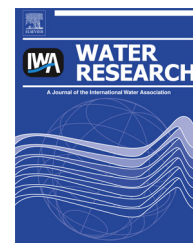




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Applications of nanotechnology in water and wastewater treatment

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ABSTRACT

Providing clean and affordable water to meet human needs is a grand challenge of the 21st century. Worldwide, water supply struggles to keep up with the fast growing demand, which is exacerbated by population growth, global climate change, and water quality deterioration. The need for technological innovation to enable integrated water management cannot be overstated. Nanotechnology holds great potential in advancing water and wastewater treatment to improve treatment efficiency as well as to augment water supply through safe use of unconventional water sources. Here we review recent development in nanotechnology for water and wastewater treatment. The discussion covers candidate nanomaterials, properties and mechanisms that enable the applications, advantages and limitations as compared to existing processes, and barriers and research needs for commercialization. By tracing these technological advances to the physicochemical properties of nanomaterials, the present review outlines the opportunities and limitations to further capitalize on these unique properties for sustainable water management.

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1. Introduction

Water is the most essential substance for all life on earth and a precious resource for human civilization. Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the 21st century.

Our current water supply faces enormous challenges, both old and new. Worldwide, some 780 million people still lack access to improved drinking water sources (WHO, 2012). It is urgent to implement basic water treatment in the affected areas (mainly in developing countries) where water and

wastewater infrastructure are often non-existent. In both developing and industrialized countries, human activities play an ever-greater role in exacerbating water scarcity by contaminating natural water sources. The increasingly stringent water quality standards, compounded by emerging contaminants, have brought new scrutiny to the existing water treatment and distribution systems widely established in developed countries. The rapidly growing global population and the improvement of living standard continuously drive up the demand. Moreover, global climate change accentuates the already uneven distribution of fresh water, destabilizing the supply. Growing pressure on water supplies makes using

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unconventional water sources (e.g., stormwater, contaminated fresh water, brackish water, wastewater and seawater) a new norm, especially in historically water-stressed regions. Furthermore, current water and wastewater treatment technologies and infrastructure are reaching their limit for providing adequate water quality to meet human and environmental needs.

Recent advances in nanotechnology offer leapfrogging opportunities to develop next-generation water supply systems. Our current water treatment, distribution, and discharge practices, which heavily rely on conveyance and centralized systems, are no longer sustainable. The highly efficient, modular, and multifunctional processes enabled by nanotechnology are envisaged to provide high performance, affordable water and wastewater treatment solutions that less rely on large infrastructures (Qu et al., 2013). Nanotechnology-enabled water and wastewater treatment promises to not only overcome major challenges faced by existing treatment technologies, but also to provide new treatment capabilities that could allow economic utilization of unconventional water sources to expand the water supply.

Here, we provide an overview of recent advances in nanotechnologies for water and wastewater treatment. The major applications of nanomaterials are critically reviewed based on their functions in unit operation processes. The barriers for their full-scale application and the research needs for overcoming these barriers are also discussed. The potential impact of nanomaterials on human health and ecosystem as well as any potential interference with treatment processes are beyond the scope of this review and thus will not be detailed addressed here.

2. Current and potential applications for water and wastewater treatment

Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimension. At this scale, materials often possess novel size-dependent properties different from their large counterparts, many of which have been explored for applications in water and wastewater treatment. Some of these applications utilize the smoothly scalable size-dependent properties of nanomaterials which relate to the high specific surface area, such as fast dissolution, high reactivity, and strong sorption. Others take advantage of their discontinuous properties, such as superparamagnetism, localized surface plasmon resonance, and quantum confinement effect. These applications are discussed below based on nanomaterial functions in unit operation processes (Table 1). Most applications discussed below are still in the stage of laboratory research. The pilot-tested or field-tested exceptions will be noted in the text.

2.1. Adsorption

Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment. Efficiency of conventional adsorbents is usually limited by the surface area or active sites, the lack of selectivity, and the adsorption kinetics. Nano-adsorbents offer

significant improvement with their extremely high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry.

2.1.1. Carbon based nano-adsorbents

2.1.1.1. *Organic removal.* CNTs have shown higher efficiency than activated carbon on adsorption of various organic chemicals (Pan and Xing, 2008). Its high adsorption capacity mainly stems from the large specific surface area and the diverse contaminant–CNT interactions. The available surface area for adsorption on individual CNTs is their external surfaces (Yang and Xing, 2010). In the aqueous phase, CNTs form loose bundles/aggregates due to the hydrophobicity of their graphitic surface, reducing the effective surface area. On the other hand, CNT aggregates contain interstitial spaces and grooves, which are high adsorption energy sites for organic molecules (Pan et al., 2008). Although activated carbon possesses comparable measured specific surface area as CNT bundles, it contains a significant number of micropores inaccessible to bulky organic molecules such as many antibiotics and pharmaceuticals (Ji et al., 2009). Thus CNTs have much higher adsorption capacity for some bulky organic molecules because of their larger pores in bundles and more accessible sorption sites.

A major drawback of activated carbon is its low adsorption affinity for low molecular weight polar organic compounds. CNTs strongly adsorb many of these polar organic compounds due to the diverse contaminant–CNT interactions including hydrophobic effect, π – π interactions, hydrogen bonding, covalent bonding, and electrostatic interactions (Yang and Xing, 2010). The π electron rich CNT surface allows π – π interactions with organic molecules with C=C bonds or benzene rings, such as polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds (Chen et al., 2007; Lin and Xing, 2008). Organic compounds which have –COOH, –OH, –NH₂ functional groups could also form hydrogen bond with the graphitic CNT surface which donates electrons (Yang et al., 2008). Electrostatic attraction facilitates the adsorption of positively charged organic chemicals such as some antibiotics at suitable pH (Ji et al., 2009).

2.1.1.2. *Heavy metal removal.* Oxidized CNTs have high adsorption capacity for metal ions with fast kinetics. The surface functional groups (e.g., carboxyl, hydroxyl, and phenol) of CNTs are the major adsorption sites for metal ions, mainly through electrostatic attraction and chemical bonding (Rao et al., 2007). As a result, surface oxidation can significantly enhance the adsorption capacity of CNTs. Several studies show that CNTs are better adsorbents than activated carbon for heavy metals (e.g., Cu²⁺, Pb²⁺, Cd²⁺, and Zn²⁺) (Li et al., 2003; Lu et al., 2006) and the adsorption kinetics is fast on CNTs due to the highly accessible adsorption sites and the short intraparticle diffusion distance.

Overall, CNTs may not be a good alternative for activated carbon as wide-spectrum adsorbents. Rather, as their surface chemistry can be tuned to target specific contaminants, they may have unique applications in polishing steps to remove recalcitrant compounds or in pre-concentration of trace organic contaminants for analytical purposes. These applications require small quantity of materials and hence are less sensitive to the material cost.

Table 1 – Current and potential applications of nanotechnology in water and wastewater treatment.

