivation. (Reproduced with permission from reference (103). Copyright 2015 Elsevier.)

The idea of constructing nanopores in graphene sheets deems it a promising material in the area of water filtration and desalination. The porous materials having narrow distributed pores with a very small pore size ranging between 1-5 Å are very useful for molecular sieving and separation purposes (104). The ease of fabrication, good mechanical strength and presence of an interlayer separation of approx. 6 Å helps them to accommodate water molecules, and in-turn makes them a good candidate for water purification. Graphene sheets with tiny perforations allow the passage of water molecules but restrict the passage of contaminants and pollutants.

Graphene is an impermeable membrane due to the delocalized π -orbital cloud (105). The π -orbital cloud can block the entry of very small molecules such as hydrogen, helium *etc.* (4) If it is possible to make pores in graphene, while retaining its structural integrity, graphene can be a good material for the purification of gases and liquids. Studies have proven that the water flux through nanoporous graphene is greatly dependent on the diameter and functionalization of the pores (106). The water flow rate through graphene increases with an increase in pore diameter and applied pressure. The incorporation of charged species into graphene pores, either by chemical oxidation or by functionalization, can contribute positively to water desalination (107). Wang and Karnik reported that water permeation through graphene nanopores is based on the principle of reverse osmosis (RO) and the selectivity can be increased by hydrogen functionalization of the graphene pores. Hydroxyl group functionalization increases the speed of water transport (Figure 5) (108).

Figure 5. A graphene membrane with subnanometer pores is a promising RO membrane. High pressure applied to the salt water (left) drives water molecules across the graphene membrane (right), while salt ions (spheres) are blocked. (Reproduced with permission from reference (108). Copyright 2012 Nature Publishing Group.)

Sint *et al.* reported that nanopores functionalized in graphene layers can act as ion sieves of high selectivity (109). The negatively charged fluorine or nitrogen terminated nanopores favor the flow of cations and positively charged hydrogen

functionalization favors the passage of anions. These nanopores can be generated by ion etching (*110*) or chemical functionalization. The ion selectivity and passage through the nanopores depend upon the size, shape and the nature of functional groups attached to the pores.

Many theoretical studies have proven that thin layer graphene can act as a superior separation membrane for gases, various ions, water *etc.* Cohen-Tanugi and Grossman reported that the nanopores in single layer graphene sheets can filter sodium chloride salt from water in an effective way (*111*). Using classical molecular dynamics they proved that the pore diameter and adequate pore size distribution aid the nanosheet in preventing the passage of salt but permit the flow of water. Also, their studies suggest that the functional groups in the graphene sheets, such as the hydroxyl group, can double the water flux due to its high hydrophilicity. Their work states that atomically thin, periodic nanostructures like graphene, prepared using the bottom up technique, and along with the redesign of desalination membranes, can overcome the drawbacks of current water purification technologies. A schematic representation of the desalination of salt water is shown in Figure 6.

*Figure 6. Schematic representation of the desalination of salt water. **Right side:** Water molecules and sodium and chlorine ions in saltwater. **Center:** sheet of graphene (pale blue). **Left side:** water molecules (left side)). (Reproduced with permission from reference (*111*). Copyright 2012 American Chemical Society.)*

R. K. Joshi *et al.* studied the permeation of water through micrometer thick GO laminates prepared using a vacuum filtration technique (*112*). The GO laminates act like a molecular sieve which block all solute particles possessing a hydrated diameter greater than 4.5 Å. It was claimed that the membrane permeates molecules of lesser size, one thousand times faster than that by simple diffusion and this behavior is due to the network of nanocapillaries in graphene which exerts high pressure on ions inside the pores.

Ultrafast water permeation membranes of nanostrand channeled GO membranes, possessing nanochannels of a diameter of 3-5 nm has been reported by Huang *et al.* (113) As prepared nanostrand GO membranes have ten times higher permeation rate than simple GO membranes and one hundred times higher than that of commercially available ultra-filtration membranes. The authors prepared the nanostrand channeled GO using a multi-step process in which a dispersion of positively charged copper hydroxide nanostrands (CHNs) and negatively charged GO sheets is prepared on a porous support, followed by hydrazine reduction, and finally the CHN is removed by EDTA washing. Recent research studies state that the ultrafast permeation of water through graphene-based nanochannels is possible. Sun *et al.* studied the permeation of water through graphene nanochannels without external hydrostatic pressures (114). Their research work focused on using an isotope labeling technique to study the water permeation through nanocapillaries and to evaluate the transport properties of solvent water in the presence of dissolved ions. The authors were able to prove that liquid water can undergo an ultrafast permeation through the nanocapillaries in the GO membrane and that the water permeation is lowered when it is mixed with ions. Figure 7 shows the preparation of nanocapillaries on GO membranes using the vacuum filtration technique and the permeation of water through this membrane.

Han *et al.* fabricated ultrathin graphene membranes with 2D nanochannels having a high water flux of $21.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with the support of PVDF based filtration membranes (115). The membranes showed a high retention rate for dyes but moderate rates for salts. The as prepared membranes demonstrated properties of graphene such as high thermal stability, excellent mechanical properties, and those of PVDF such as high flexibility, processability *etc.* Similarly, when GO is blended with polysulfone, it shows high salt rejection rate (116). The hydrophilicity, water flux and salt rejection properties of the membrane were enhanced by increasing the loading content of GO in the polymer matrix. The authors have shown that approx. 72% of salt rejection (for 1000 ppm sodium sulfate solution) is exhibited by 2000 ppm GO membrane. They also claimed that the rate of salt rejection is dependent upon the pH of the solution; the higher the pH, the greater the rejection rate.

In many countries contamination of ground water with arsenic, which is considered to be one of the most toxic and carcinogenic elements, has led to mass epidemic diseases. In this context, many researchers are focusing on water filtration technology to reduce the arsenic content in water. Chandra *et al.* synthesized water dispersible magnetite (M)/RGO composites for the removal of arsenic from ground water. They have chemically synthesized M/RGO composites possessing super paramagnetic properties at room temperature with an average particle size of approx. 10 nm for magnetite. Based on the adsorption studies, they reported that the removal capacity of As(III) is higher than that of As(V) with this composite. The composite exhibits nearly 99.9% arsenic removal from water (117). The presence of humic acid (HA) in natural water will adversely affect the ability to remove arsenic. To overcome this negative influence of HA, Paul *et al.* synthesized a magnetic nanocomposite of Fe_3O_4 and graphene using a co-precipitation technique (118). They claimed that their nanocomposite

reverses the role of HA to a positive influence, which open up a new graphene nanotechnology for the removal of arsenic from water. The maximum uptake of arsenate and arsenite observed in the presence of RGO-Fe-HA is 16 and 7.5 mg g⁻¹, respectively. This positive observation for the HA present during the removal of arsenic using the GO-Fe₃O₄ nanocomposite materials is not only surprising but also very motivating for the future of nanotechnology in water research. Their work confirmed that the HA coating significantly enhances the arsenic adsorption mechanism through π - π interactions of aromatic amine groups of humic acid with RGO.

Figure 7. (a) Left panel: schematic drawing of the fabrication of GO membranes using vacuum-filtration. **Right panel:** a photograph of the as-synthesized GO membrane and a schematic diagram of its cross-sectional structure. **(b, c)** Photographs of the home-made permeation apparatus and the D₂O labelled water transmembrane permeation process. **(d)** White light interference characterization for the interface between GO with cellulose membrane and microfilter membranes. **(e)** An optical image of the cross-section of a cellulose microfilter. The inset shows a photograph of the microfilter used in the experiments. (Reproduced with permission from reference (114). Copyright 2015 Royal Society of Chemistry.)

Hu and Mi have synthesized a new water filtration system using GO nanosheets. The nanosheets are fabricated by a layer-by-layer deposition technique, in which the GO layers were cross-linked by using 1,3,5-benzenetricarbonyl trichloride on a polydopamine-coated polysulfone support (119). Water can flow through the nanochannels between each GO layers, while the unwanted solute/foreign particles are simultaneously rejected by size exclusion

and charge effects. The water flux and rejection performance of the as prepared GO membrane was tested using a dead end membrane filtration system and the flux was roughly 4-10 times higher than that of most commercial nanofiltration membranes. They also found that the developed GO membrane exhibited a low rejection of monovalent and divalent salts (6-46%), a moderate rejection rate of Methylene Blue (46-66%) and a high rejection rate of Rhodamine-WT (93-95%). The main benefit of graphene nanomaterials over other carbon based nanomaterials is its economic advantages; graphene can be produced at a price that is almost negligible cost from inexpensive graphite (120, 121).