Applications	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies
Adsorption	Carbon nanotubes	High specific surface area, highly assessable adsorption sites, diverse contaminant-CNT interactions, tunable surface chemistry, easy reuse	Contaminant preconcentration/detection, adsorption of recalcitrant contaminants
	Nanoscale metal oxide	High specific surface area, short intraparticle diffusion distance, more adsorption sites, compressible without significant surface area reduction, easy reuse, some are superparamagnetic	Adsorptive media filters, slurry reactors
	Nanofibers with core–shell structure	Tailored shell surface chemistry for selective adsorption, reactive core for degradation, short internal diffusion distance	Reactive nano-adsorbents
Membranes and membrane processes	Nano-zeolites	Molecular sieve, hydrophilicity	High permeability thin film nanocomposite membranes
	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans	Anti-biofouling membranes
	Carbon nanotubes	Antimicrobial activity (unaligned carbon nanotubes) Small diameter, atomic smoothness of inner surface, tunable opening chemistry, high mechanical and chemical stability	Anti-biofouling membranes Aligned carbon nanotube membranes
	Aquaporin Nano-TiO ₂	High permeability and selectivity Photocatalytic activity, hydrophilicity, high chemical stability	Aquaporin membranes Reactive membranes, high performance thin film nanocomposite membranes
	Nano-magnetite Nano-TiO ₂	Tunable surface chemistry, superparamagnetic Photocatalytic activity in UV and possibly visible light range, low human toxicity, high stability, low cost	Forward osmosis Photocatalytic reactors, solar disinfection systems
Disinfection and microbial control	Fullerene derivatives	Photocatalytic activity in solar spectrum, high selectivity	Photocatalytic reactors, solar disinfection systems
	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans, ease of use	POU water disinfection, anti-biofouling surface
	Carbon nanotubes	Antimicrobial activity, fiber shape, conductivity	POU water disinfection, anti-biofouling surface
Sensing and monitoring	Nano-TiO ₂	Photocatalytic ROS generation, high chemical stability, low human toxicity and cost	POU to full scale disinfection and decontamination
	Quantum dots	Broad absorption spectrum, narrow, bright and stable emission which scales with the particle size and chemical component	Optical detection
	Noble metal nanoparticles	Enhanced localized surface plasmon resonances, high conductivity	Optical and electrochemical detection
	Dye-doped silica nanoparticles	High sensitivity and stability, rich silica chemistry for easy conjugation	Optical detection
	Carbon nanotubes	Large surface area, high mechanical strength and chemical stability, excellent electronic properties	Electrochemical detection, sample preconcentration
	Magnetic nanoparticles	Tunable surface chemistry, superparamagnetism	Sample preconcentration and purification

Produced by exfoliating graphite with strong acids and oxidizers, graphite oxide is a potentially low-cost adsorbent. It was recently reported that sand granules coated with graphite oxide was efficient in removing Hg²⁺ and a bulky dye molecule (Rhodamine B); its performance was comparable to commercial activated carbon (Gao et al., 2011).

2.1.1.3. Regeneration and reuse. Regeneration is an important factor that determines the cost-effectiveness of adsorbents. Adsorption of metal ions on CNTs can be easily reversed by

reducing the solution pH. The metal recovery rate is usually above 90% and often close to 100% at pH < 2 (Li et al., 2005; Lu et al., 2006). Moreover, the adsorption capacity remains relatively stable after regeneration. Lu et al. reported that Zn²⁺ adsorption capacity of SWNT and MWNT decreased less than 25% after 10 regeneration and reuse cycles, while, that of activated carbon was reduced by more than 50% after one regeneration (Lu et al., 2006). A statistical analysis based on the best-fit regression of Zn²⁺ adsorption capacity and the number of regeneration and reuse cycles suggested that CNT

nano-adsorbents can be regenerated and reused up to several hundred times for Zn^{2+} removal while maintaining reasonable adsorption capacity (Lu et al., 2007).

2.1.2. Metal based nano-adsorbents

Metal oxides such as iron oxide, titanium dioxide and alumina are effective, low cost adsorbents for heavy metals and radionuclides. The sorption is mainly controlled by complexation between dissolved metals and the oxygen in metal oxides (Koeppenkastrop and Decarlo, 1993). It is a two-step process: fast adsorption of metal ions on the external surface, followed by the rate-limiting intraparticle diffusion along the micropore walls (Trivedi and Axe, 2000). Their nanoscale counterparts have higher adsorption capacity and faster kinetics because of the higher specific surface area, shorter intraparticle diffusion distance and larger number of surface reaction sites (i.e., corners, edges, vacancies). For instance, as the particle size of nano-magnetite decreased from 300 to 11 nm, its arsenic adsorption capacity increased more than 100 times (Yean et al., 2005). Much of this observed increase in adsorption was attributed to the increase in specific surface area as the 300-nm and 20-nm magnetite particles have similar surface area normalized arsenic adsorption capacity ($\sim 6 \mu\text{mol m}^{-2}$ or $3.6 \text{ atoms nm}^{-2}$) (Auffan et al., 2009, 2008). However, when particle size was reduced to below 20 nm, the specific surface area normalized adsorption capacity increased, with 11-nm magnetite nanoparticles absorbing three times more arsenic ($\sim 18 \mu\text{mol m}^{-2}$ or 11 atoms nm^{-2}), suggesting a “nanoscale effect”. This “nanoscale effect” was attributed to the change of magnetite surface structure which creates new adsorption sites (vacancies) (Auffan et al., 2009).

In addition to high adsorption capacity, some iron oxide nanoparticles, e.g., nano-maghemite and nano-magnetite, can be superparamagnetic. Magnetism is highly volume-dependent as it stems from the collective interaction of atomic magnetic dipoles. If the size of a ferro- or ferri-magnet decreases to the critical value ($\sim 40 \text{ nm}$), the magnet changes from multiple domains to single domain with higher magnetic susceptibility (Yavuz et al., 2006). As the size further decreases, magnetic particles become superparamagnetic, losing permanent magnetic moments while responding to an

external magnetic field, which allows easy separation and recovery by a low-gradient magnetic field. These magnetic nanoparticles can be either used directly as adsorbents or as the core material in a core–shell nanoparticle structure where the shell provides the desired function while the magnetic core realizes magnetic separation (Fig. 1).

Metal oxide nanocrystals can be compressed into porous pellets without significantly compromising their surface area when moderate pressure is applied (Lucas et al., 2001). The pore volume and pore size can be controlled by adjusting the consolidation pressure. Thus, they can be applied in forms of both fine powders and porous pellets, which are the likely forms to be used in industry.

Metal based nanomaterials have been explored to remove a variety of heavy metals such as arsenic, lead, mercury, copper, cadmium, chromium, nickel, and have shown great potential to outcompete activated carbon (Sharma et al., 2009). Among them, the application for arsenic removal has attracted much attention. Although a good adsorbent for many organic and inorganic contaminants, activated carbon has limited capacity for arsenic, especially for As(V) (Daus et al., 2004). Several metal oxide nanomaterials including nano-sized magnetite and TiO_2 have shown arsenic adsorption performance superior to activated carbon (Deliyanni et al., 2003; Mayo et al., 2007). Metal (hydr)oxide nanoparticles also can be impregnated onto the skeleton of activated carbon or other porous materials to achieve simultaneously removal of arsenic and organic co-contaminants, which favors point-of-use (POU) applications (Hristovski et al., 2009a, 2009b).

2.1.2.1. Regeneration and reuse. Metal oxide nano-adsorbents can be easily regenerated by changing solution pH (Sharma et al., 2009). In many cases, the adsorption capacity of metal oxide nano-adsorbents is well maintained after several regeneration and reuse cycles (Hu et al., 2006). However, reduced adsorption capacity after regeneration has also been reported (Deliyanni et al., 2003).

Above all, metal based nano-adsorbents can be produced at relatively low cost. The high adsorption capacity, low cost, easy separation and regeneration make metal based nano-adsorbents technologically and economically advantageous.