The antimicrobial properties, fibrous shape, and high conductivity of carbon nanotubes (CNTs) allow for the use of novel CNT filters for the removal of pathogenic bacterial and viral species. The thin layer of CNTs effectively removes bacteria by size exclusion and viruses by depth filtration (122). Iron oxides have been widely used in the environmental field as potential adsorbents due to their redox cycle, ion exchange, high affinity for contaminants and magnetic properties. Additionally, after the removal of the contaminants, magnetic oxides can be recovered from aqueous media, allowing for a more economical, cost-effective cleaning process (123). In relation to environmental remediation, nanomaterials have proven more effective than standard approaches, an advantage attributed to their elevated reactivity and increased surface-to-volume ratio (124). Such technologies reduce the concentration of contaminants to parts per billion (ppb) levels and aid in meeting water quality standards.

Due to advances in the area of desalination and the use of nanomaterials, seawater has become a realistic source of potable water for consumption and industrial use. Indeed, developments in the area of nanotechnology indicates that many of the current issues associated with water quality could be resolved or at least significantly amended using nanocatalysts, nanosorbents, bioactive NPs, nanostructured catalytic membranes and NP enhanced filtration methods. The RO process is used in many desalination plants in order to convert seawater to potable water. This method operates by forcing saltwater under pressure through a membrane, typically a polymer with many nanosize pores, allowing water through the pores but stopping the passage of salts and bacteria. In order to produce desalinated water, the osmotic pressure of the feed water needs to be exceeded. Therefore, RO systems require pumps to maintain sufficient pressure to force the water through the membrane as well as cleaning procedures to clean bacteria that grows on the saltwater side of the membrane. Recent studies focus on the use of nanomaterials to decrease the pressure needed to forcefully pass water through the filter and to reduce the capability of bacteria to colonize the membrane resulting in membrane fouling (125). The preparation of membranes incorporating NPs or nanotubes allows for an interaction between the NP surfaces and the polymer chains, resulting in the formation of desirable structured membranes. These modifications of membrane structure result in favorable selectivity, permeability, and satisfactory performance in ultra-filtration and nano-filtration membranes. Furthermore, it is thought that the hydrophilic properties of the NP functional groups are able to control membrane fouling which is a major drawback of membrane separation technology (126). The use of CNTs for water cleaning has shown great potential due to their capacity to act as an adsorbent substance

aiding in the elimination of undesirable contaminants of chemical and biological origin. This ability can be attributed to their structural and function properties. Additionally, due to their antimicrobial properties, CNTs possess a remarkable biofouling resistance that is a major advantage for desalination applications (127). Consequently, NPs will allow for the use of more economical materials than those currently available, thereby reducing the financial costs associated with water desalination (128). At present there is an abundance of desalination methods which use nanomaterials as functional components, currently these methods are being developed to market level. CNTs have been evaluated for desalination due to their rapid water transport properties, large surface area and ease of functionalization (124).

Nanomaterials Based Sensors for Water Technologies

In recent years, the advances in synthesis and functionalization of nanomaterials have allowed the application of these materials as functional probes for the detection of pollutants in water. In this section, the use of metal NPs, quantum dots (QDs) and CNTs for water quality monitoring will be reviewed.

Metal Nanoparticles

Noble metal NPs have attracted much attention for their potential use in sensing due to their unique optical properties. They exhibit localized surface plasmon resonances (LSPRs) due to the collective oscillation of the conduction electrons of the particle in response to light irradiation (127). This process is illustrated in Figure 8. For noble metal NPs, this phenomenon occurs at specific wavelengths in the visible region. This LSPR is dependent not only on the size, shape and composition of the particles but also upon the separation distance between the particles and the dielectric environment of the surrounding medium (128). Thus, changes in the interparticle distance or changes in the environment at the particle surface can lead to changes in the SPR which can be manifested as a color change that is visible to the naked eye.