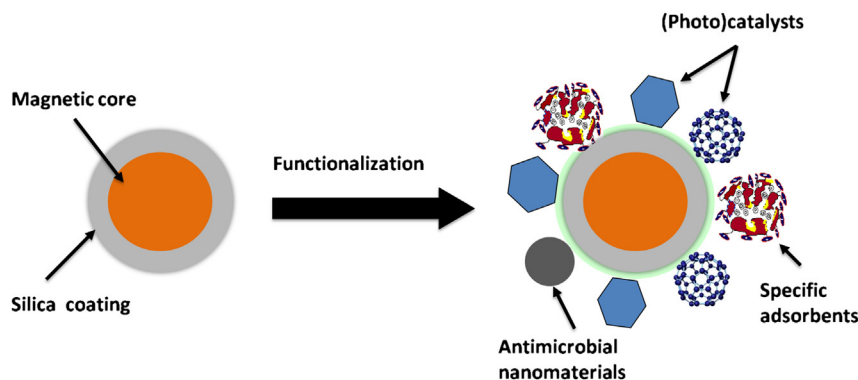


Fig. 1 – Multifunctional magnetic nanoparticles. Magnetic nanoparticles are used as the core material in a core–shell nanoparticle structure where the shell provides the desired function while the magnetic core realizes magnetic separation. Silica coating helps functionalization due to the rich silica chemistry.

2.1.3. Polymeric nano-adsorbents

Dendrimers are tailored adsorbents that are capable of removing both organics and heavy metals. Their interior shells can be hydrophobic for sorption of organic compounds while the exterior branches can be tailored (e.g., hydroxyl- or amine-terminated) for adsorption of heavy metals. The sorption can be based on complexation, electrostatic interactions, hydrophobic effect, and hydrogen bonding (Crooks et al., 2001). A dendrimer-ultrafiltration system was designed to recover metal ions from aqueous solutions (Diallo et al., 2005). The system achieved almost complete removal of Cu^{2+} ions with initial concentration of 10 ppm and Cu^{2+} to PAMAM dendrimer- NH_2 ratio of 0.2. After adsorption, the metal ion laden dendrimers were recovered by ultrafiltration and regenerated by decreasing pH to 4.

2.1.4. Potential application in water treatment

Nano-adsorbents can be readily integrated into existing treatment processes in slurry reactors or adsorbents. Applied in the powder form, nano-adsorbents in slurry reactors can be highly efficient since all surfaces of the adsorbents are utilized and the mixing greatly facilitates the mass transfer. However, an additional separation unit is required to recover the nanoparticles. Nano-adsorbents can also be used in fixed or fluidized adsorbents in the form of pellets/beads or porous granules loaded with nano-adsorbents. Fixed-bed reactors are usually associated with mass transfer limitations and head loss; but it doesn't need future separation process. Applications of nano-adsorbents for arsenic removal have been commercialized, and their performance and cost have been compared to other commercial adsorbents in pilot tests (Aragon et al., 2007). ArsenX^{np} is a commercial hybrid ion exchange medium comprising of iron oxide nanoparticles and polymers. ADSORBISIA[™] is a nanocrystalline titanium dioxide medium in the form of beads from 0.25 to 1.2 mm in diameter. Both nano-adsorbents were highly efficient in removing arsenic and ArsenX^{np} required little backwash (Aragon et al., 2007; Sylvester et al., 2007). The estimated treatment cost for ArsenX^{np} is \$0.25~\$0.35/1000 gal if the medium is regenerated, similar to \$0.37/1000 gal of Bayoxide E33, a high-performance granular iron oxide adsorbent (Aragon et al., 2007; Westerhoff et al., 2006). ArsenX^{np} and ADSORBISIA[™] have been employed in small to medium scale drinking water treatment systems and were proven to be cost-competitive.

2.2. Membranes and membrane processes

The basic goal of water treatment is to remove undesired constituents from water. Membranes provide a physical barrier for such constituents based on their size, allowing use of unconventional water sources. As the key component of water treatment and reuse, they provide high level of automation, require less land and chemical use, and the modular configuration allows flexible design (Qu et al., 2013).

A major challenge of the membrane technology is the inherent tradeoff between membrane selectivity and permeability. The high energy consumption is an important barrier to the wide application of pressure driven membrane processes. Membrane fouling adds to the energy consumption

and the complexity of the process design and operation. Furthermore, it reduces the lifetime of membranes and membrane modules.

The performance of membrane systems is largely decided by the membrane material. Incorporation of functional nanomaterials into membranes offers a great opportunity to improve the membrane permeability, fouling resistance, mechanical and thermal stability, as well as to render new functions for contaminant degradation and self-cleaning.

2.2.1. Nanofiber membranes

Electrospinning is a simple, efficient and inexpensive way to make ultra fine fibers using various materials (e.g., polymers, ceramics, or even metals) (Cloete et al., 2010; Li and Xia, 2004). The resulting nanofibers have high specific surface area and porosity and form nanofiber mats with complex pore structures. The diameter, morphology, composition, secondary structure, and spatial alignment of electrospun nanofibers can be easily manipulated for specific applications (Li and Xia, 2004). Although nanofiber membranes have been commercially employed for air filtration applications, their potential in water treatment is still largely unexploited. Nanofiber membranes can remove micron-sized particles from aqueous phase at a high rejection rate without significant fouling (Ramakrishna et al., 2006). Thus they have been proposed to be used as pretreatment prior to ultrafiltration or reverse osmosis (RO). Functional nanomaterials can be easily doped into the spinning solutions to fabricate nanoparticle impregnated nanofibers or formed in situ (Li and Xia, 2004). The outstanding features and tunable properties make electrospun nanofibers an ideal platform for constructing multifunctional media/membrane filters by either directly using intrinsically multifunctional materials such as TiO_2 or by introducing functional materials on the nanofibers. For example, by incorporating ceramic nanomaterials or specific capture agents on the nanofiber scaffold, affinity nanofiber membranes can be designed to remove heavy metals and organic pollutants during filtration.

2.2.2. Nanocomposite membranes

A significant number of studies on membrane nanotechnology have focused on creating synergism or multifunction by adding nanomaterials into polymeric or inorganic membranes. Nanomaterials used for such applications include hydrophilic metal oxide nanoparticles (e.g., Al_2O_3 , TiO_2 , and zeolite), antimicrobial nanoparticles (e.g., nano-Ag and CNTs), and (photo)catalytic nanomaterials (e.g., bi-metallic nanoparticles, TiO_2).

The main goal of adding hydrophilic metal oxide nanoparticles is to reduce fouling by increasing the hydrophilicity of the membrane. The addition of metal oxide nanoparticles including alumina (Maximous et al., 2010), silica (Bottino et al., 2001), zeolite (Pendergast et al., 2010) and TiO_2 (Bae and Tak, 2005) to polymeric ultrafiltration membranes has been shown to increase membrane surface hydrophilicity, water permeability, or fouling resistance. These inorganic nanoparticles also help enhance the mechanical and thermal stability of polymeric membranes, reducing the negative impact of compaction and heat on membrane permeability (Ebert et al., 2004; Pendergast et al., 2010).

Antimicrobial nanomaterials such as nano-Ag and CNTs can reduce membrane biofouling. Nano-Ag has been doped or surface grafted on polymeric membranes to inhibit bacterial attachment and biofilm formation (Mauter et al., 2011; Zodrow et al., 2009) on the membrane surface as well as inactivate viruses (De Gussemme et al., 2011). However, its long-term efficacy against membrane biofouling has not been reported. Appropriate replenishment of nano-Ag needs to be addressed for practical application of this technology. CNTs inactivate bacteria upon direct contact (Brady-Estevez et al., 2008). High bacterial inactivation (>90%) has been achieved using polyvinyl-N-carbazole-SWNT nanocomposite at 3 wt% of SWNT (Ahmed et al., 2012). As CNTs are insoluble in water and not consumed, there is no need for replenishment. However, as direct contact is required for inactivation, long term filtration experiments are needed to determine the impact of fouling on the antimicrobial activity of CNTs. Addition of oxidized MWNT at low weight percentage (up to 1.5 wt%) also increases the hydrophilicity and permeability of polysulfone membranes (Choi et al., 2006b).