For example, Liu *et al.* developed a gold NP based sensor for lead ions (129). This sensor consisted of 13 nm gold NPs modified with an oligonucleotide, a DNAzyme (called 17E) and a substrate DNA sequence. The substrate DNA sequence was designed to incorporate regions which hybridize to the DNA sequence on the NPs and a recognition region for the enzyme. In the absence of lead ions, the substrate DNA hybridizes to the DNA on the NPs, leading to aggregation of the NPs and a visible blue color. However, the addition of lead ions results in the hydrolytic cleavage of the substrate DNA sequence by 17E, thus preventing the formation of NP aggregates. Thus, a red color appears as a result. The components of the sensor and the process by which the color change occurs are shown in Figure 9. The color change of the sensor, induced by the presence of lead ions, could be monitored using UV-Vis spectroscopy. It was reported that the non-optimized sensor could detect lead ion concentrations in the range of 0.1–4.0 μM .

a. cleavage site substrate strand 17DS

3'-G T A G A G A A G G - r A T A T C A C T C A -5'

5'-C A T C T C T C T T C T A T A G T G A G T -3'

enzyme strand 17E

b. Pb(II)

c. aggregate 50°C

no Pb(II) anneal

Pb(II) anneal

17E = 5'-TGTCAACTCGTG ACTCACTAT rA GGAAAGAGATG TGTCAACTCGTG-3'

DNA_{Au} = S-(CH₂)₁₆-5'-CACGAGTTGACA-3'

Sub_{Au} = 5'-TGTCAACTCGTG ACTCACTAT rA GGAAAGAGATG TGTCAACTCGTG-3'

In Water Challenges and Solutions on a Global Scale; Loganathan, et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

A similar methodology was employed by these researchers to develop a gold NP based sensor for copper ions (130). However, to prevent interference in samples resulting from non-specific nucleic acid cleavage, a DNA ligation enzyme was used, rather than a DNA cleavage enzyme. Thus, the presence of copper ion was signaled by the formation of gold NP aggregates, resulting in a color change from red to blue. It was demonstrated that the system was sensitive enough to detect Cu^{2+} in drinking water, at the limits specified by the U.S. Environmental Protection Agency (EPA) and the WHO *i.e.* at 20 and 30 μM respectively.

Annadhasan *et al.* reported the use of tyrosine stabilized silver NPs for the colorimetric detection of mercury ions and manganese ions in drinking water (131). The limit of detection for Hg^{2+} ions was found to be 19 nM and the limit of detection for Mn^{2+} ions was found to be 23 nM. A gold NP based sensor for colorimetric detection of cholera toxin in water was developed by Scholfield *et al.* (132) The surface of the NPs was functionalized with a lactose derivative. Binding of the cholera toxin to the lactose induced aggregation of the NPs and consequent color change from red to purple. Gold nanorod assemblies were used for the detection of microcystin-LR toxin in water (133). This toxin originates from common blue-green algae. It has been reported that sustained exposure to small concentrations of this toxin in drinking water can cause liver cancer (134). Two types of protein functionalized gold nanorods were prepared which self-assembled into side-by-side or end-to-end assemblies. The addition of the microcystin-LR toxin resulted in disruption of these assemblies and consequently changes in the UV-Vis absorption spectra of the nanorods. Newman *et al.* reported the use of zirconium phosphate modified gold NPs for the detection of organophosphates (135). The binding of the organophosphate resulted in a blue shift of the SPR of the gold NPs. It was noted that the SPR shift was independent of the organophosphate concentration beyond a threshold concentration of 5×10^{-7} M for diethylchlorophosphate. Therefore, this sensor is designed to be a presumptive test for the presence or absence of organophosphate, rather than for quantitative analysis of organophosphate. Anti-*E. coli* antibody conjugated gold nanorods were used to detect *E. coli* bacteria in water at concentrations of 50 Colony Forming Units mL^{-1} (136). The detection mechanism was based on the increased two photon Rayleigh scattering observed after addition of *E. coli* bacteria to the NPs. It was reported that this method showed much greater sensitivity (2 orders of magnitude more sensitive) than the usual colorimetric techniques, which are typically used. This sensor also had the advantage of offering more rapid results than conventional methods for detection of *E. coli* in water.

The LSPRs of metal NPs can also be exploited for the detection of species of interest by use of surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman spectroscopy (SERRS). When Raman scattering molecules are in close proximity to metal NPs, their scattering can be intensely enhanced upon excitation of the NP LSPR. This can result in a Raman signal enhancement of up to 10^{14} , allowing single molecule detection (137). Cysteine modified gold NPs were used as a SERS probe for the detection of trinitrotoluene (TNT) in water at 2 picomolar concentration (138). SERRS

has been used for the detection of *C. parvum* and *Giardia lamblia* (139). Gold NPs were functionalized with antibodies specific to *C. parvum* or *G. lamblia* and further functionalized with Raman active dye molecules. After incubation with the antibody-NP conjugates, *C. parvum* oocysts and *G. lamblia* could easily be analyzed using Raman spectroscopy.