(Photo)catalytic nanoparticle incorporated membranes (a.k.a. reactive membranes) combine their physical separation function and the reactivity of a catalyst toward contaminant degradation. Much effort has been devoted to develop photocatalytic inorganic membranes consisting of nanophotocatalysts (normally nano-TiO₂ or modified nano-TiO₂) (Choi et al., 2006a). Metallic/bi-metallic catalyst nanoparticles such as nano zero-valent iron (nZVI) and noble metals supported on nZVI have been incorporated into polymeric membranes for reductive degradation of contaminants, particularly chlorinated compounds (Wu et al., 2005; Wu and Ritchie, 2008). nZVI serves as the electron donor and the noble metals catalyze the reaction.

2.2.3. Thin film nanocomposite (TFN) membranes

Development of TFN membranes mainly focuses on incorporating nanomaterials into the active layer of thin film composite (TFC) membranes via doping in the casting solutions or surface modification. Nanomaterials that have been researched for such applications include nano-zeolites, nano-Ag, nano-TiO₂, and CNTs. The impact of nanoparticles on membrane permeability and selectivity depends on the type, size and amount of nanoparticles added.

Nano-zeolites are the most frequently used dopants in TFN and have shown potential in enhancing membrane permeability. The addition of nano-zeolites leads to more permeable, negatively charged, and thicker polyamide active layer (Lind et al., 2009a). One study reported water permeability increased up to 80% over the TFC membrane, with the salt rejection largely maintained (93.9 ± 0.3%) (Jeong et al., 2007). TFN membranes doped with 250 nm nano-zeolites at 0.2 wt% achieved moderately higher permeability and better salt rejection (>99.4%) than commercial RO membranes (Lind et al., 2010). It was hypothesized that the small, hydrophilic pores of nano-zeolites create preferential paths for water. However, water permeability increased even with pore-filled zeolites, although less than the pore-open ones, which could be attributed to defects at the zeolite–polymer interface. Nano-zeolites were also used as carriers for antimicrobial agents such as Ag⁺, which imparts anti-fouling property to the

membrane (Lind et al., 2009b). The zeolite TFN technology has reached the early stage of commercialization. QuantumFlux, a seawater TFN RO membrane, is now commercially available (www.nanoH2O.com).

Incorporation of nano-TiO₂ (up to 5 wt%) into the TFC active layer slightly increased the membrane rejection while maintaining the permeability (Lee et al., 2008). When the concentration of nano-TiO₂ exceeded 5 wt%, the water flux increased in the cost of reducing rejection, suggesting defect formation in the active layer. Upon UV irradiation, TiO₂ can degrade organic contaminants and inactivate microorganisms. This helps reduce organic and biological fouling as well as remove contaminants that are not retained by the membrane. However, the close adjacency between the photocatalyst and the membrane may also lead to detrimental effects on polymeric membrane materials, which needs to be addressed for long-term efficacy (Chin et al., 2006).

CNTs (unaligned) also found their application in TFN membranes due to their antimicrobial activities. Tiraferri et al. covalently bonded SWNTs to a TFC membrane surface (Tiraferri et al., 2011). This approach is advantageous as it uses relatively small amount of the nanomaterial and minimizes perturbation of the active layer. The resulting TFN membrane exhibited moderate anti-bacterial properties (60% inactivation of bacteria attached on the membrane surface in 1 h contact time), potentially reducing or delaying membrane biofouling.

2.2.4. Biologically inspired membranes

Many biological membranes are highly selective and permeable. Aquaporins are protein channels that regulate water flux across cell membranes. Their high selectivity and water permeability makes their use in polymeric membranes an attractive approach to improve membrane performance. Aquaporin-Z from *Escherichia coli* has been incorporated into amphiphilic triblock-polymer vesicles (Kumar et al., 2007), which exhibit water permeability at least an order of magnitude over the original vesicles with full rejection to glucose, glycerol, salt, and urea. One potential design is to coat aquaporin incorporated lipid bilayers on commercial nanofiltration membranes. On this front, limited success was achieved (Kaufman et al., 2010).

Aligned CNTs have been shown both experimentally and theoretically to provide water permeation much faster than what the Hagen–Poiseuille equation predicts, owing to the atomic smoothness of the nano-sized channel, and the one dimensional single-file ordering of water molecules while passing through the nanotubes (Holt et al., 2006; Hummer et al., 2001). It was predicted that a membrane containing only 0.03% surface area of aligned CNTs will have flux exceeding current commercial seawater RO membranes (Pendergast and Hoek, 2011). However, high rejection for salt and small molecules is challenging for aligned CNT membranes due to the lack of CNTs with uniformly sub-nanometer diameter. Functional group gating at the nanotube opening has been proposed to enhance the selectivity of aligned CNT membranes (Mauter and Elimelech, 2008). By grafting carboxyl functional groups on sub-2-nm CNT openings, 98% rejection of Fe(CN)₆³⁻ was achieved at low ionic strength by Donnan exclusion (Fornasiero et al., 2008). However, KCl rejection was only 50% at 0.3 mM, and decreased to almost zero at 10 mM.

Grafting bulky functional groups at the tube opening could physically exclude salts. However, steric exclusion will significantly reduce membrane permeability (Nednoor et al., 2005). Thus at the current stage, aligned CNT membranes are not capable of desalination. To achieve reliable salt rejection, the CNT diameter must be uniformly smaller than 0.8 nm (Hinds, 2012).

A key barrier for both aquaporin and aligned CNT membranes is the scale-up of the nanomaterial production and membrane fabrication. Large-scale production and purification of aquaporins are very challenging. To date, chemical vapor deposition (CVD) is the most common way to make aligned nanotubes. A continuous high-yield CVD prototype has been designed for producing vertically aligned CNT, paving the way for large-scale production (de Villoria et al., 2011). A post-manufacturing alignment method using magnetic field was also developed (Mauter et al., 2010).

Nanocomposite and TFN membranes have good scalability as they can be fabricated using current industrial manufacturing processes. The high water permeability can reduce the applied pressure or required membrane area and consequently cut cost. This strategy may greatly improve the energy efficiency for treatment of waters with low osmosis pressure, but it may have limited advantage in seawater RO, whose energy consumption is already close to the thermodynamic limit (Elimelech and Phillip, 2011). A recent review ranked current membrane nanotechnologies based on their potential performance enhancement and state of commercial readiness (Pendergast and Hoek, 2011).

2.2.5. Forward osmosis

Forward osmosis (FO) utilizes the osmotic gradient to draw water from a low osmotic pressure solution to a high osmotic pressure one (i.e., the draw solution). The diluted draw solution is then treated by reverse osmosis or thermal processes to generate pure water. FO has two major advantages over the pressure-driven reverse osmosis: it does not require high pressure, and the membrane is less prone to fouling.

The key to FO is to have a draw solute with high osmolality and easily separable from water. Chemicals currently employed for draw solutions include NaCl and ammonia

bicarbonate. Therefore, RO or thermal treatment, both energy intensive, is required to recover water from the draw solution. Magnetic nanoparticles were recently explored as a new type of draw solute for its easy separation and reuse. Hydrophilic coating was employed to aid dissolution and increase osmotic pressure. An FO permeate flux higher than $10 \text{ L m}^{-2} \text{ h}^{-1}$ was achieved using 0.065 M poly(ethylene glycol) diacid-coated magnetic nanoparticles when deionized water was used as the feed solution (Ge et al., 2011). Magnetic nanoparticles were also applied to recover draw solutes. In a recent study, magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) were used to recover $\text{Al}_2(\text{SO}_4)_3$ (the draw solute) through flocculation (Liu et al., 2011c).

2.3. (Photo)catalysis

Photocatalytic oxidation is an advanced oxidation process for removal of trace contaminants and microbial pathogens. It is a useful pretreatment for hazardous and non-biodegradable contaminants to enhance their biodegradability. Photocatalysis can also be used as a polishing step to treat recalcitrant organic compounds. The major barrier for its wide application is the slow kinetics due to limited light fluence and photocatalytic activity. Current research focuses on increasing photocatalytic reaction kinetics and photoactivity range (Table 2).

2.3.1. Nano-photocatalyst optimization

TiO_2 is the most widely used semiconductor photocatalyst in water/wastewater treatment owing to its low toxicity, chemical stability, low cost, and abundance as raw material. It generates an electron/hole (e^-/h^+) pair upon absorbing a UV photon, which later either migrate to the surface and form reactive oxygen species (ROS) or undergo undesired recombination. The photoactivity of nano- TiO_2 can be improved by optimizing particle size and shape, reducing e^-/h^+ recombination by noble metal doping, maximizing reactive facets, and surface treatment to enhance contaminant adsorption.

The size of TiO_2 plays an important role in its solid-phase transformation, sorption, and e^-/h^+ dynamics. Among the crystalline structures of TiO_2 , rutile is the most stable for

Table 2 – TiO_2 photocatalyst optimization.

Optimization objectives	Optimization approaches	Optimization mechanisms	Water treatment applications
Enhance photocatalytic reaction kinetics	Size	More surface reactive sites, higher reactant adsorption, lower electron-hole recombination	High performance UV activated photocatalytic reactors
	Nanotube morphology	Shorter carrier-diffusion paths in the tube walls, higher reactant mass transfer rate toward tube surface	
	Noble metal doping	Better electron-hole separation, lower electron-hole recombination	
Expand photoactivity range	Reactive crystallographic facets	Higher reactant sorption, better electron-hole separation, lower electron-hole recombination	Low energy cost solar/visible light activated photocatalytic reactors
	Metal impurity doping	Impurity energy levels	
	Anion doping	Band gap narrowing	
	Dye sensitizer doping	Electron injection	
	Narrow band-gap semiconductors doping	Electron injection	

particles larger than 35 nm, while anatase, which is more efficient in producing ROS, is the most stable for particles smaller than 11 nm (Fujishima et al., 2008; Zhang and Banfield, 2000). A major cause for the slow reaction kinetics of TiO₂ photocatalysis is the fast recombination of e⁻ and h⁺. Decreasing TiO₂ particle size lowers volume recombination of e⁻/h⁺, and enhances interfacial charge carrier transfer (Zhang et al., 1998). However, when particle size is reduced to several nanometers, surface recombination dominates, decreasing photocatalytic activity. Therefore, the photocatalytic activity of TiO₂ has a maximum due to the interplay of the aforementioned mechanisms, which lies in the nanometer range. TiO₂ nanotubes were found to be more efficient than TiO₂ nanoparticles in decomposition of organic compounds (Macak et al., 2007). The higher photocatalytic activity was attributed to the shorter carrier-diffusion paths in the tube walls and faster mass transfer of reactants toward the nanotube surface.

Noble metal doping can reduce the e⁻/h⁺ recombination because the photo-excited electrons tend to migrate to the noble metals with lower Fermi levels while the holes stay in TiO₂ (Ni et al., 2007). The photocatalytic activity of TiO₂ can also be promoted by creating highly reactive crystallographic facets. Because high-energy {001} facets diminish quickly during crystal growth, anatase TiO₂ is usually dominated by the low-energy {101} facets. Using specific capping agent (usually fluoride), the percentage of {001} facets can be increased from less than 10% to up to 89% (Han et al., 2009), substantially enhancing hydroxyl radical production and organic compound decomposition (Han et al., 2009; Murakami et al., 2009). The enhanced activity stems from the strong adsorption of reactants on high-energy facets (Liu et al., 2011b) and the spatial separation of electrons and holes on specific crystal facets (Murakami et al., 2009). The optimal percentage of {001} facets for photocatalysis is still debated (Liu et al., 2011b). Improving contaminant adsorption by modifying photocatalyst surface is another way to enhance photocatalytic activity due to the short life time of ROS. However, little has been done in this area.

Another actively pursued research area is to extend the excitation spectrum of TiO₂ to include visible light. The general strategy is doping metal impurities, dye sensitizers, narrow band-gap semiconductors, or anions into nano-TiO₂ to form hybrid nanoparticles or nanocomposites (Fujishima et al., 2008; Ni et al., 2007). Metals and anions create impurity energy levels or narrow the band gap; upon visible light excitation, dye sensitizers and narrow band-gap semiconductors inject electrons into TiO₂ to initiate the catalytic reactions. Among these methods, anions (especially nitrogen) doping, was considered most cost-effective and feasible for industrial applications (Fujishima et al., 2008), although their stability and long-term efficacy has not been tested. Decreased nitrogen concentration during photocatalysis has been reported (Kitano et al., 2006).

Other than TiO₂, WO₃ and some fullerene derivatives also have the potential to be used in photocatalytic water treatment. WO₃ has a narrower band gap than TiO₂, allowing it to be activated by visible light (<450 nm) (Kominami et al., 2001). Pt doping further enhances WO₃ reactivity by facilitating multi-electron reduction of O₂ and improving e⁻/h⁺ separation (Kim et al., 2010). Aminofullerenes generate ¹O₂ under visible

light irradiation (<550 nm) (Lof et al., 1995) and has been studied to degrade pharmaceutical compounds and inactivate viruses (Lee et al., 2010). Fullerol and C₆₀ encapsulated with poly(N-vinylpyrrolidone) can produce ¹O₂ and superoxide under UVA light (Brunet et al., 2009). Aminofullerenes are more amenable to immobilization than fullerol and are more effective for disinfection purposes due to their positive charge. ¹O₂ has lower oxidation potential than hydroxyl radicals produced by TiO₂, while it is a more selective ROS and consequently less susceptible to quenching by non-target background organic matter. Fullerenes are currently much more expensive and not as readily available as TiO₂.

2.3.2. Potential applications in water treatment

The overall efficiency of a photocatalytic water treatment process strongly depends on the configuration and operation parameters of the photo-reactor. Two configurations are commonly used: slurry reactors and reactors using immobilized TiO₂. Various dispersion/recovery or catalyst immobilization techniques are being pursued to maximize its efficiency. Extensive investigation on operating parameters has been carried out with these lab or pilot scale systems. A recent critical review outlines the effects of water quality and a wide range of operating parameters including TiO₂ loading, pH, temperature, dissolved oxygen, contaminant type and concentration, light wavelength and intensity (Chong et al., 2010). Readers are referred to this review for details regarding process optimization. A commercial product, Purifics Photo-Cat™ system, has treatment capacity as high as 2 million gallon per day with a small footprint of 678 ft². Pilot tests showed that the Photo-Cat™ system is highly efficient for removing organics without producing waste streams and it operates with relatively low specific power consumption of about 4 kWh/m³ (Al-Bastaki, 2004; Benotti et al., 2009; Westerhoff et al., 2009). Nano-TiO₂ facilitated solar disinfection (SODIS) has been extensively tested and appears to be a feasible option to produce safe drinking water in remote areas of developing countries. The SODIS system can be small scale for one person or scaled up to medium size solar compound parabolic collectors.