Metal NPs can also be used for the electrochemical detection of species in water. A multilayer assembly of polyelectrolyte gold NPs has been used for the detection of arsenic ions which exhibited a limit of detection of $0.48 \mu\text{M}$ (140). Also, a silver NP based electrochemical sensor, used for the detection of nitrite ion, has been developed by Rastogi *et al.* (141) They reported that this system offered nitrite ion detection over a wide linear range, with a lower limit of detection, higher sensitivity and faster response time than that of other previously reported nitrite sensors.

An enzyme amplified sandwich electrochemical immunosensor, using dual labeled gold NPs (alkaline phosphatase (ALP) and anti-oocysts monoclonal antibody (McAb)) in indium tin oxide (ITO), was used to detect *C. parvum* (142), as illustrated in Figure 10. Anti-oocysts McAb were immobilized on a Au NP functionalized ITO electrode. The subsequent binding of analytes and dual labeled gold NP probe resulted in detection of the *C. parvum* target. This yielded very sensitive detection (a limit of detection of 3 oocysts mL^{-1}) in a short processing time.

Figure 10. Electrochemical detection of *C. parvum* using antibody functionalized Au NPs. (Reproduced with permission from reference (142). Copyright 2011 Royal Society of Chemistry.)

Quantum Dots

So far, the use of NPs for SPR based sensing and electrochemical detection has been discussed. However, changes in fluorescence intensity can also be exploited for sensing applications. Recent advances in the synthesis of QDs have enabled the development of novel fluorescent probes for the detection of species of interest.

QDs are semiconductor NPs which have emission wavelengths that scale with size. The emission spectrum of QDs has been shown to be ten to twenty times brighter than organic fluorophores (143). Water-soluble mercaptoacetic acid-capped CdS and CdS/ZnS QDs were developed for the fluorescent detection of Hg^{2+} ions. The presence of the mercury ion was signaled by the fluorescence quenching of the QDs which was shown to be linearly proportional to the mercury ion concentration. Limits of detection in the nanomolar range were reported for these sensors (144). However, due to concerns related to the potential toxicity of cadmium, a modified mercury sensor was developed. *N*-acetyl-cysteine coated zinc sulfide NPs were prepared by a one-step synthetic method in an aqueous medium (145). These NPs were used for the trace detection of Hg^{2+} ions in water, yielding a limit of detection of 5 nM.

Similarly, glutathione-capped ZnSe QDs were prepared and used for the determination of lead ions (146). This system demonstrated improved sensitivity and selectivity for the detection of trace Pb^{2+} in water, such that a detection limit of 0.71 nM was achieved. The U.S. EPA stipulates that the maximum level of lead allowed in drinking water is 72 nM (15 ppb) (147). Therefore this nanosensor could be used to ensure compliance with this level. In a method similar to the strategy of Liu *et al.* (129, 130), a QD-DNAzyme sensor for the detection of Pb^{2+} and Cu^{2+} ions has been reported (148). Quencher-labeled DNAzymes were synthesised and attached to the surface of CdSe/ZnS QDs. Since the quencher molecule was close to the NP surface, the QD fluorescence of the QD was quenched. However, the addition of lead ions resulted in cleavage of the quencher-labeled DNAzymes from the QD and resultant restoration of the QD fluorescence. Using this strategy, it was also possible to simultaneously detect lead and copper ions using two different colors of QDs, with minimal cross talk between the Pb^{2+} detection and Cu^{2+} detection. The limits of detection of 0.2 and 0.5 nM were reported for Pb^{2+} and Cu^{2+} , respectively.

While using flow cytometry, Hahn *et al.* reported that the use of CdSe/ZnS core/shell bioconjugates, resulted in increased fluorescence intensities, lower limits of detection and improved accuracy when analyzing a mixture of pathogenic *E. coli* O157:H7 and harmless *E. coli* DH5 α , when compared to results using a green organic dye (149).