Photocatalysis has shown great potential as a low-cost, environmental friendly and sustainable water treatment technology. However, there are several technical challenges for its large scale application, including 1) catalyst optimization to improve quantum yield or to utilize visible light; 2) efficient photocatalytic reactor design and catalyst recovery/immobilization techniques; 3) better reaction selectivity.

Metal oxide nanomaterials such as TiO₂ and CeO₂ as well as carbon nanotubes have been studied as catalysts in heterogeneous catalytic ozonation processes that provide fast and comparatively complete degradation of organic pollutants. Both radical-mediated and non-radical-mediated reaction pathways have been proposed (Nawrocki and Kasprzyk-Hordern, 2010). The adsorption of ozone and/or pollutants on the catalyst surface plays a critical role in both mechanisms. Nanomaterials have large specific surface area and an easily accessible surface, leading to high catalytic activity. Some nanomaterials were also reported to promote decomposition of ozone into hydroxyl radicals, facilitating degradation process through radical-mediated routes (Orge et al.,

2011). For future industrial scale applications, a better understanding of the mechanism of nanomaterial enabled catalytic ozonation is in critical need.

2.4. Disinfection and microbial control

The dilemma between effective disinfection and formation of toxic disinfection by-products (DBPs) poses a great challenge for the water industry. It is now well recognized that conventional disinfectants, such as chlorine disinfectants and ozone can form toxic DBPs (e.g., halogenated disinfection byproducts, carcinogenic nitrosamines, bromate, etc.). UV disinfection emerged as an alternative for oxidative disinfection as it produces minimal DBPs, while it requires high dosage for certain viruses (e.g., adenoviruses). These limitations urge the development of alternative methods that can enhance the robustness of disinfection while avoiding DBP formation.

Our previous review on antimicrobial nanomaterials highlighted the potential of nanotechnology in disinfection and microbial control (Li et al., 2008). Many nanomaterials, including nano-Ag, nano-ZnO, nano-TiO₂, nano-Ce₂O₄, CNTs, and fullerenes, exhibit antimicrobial properties without strong oxidation, and hence have lower tendency to form DBPs (Table 3). The antimicrobial mechanisms of these nanomaterials, their merits, limitations, and applicability for water treatment, and the critical research needs are thoroughly discussed in that review paper (Li et al., 2008). Thus only a brief update mainly regarding nano-Ag and carbon based nanomaterials will be provided here.

2.4.1. Antimicrobial mechanisms

Nano-Ag is currently the most widely used antimicrobial nanomaterial. Its strong antimicrobial activity, broad antimicrobial spectrum, low human toxicity, and ease of use make it a promising choice for water disinfection and microbial control. It is now well accepted that the antimicrobial activity of nano-silver largely stems from the release of silver ions (Xiu et al., 2011, 2012). Silver ions can bind to thiol groups in vital proteins, resulting in enzyme damage (Liau et al., 1997). It also has been reported that silver ions can prevent DNA replication and induce structural changes in the cell envelope (Feng et al.,

2000). Thus, the release rate and bioavailability of silver ions is crucial for the toxicity of nano-Ag. Studies have suggested that physicochemical properties of nano-Ag play an important role in its antimicrobial activity. However, the influence of the size, shape, coating, and crystallographic facet appears to be mainly related to different release kinetics of silver ions. The presence of common ligands reduces the bioavailability of silver ions and mitigates its toxicity (Xiu et al., 2011). A recent study found that low concentration (sublethal) of silver ions or nano-Ag enhances *E. coli* growth, suggesting a hormetic response that could be counterproductive to its antimicrobial applications (Xiu et al., 2012).

CNTs kill bacteria by causing physical perturbation of the cell membrane, oxidative stress, or disruption of a specific microbial process via disturbing/oxidizing a vital cellular structure/component (Vecitis et al., 2010) upon direct contact with bacterial cells. Graphene and graphite materials exhibit antimicrobial properties through similar mechanisms (Liu et al., 2011a). The cytotoxicity of CNTs strongly depends on their physicochemical properties. Short, dispersed, and metallic CNTs with small diameters are more toxic (Kang et al., 2008a, 2008b; Vecitis et al., 2010).

2.4.2. Potential applications in water treatment

Antimicrobial nanomaterials are envisaged to find their applications in three critical challenges in water/wastewater systems: disinfection, membrane biofouling control, and biofilm control on other relevant surfaces.

Nano-Ag has good potential for application in POU treatment. It can improve water quality for high-end use, or provide another barrier against waterborne pathogens for vulnerable population. Commercial devices utilizing nano-Ag are already available, e.g., MARATHON[®] and Aquapure[®] systems. Nano-Ag has also been incorporated into ceramic microfilters as a barrier for pathogens, which can be employed in remote areas in developing countries (Peter-Varbanets et al., 2009).

The antimicrobial properties, fibrous shape, and high conductivity of CNTs enable novel CNT filters for both bacteria and virus removal: The thin layer of CNTs effectively remove bacteria by size exclusion and viruses by depth filtration (Brady-Estevez et al., 2010); the retained bacteria are largely inactivated by CNTs within hours. With a small intermittent voltage (2–3 V), MWNTs can directly oxidize attached bacteria and viruses and lead to inactivation in seconds (Rahaman et al., 2012; Vecitis et al., 2011). The applied electric potential also enhances viral transport to the anodic CNTs (Rahaman et al., 2012). Such CNT filters can be used as high performance POU devices for water disinfection with minimal to no power requirement.

The application of nanomaterials in membrane biofouling control is detailed in Section 2.2. They can also be used in other water treatment related surfaces such as storage tanks and distribution pipes to control pathogen contamination, biofilm formation, and microbial influenced corrosion. Affordable coating techniques that can economize nanomaterial use and maximize its efficacy while allowing for regeneration are in critical need. An alternative approach is to employ nanoscale biofouling resistant surface structures, a strategy used by marine organisms (dolphins and sharks) and

Table 3 – Nanomaterial antimicrobial mechanisms.

Nanomaterials	Antimicrobial mechanisms
Nano-Ag	Release of silver ions, protein damage, suppression of DNA replication, membrane damage
Nano-TiO ₂	Production of ROS
Nano-ZnO	Release of zinc ions, production of H ₂ O ₂ , membrane damage
Nano-MgO	Membrane damage
Nano-Ce ₂ O ₄	Membrane damage
nC ₆₀	ROS-independent oxidation
Fullerol and aminofullerene	Production of ROS
Carbon nanotubes	Membrane damage, oxidative stress
Graphene-based nanomaterials	Membrane damage, oxidative stress

plants (lotus leaves). A common disadvantage of many nanomaterial enabled disinfection approaches is the lack of disinfection residue, which is crucial for controlling microbial growth during water storage and distribution. Nevertheless, nanotechnology enabled disinfection can reduce DBP formation as chlorine or other chemical disinfectants are only needed as secondary disinfectants. Long term efficacy is another major uncertainty for all the aforementioned technologies. Antimicrobial nanomaterials that rely on release of biocidal ions will be eventually depleted. Controlled release and the replenish strategies are thus needed. A potential “on-demand” release strategy is to encapsulate antimicrobial agents into a matrix gated by materials responsive to the presence of microorganisms or biofilms. This “on-demand” mechanism can be further coupled with recognition mechanisms for targeted release (Fig. 2). For nanomaterials relying on direct contact, fouling may largely suppress or even eliminate their antimicrobial activity.