Agrawal *et al.* used a QD-magnetic NP based sensor for the detection of the waterborne pathogens *E. coli* and *Salmonella typhimurium* (150). Firstly, they prepared magnetic NPs tagged with anti-*E. coli* and anti-*S. typhimurium* antibodies. They also prepared green fluorescent cadmium telluride QDs tagged with anti-*E. coli* antibodies and red fluorescent QDs tagged with anti-*S. typhimurium* antibodies. The antibody-tagged magnetic NPs were injected into microchannels that were preloaded with bacterial samples and also a solution of antibody-tagged QDs. Removal of the magnets from the pre-capture zone

allowed the flow of the antibody-tagged magnetic NPs towards the capture zone, along the flow of bacterial samples. Removal of the magnets from capture zone caused the antibody-tagged QDs to flow. In the detection zone, QDs, bacterial samples and magnetic NPs formed a complex that fluoresced when irradiated with visible light.

Carbon Nanotubes and Graphene

The unique electrical properties and high surface area of CNTs have been exploited for the detection of a wide variety of water pollutants. For example, an electrode array composed of CNTs and coated with a bismuth film was used for the voltammetric detection of cadmium(II) and lead(II) at concentrations below the ppb level (151). A limit of detection of $0.04 \mu\text{g L}^{-1}$ was reported. Cysteine coated CNTs were used in the construction of an electrochemical sensor for the simultaneous detection of lead and copper ions (152). Detection limits of 1 ppb and 15 ppb were reported for Pb^{2+} and Cu^{2+} respectively. This sensor was deployed for the determination of Pb^{2+} and Cu^{2+} in spiked lake water samples. Average recoveries of 96.2% and 94.5% were reported for Pb^{2+} and Cu^{2+} respectively. Organophosphate pesticides have been detected using self-assembled layers of acetylcholinesterase immobilized on a CNT modified glassy carbon electrode (153). Single walled CNTs and antibodies have been combined to create a paper based sensor for the detection of microcystin-LR toxin (154). This nanosensor achieved a limit of detection of 0.6 ppb with a response time that was 28 times quicker than that obtained using an enzyme linked immunosorbent assay. A CNT based electrochemical biosensor, for the detection of bacteriophage MS2, was recently reported by Prieto-Simon *et al.* (155) This virus is often detected in sewage impacted water supplies. Excellent sensitivity and limit of detection (9.3 and 9.8 pfu mL^{-1} in buffer and in river water, respectively) were achieved using this sensor.

Another allotrope of carbon; graphene, has been used for the development of sensors for water contaminants. Even though it was only first produced in the laboratory in 2003 (156), graphene based sensors have since been utilized for the detection of heavy metals, pathogenic bacteria and organic pollutants. The reason for the intense interest in graphene lies in its unique physical and chemical properties: high surface area (theoretically $2630 \text{ m}^2 \text{ g}^{-1}$ for single-layer graphene) (101), superior thermal conductivity (157) and electric conductivity (158), and excellent mechanical strength (159).

A nanocomposite of graphene sheets modified with Nafion was used for the detection of cadmium ions using differential pulse anodic stripping voltammetry (160). This system provided detection of Cd^{2+} in the range of $0.25\text{--}5.00 \mu\text{g L}^{-1}$, with a limit of detection of $3.50 \mu\text{g L}^{-1}$. Additionally, the sensor could differentiate between cadmium ions and interferents such as magnesium and zinc salts. This sensor was deemed to offer several advantages compared to existing methods for cadmium analysis, namely that it was more cost effective, portable and reliable and more suited to on-site detection. A copper NP -GO hybrid was used for

the electrochemical detection of 2-naphthol in river water (161). 2-naphthol is widely used in the syntheses of azo-dyes, rubber antioxidants, bactericides, mildew preventives and antiseptic substances. The sensor was successfully used to detect 2-naphthol in the linear ranges of 0.1–4.0 μM and 4.0–130 μM , with a limit of detection of 5.0 nM. An electrochemical sensor for the simultaneous detection of nitrite and sulfite in water was prepared using potassium doped graphene (162). The sensor showed excellent sensitivity and selectivity towards nitrite and sulfite and superior antifouling properties compared to other systems developed for this purpose.