2.5. Sensing and monitoring

A major challenge for water/wastewater treatment is water quality monitoring due to the extremely low concentration of certain contaminants, the lack of fast pathogen detection, as well as the high complexity of the water/wastewater matrices. Innovative sensors with high sensitivity and selectivity, and fast response are in great need.

2.5.1. Pathogen detection

Pathogen detection is of critical importance as it's directly related to public health. Conventional indicator systems such as coliform bacteria is slow and fail to monitor the presence of some important or emerging pathogens including viruses (hepatitis A and E, coxsackieviruses, echoviruses, adenoviruses, and Norwalk viruses), bacteria (*Legionella* and *Helicobacter*), and protozoan (*Cryptosporidium* and *Giardia*) (Theron et al., 2010). Many of these pathogens are etiologic agents in

outbreaks associated with drinking water. Additionally, pathogen detection is the key component of diagnosis-based water disinfection approach, in which disinfection is triggered by the detection of target microorganisms.

Active research is going on developing nanomaterial enabled pathogen sensors. These sensors usually consist of three major components: recognition agents, nanomaterials, and a signal transduction mechanism (Vikesland and Wigginton, 2010). Recognition agents that specifically interact with antigens or other epitopes on the pathogen surface provide the selectivity. Sensitivity and fast response are achieved by the nanomaterial related signal transduction upon the recognition event. A wide range of recognition agents have been utilized, including antibodies, aptamers, carbohydrates, and antimicrobial peptides (Vikesland and Wigginton, 2010). Nanomaterials improve the sensitivity and speed of detection and achieve multiplex target detection owing to their unique physicochemical properties, especially electrochemical, optical, and magnetic properties. These sensors can be employed to detect whole cells (Vikesland and Wigginton, 2010) as well as biomolecules (Theron et al., 2010).

The most commonly used nanomaterials in pathogen detection are magnetic nanoparticles, Quantum dots (QDs), noble metals, dye-doped nanoparticles and CNTs. Magnetic nanoparticles and CNTs have been extensively studied for sample concentration and purification. A commercial magnetic nanocomposite, Dynabead[®], is available for developing various pathogen detection kits.

QDs are fluorescent nanocrystals of semiconducting materials (e.g., CdSe) whose electronic characteristics depend on the size and shape of the individual crystals. QD particles with smaller sizes have wider band gaps and thus need more energy to excite and emit light with shorter wavelength. QDs have broad absorption spectra but narrow and stable fluorescent emission spectra. Thus QDs are especially suitable for multiplex detection using one excitation light source. The emission spectrum of QDs is ~10–20 times brighter than an

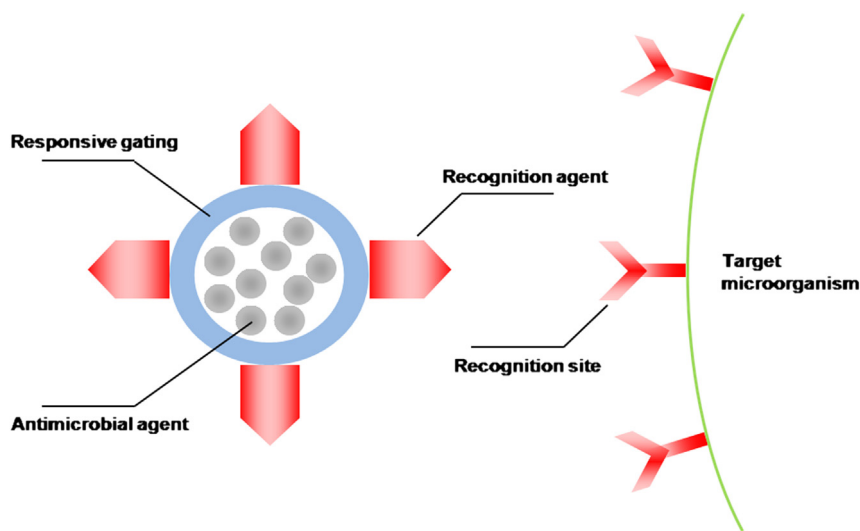


Fig. 2 – Schematic mechanism for “on-demand” microbial control. “On-demand” microbial control can be achieved by using recognition agents that target specific microorganism. The responsive gating material is designed to release the antimicrobial agent after the recognition event.

organic fluorophore (Yan et al., 2007) and up to thousands of times more stable than conventional dyes (Sukhanova et al., 2004).

Noble metal nanomaterials have been widely used in sensors mainly due to their enhanced localized surface plasmon resonance (LSPR), which depends on the size, shape, composition, and separation distance of nanoparticles, as well as the dielectric environment of the surrounding medium (Petryayeva and Krull, 2011). The high conductivity of noble metal nanoparticles also promotes the electron transfer between electrode surface and the analyte (Lei and Ju, 2012). The presence of enhanced LSPR leads to high molar extinction coefficient and Rayleigh scattering, as well as enhanced local electromagnetic fields near the nanoparticle surface. Based on theoretical calculation, nano-Au spheres of ~40 nm in diameter have an absorption cross-section 5 orders of magnitude higher than conventional dyes, while 80-nm nano-Au spheres scatter light 5 orders of magnitude more than fluorescence dyes (Jain et al., 2006). Noble metals were used mainly in colorimetric and surface-enhanced Raman spectroscopy (SERS) sensing. Colorimetric assays are fast and simple. The signal transduction relies on the color change of the nanoparticle suspension due to different interparticle distance or aggregation state (Kelly et al., 2003). It has been studied for detection of DNA, diagnosis of pathogen infection and pathogen monitoring in water samples. However, the aggregation state of nanoparticles is sensitive to the solution chemistry and difficult to control. The coexisting water/wastewater constituents will greatly affect results, reducing reproducibility. The SERS phenomenon is attributed to both electromagnetic effect and chemical mechanisms related to the charge transfer between the noble metals and the target molecules (Moskovits, 2005). As a result, the efficiency of Raman scattering can be enhanced more than 10^{14} fold, which is even capable of detecting a single molecule (Nie and Emery, 1997).

Silica nanoparticles doped with either organic or inorganic luminescent dyes have been developed for ultra-sensitive sensors. The large number of dye molecules confined in a single silica particle guarantees huge improvement in sensitivity. Moreover, the silica matrix protects the dye molecules from the external environment, largely suppressing photobleaching and photodegradation. The outstanding photostability makes dye-doped silica nanoparticles especially advantageous for applications that require high intensity or prolonged excitations (Yan et al., 2007). The rich silica chemistry (e.g., silane chemistry) also helps future surface modification and conjugation.

The high conductivity along the length makes CNTs outstanding electrode materials. As a result, CNTs can greatly facilitate electrochemical detection by promoting electron transfer (McCreery, 2008) and electrode–analyte interactions. They have been incorporated into electrodes via random or aligned coating, or used as a single CNT electrode (Yang et al., 2010b). Semiconducting CNTs can be used in nano-scale field-effect transistor (Heller et al., 2008). Besides their excellent electronic properties, the high adsorption capacity of CNTs increases detection sensitivity (Collins et al., 2000). The major challenge for CNT based sensors is the heterogeneity of CNTs. Separation of metallic and semiconducting SWNT has been

extensively studied but still far from perfect. The production and purification processes of CNTs often introduce impurities, contaminants, and even degradation of the CNT structure. Therefore, better synthesis, purification and separation are required to produce more homogeneous CNTs.

Although most of these nanosensors possess excellent photostability and sensitivity, nonspecific binding is still a major challenge for their application in water and wastewater. Strategies to reduce nonspecific binding and prevent undesired nanoparticle aggregation are in critical need.

2.5.2. Trace contaminant detection

In trace organic or inorganic contaminant detection, nanomaterials can be used in both concentration and detection. CNTs have great potential for environmental analysis of trace metal or organic pollutants as they offer high adsorption capacity and recovery rate as well as fast kinetics as discussed in Section 2.1.1. The pre-concentration factors for metal ions were found to be between 20 and 300 with fast adsorption kinetics (Duran et al., 2009). CNTs have also been extensively studied for preconcentrating a variety of organic compounds, many of which were done in real water samples (Cai et al., 2003). Adsorption of charged species to CNTs results in changes of conductance, providing the basis for the correlation between analyte concentration and current fluctuation (Mauter and Elimelech, 2008).

Other nanomaterials such as nano-Au and QDs have also been used. Nano-Au was used to detect pesticides at ppb levels in a colorimetric assay (Lisha et al., 2009); modified nano-Au was shown to detect Hg^{2+} and CH_3Hg^+ rapidly with high sensitivity and selectivity (Lin and Tseng, 2010). QD modified TiO_2 nanotubes lowered the detection limits of PAHs to the level of pica-mole per liter based on fluorescence resonance energy transfer (Yang et al., 2010a). A nanosensor based on CoTe QDs immobilized on a glassy carbon electrode surface was reported to detect Bisphenol A in water at concentrations as low as ~10 nM within 5 s (Yin et al., 2010).

2.6. Multifunctional devices

The advance in functional nanomaterials and their convergence with conventional technologies bring opportunities in designing a new family of nanotechnology enabled multifunctional water treatment devices which are capable of performing multiple tasks in one device. Such multifunctional systems can enhance the overall performance and avoid excessive redundancy, miniaturizing the footprint. Therefore, the multifunctional concept is especially advantageous in decentralized and small-scale applications. Different functional nanomaterials can be integrated onto a common platform based on treatment requirement. Beside magnetic nanoparticles, membranes are a good and extensively studied platform to construct multifunctional devices. Notably, electrospun nanofibers have drawn much attention as an excellent nanomaterial carrier. Owing to the high performance, small footprint, and modular design of nanotechnology enabled devices, it is envisaged that different functionalities can be assembled in layers of a cartridges or as modules arranged in series, allowing optimization/regeneration of each functionality separately (Qu et al., 2013). The

capacity and functionality of such nanotechnology enabled system can be easily manipulated by plugging in or pulling out modules.

3. Retention and reuse of nanomaterials

The retention and reuse of nanomaterials is a key aspect of nanotechnology enabled device design due to both cost and public health concerns. It can be usually achieved by applying a separation device or immobilizing nanomaterials in the treatment system. A promising separation process is membrane filtration which allows continuous operation with small footprint and chemical use. Ceramic membranes are more advantageous than polymeric membranes in photocatalytic or catalytic ozonation applications as they are more resistant to UV (Chin et al., 2006) and chemical oxidants. The suspended particles in the receiving water are detrimental to reactor-membrane hybrid systems as they can be retained by the membrane and significantly reduce the reaction efficiency. Thus raw water pretreatment is usually required to reduce the turbidity. Nanomaterials also can be immobilized on various platforms such as resins and membranes to avoid further separation. However, current immobilization techniques usually result in significant loss of treatment efficiency. Research is needed to develop simple, low-cost methods to immobilize nanomaterials without significantly impacting its performance. For magnetic nanoparticles/nanocomposites, low-field magnetic separation is a possible energy-efficient option.

Little is known about the release of nanomaterials from nanotechnology enabled devices. However, the potential release is expected to be largely dependent on the immobilization technique and the separation process employed. If no downstream separation is applied, nanomaterials coated on treatment system surfaces are more likely to be released in a relatively fast and complete manner, while nanomaterials embedded in a solid matrix will have minimum release until they are disposed of. For nanomaterials that release metal ions, their dissolution needs to be carefully controlled (e.g., by coating or optimizing size and shape). The detection of nanomaterial release is a major technical hurdle for risk assessment and remains challenging. Details regarding detection techniques are beyond the scope of this paper, and readers are referred to several recent reviews on this topic (da Silva et al., 2011; Tiede et al., 2008). Few techniques can detect nanomaterials in complex aqueous matrices and they are usually sophisticated, expensive and with many limitations. Fast, sensitive and selective nanomaterial analytical techniques are in great need.

4. Barriers and research needs

Although nanotechnology enabled water/wastewater treatment processes have shown great promise in laboratory studies, their readiness for commercialization varies widely. Some are already on the market, while others require significant research before they can be considered for full scale applications. Their future development and commercialization face a variety of challenges including technical hurdles,

cost-effectiveness, and potential environmental and human risk.

There are two major research needs for full-scale applications of nanotechnology in water/wastewater treatment. First, the performance of various nanotechnologies in treating real natural and waste waters needs to be tested. Future studies need to be done under more realistic conditions to assess the applicability and efficiency of different nanotechnologies as well as to validate nanomaterial enabled sensing technologies. Secondly, the long-term efficacy of these nanotechnologies is largely unknown as most lab studies were conducted for relatively short period of time. Research addressing the long-term performance of water and wastewater treatment nanotechnologies is in great need. As a result, side-by-side comparison of nanotechnology enabled systems and existing technologies is challenging.

Despite the superior performance, the adoption of innovative technologies strongly depends on the cost-effectiveness and the potential risk involved. The current cost of nanomaterials is prohibitively high with few exceptions such as nano-TiO₂, nanoscale ion oxide, and polymeric nanofibers. There are currently two approaches to address the cost issue. One proposed approach is to use low purity nanomaterials without significantly compromising efficiency as much of the production cost is related to separation and purification (Qu et al., 2013). Alternatively, the cost-effectiveness can be improved by retaining and reusing nanomaterials. Nanomaterials possess unique challenges for risk assessment and management as they are small particles instead of molecules or ions for which risk assessment framework and protocols are already in place. Better understanding and mitigating potential hazards associated with the use of nanomaterials in water and wastewater treatment will lead to broader public acceptance, which is crucial for new technology adoption.

The compatibility between aforementioned nanotechnologies and current water and wastewater treatment processes and infrastructure also needs to be addressed. Most treatment plants and distribution systems in developed countries are expected to remain in place for decades to come. As a result, it is important to be able to implement nanotechnology with minimal changes to existing infrastructure in the near term. In the meantime, nanotechnology enabled treatment processes can be employed in places where water treatment infrastructure does not exist or in POU devices.

5. Concluding remarks

Nanotechnology for water and wastewater treatment is gaining momentum globally. The unique properties of nanomaterials and their convergence with current treatment technologies present great opportunities to revolutionize water and wastewater treatment. Although many nanotechnologies highlighted in this review are still in the laboratory research stage, some have made their way to pilot testing or even commercialization. Among them, three categories show most promise in full scale application in the near future based on their stages in research and development, commercial availability and cost of nanomaterials involved, and

compatibility with the existing infrastructure: nano-adsorbents, nanotechnology enabled membranes, and nano-photocatalysts. All three categories have commercial products, although they have not been applied in large scale water or wastewater treatment. Several other water treatment nanotechnologies have found their niche applications in POU systems.

The challenges faced by water/wastewater treatment nanotechnologies are important, but many of these challenges are perhaps only temporary, including technical hurdles, high cost, and potential environmental and human risk. To overcome these barriers, collaboration between research institutions, industry, government, and other stakeholders is essential. It is our belief that advancing nanotechnology by carefully steering its direction while avoiding unintended consequences can continuously provide robust solutions to our water/wastewater treatment challenges, both incremental and revolutionary.

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