While the majority of graphene based sensors employ electrochemical detection methods, a graphene based fluorescent nanoprobe for detection of silver ions has also been developed (163). Fluorescein labeled silver specific oligonucleotides (SSO) were prepared. In the absence of silver ions, the DNA sequence exists as a flexible single strand. The addition of silver ions results in the formation of a complex between the Ag and the cytosine bases of the oligonucleotide. This induces the formation of an inflexible hairpin structure. GO is added to selectively adsorb the unbound oligonucleotides and quench their emission. The silver ions complexed with the DNA are not adsorbed and thus, their fluorescence is not quenched. A schematic illustration of the sensor is shown in Figure 11. It was demonstrated that this sensor could differentiate silver ions in the presence of twelve other interferent metal ions, present at tenfold higher concentration.

Figure 11. Diagram of a fluorescent sensor for silver ions. In the presence of Ag(I) the fluorescein labelled oligonucleotides retain their fluorescence. In the absence of silver ion, the oligonucleotides are adsorbed onto graphene and their emission is quenched. (Reproduced with permission from reference (163). Copyright 2010 Royal Society of Chemistry.)

Conclusions

The provision of safe drinking water is a basic right of all individuals, yet people face genuine issues relating to the availability of a sufficient supply of safe and clean water, affecting their health and economic well-being. Providing a supply of clean safe water economically, is beyond the capacity of current water treatment methods. It is estimated that there are 748 million people throughout the world without access to improved water sources for drinking and many more rely on water that is not safe to consume due to contamination with pathogenic microorganisms. Furthermore, standard water treatment methods show little specificity towards contaminants; filtration (micro, nano and ultra) which leads to the requirement for the extreme use of resources and the elimination of non-harmful components (1). Additionally, this can lead to the formation of residuals/by-products which requires further processing and disposal. The reuse of wastewater is also becoming more and more important due to water scarcity throughout the globe, and it is vitally important for safety reasons to ensure that water for reuse is free from pathogenic microorganisms, particularly if used for food-crop irrigation.

Solar energy is free and ubiquitous on the Earth's surface. The utilization of solar energy for the disinfection of water is a very important area for research and development. Solar irradiation of water can result in the inactivation of pathogenic microorganisms in water due to a combination of UV and thermal effects. Nevertheless, solar disinfection alone may be slow or ineffective against different microorganisms. The addition of a photocatalyst, such as titanium dioxide, can dramatically enhance the solar disinfection of water. The photocatalytic mechanism is non-specific through the production of ROS which reduces the likelihood of resistance being developed. In order to improve upon the solar efficiency of photocatalytic disinfection, many researchers are investigating novel visible light active photocatalytic materials which can utilise more of the solar spectrum.

The study of NPs and their applications in science has become a rapidly growing sector of research and development. As the issues with supplying safe potable water are becoming increasingly evident, nanotechnology has been identified as a possible solution to this global problem. Disinfection procedures are a very significant final step in the treatment of both water and wastewater. The antimicrobial nature of some nanomaterials means that they may serve as disinfectants for water treatment, allowing for a reduction in the formation of the disinfection by-products commonly associated with chemical use. In comparison with micro-sized counterparts, NPs show a significantly higher catalytic activity in catalytic ozonation, photo-Fenton, and Fenton-like reaction, which would improve the reaction efficiency for water decontamination. The important feature of nanocatalysts is that their surface properties can deviate significantly from those of their macroscopic counterparts, as they can reach or penetrate into zones that are inaccessible to micro-sized solid catalysts. Research on novel nanocatalysts applied in heterogeneous AOPs for the degradation of emerging contaminants in water treatment is currently a very active field. A wide variety of nanomaterial based sensors for the monitoring of water quality have been

developed. These novel systems offer increased sensitivity, more rapid results and more cost effective solutions when compared with existing analytical methods. However, the suitability and robustness of all these systems under environmental conditions have not yet been established. Further work will be required to address issues such as NP stability and aggregation before such sensors can be deployed within existing water quality monitoring operations. In addition, regardless of their huge potential, the use of nanomaterials does pose some issues, such as the high cost of various nanomaterials, with the exception of TiO₂ and polymeric nanofibres. This has led to the concept of retaining and reusing nanomaterials and to the use of low purity nanomaterials, as significant costs are related to obtaining high levels of purity. Nonetheless, the rapid growth and continued advances in the area of nanomaterial based devices for water disinfection and sensing offer great promise for the challenges posed by the water quality issues.

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