

Nanotechnology for a Safe and Sustainable Water Supply: Enabling Integrated Water Treatment and Reuse

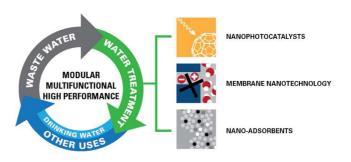
XIAOLEI QU, JONATHON BRAME, QILIN LI,* AND PEDRO J. J. ALVAREZ*

Department of Civil and Environmental Engineering, Rice University, Houston, Texas 77005, United States

RECEIVED ON JANUARY 28, 2012

CONSPECTUS

E nsuring reliable access to dean and affordable water is one of the greatest global challenges of this century. As the world's population increases, water pollution becomes more complex and difficult to remove, and global climate change threatens to exacerbate water scarcity in many areas, the magnitude of this challenge is rapidly increasing. Wastewater reuse is becoming a common necessity, even as a source of potable water, but our separate wastewater collection and water supply systems are not



designed to accommodate this pressing need. Furthermore, the aging centralized water and wastewater infrastructure in the developed world faces growing demands to produce higher quality water using less energy and with lower treatment costs. In addition, it is impractical to establish such massive systems in developing regions that currently lack water and wastewater infrastructure. These challenges underscore the need for technological innovation to transform the way we treat, distribute, use, and reuse water toward a distributed, differential water treatment and reuse paradigm (i.e., treat water and wastewater locally only to the required level dictated by the intended use).

Nanotechnology offers opportunities to develop next-generation water supply systems. This Account reviews promising nanotechnology-enabled water treatment processes and provides a broad view on how they could transform our water supply and wastewater treatment systems. The extraordinary properties of nanomaterials, such as high surface area, photosensitivity, catalytic and antimicrobial activity, electrochemical, optical, and magnetic properties, and tunable pore size and surface chemistry, provide useful features for many applications. These applications include sensors for water quality monitoring, specialty adsorbents, solar disinfection/decontamination, and high performance membranes. More importantly, the modular, multifunctional and high-efficiency processes enabled by nanotechnology provide a promising route both to retrofit aging infrastructure and to develop high performance, low maintenance decentralized treatment systems including point-of-use devices.

Broad implementation of nanotechnology in water treatment will require overcoming the relatively high costs of nanomaterials by enabling their reuse and mitigating risks to public and environmental health by minimizing potential exposure to nanoparticles and promoting their safer design. The development of nanotechnology must go hand in hand with environmental health and safety research to alleviate unintended consequences and contribute toward sustainable water management.

1. Introduction

No other resource is as necessary for life as is water. Its safety and availability are inextricably linked to global health, energy production, and economic development. Although water and wastewater treatment in the 20th century had a transformative impact, ranging from enhanced public health

to agricultural development, the global water supply faces major challenges, both old and new.

Worldwide, 884 million people lack access to adequate potable water and 1.8 million children die every year from diarrhea mainly due to water contamination. There is an urgent need to provide basic, affordable water treatment in

developing countries, where water and wastewater infrastructure are often nonexistent. Water supply systems in developed countries also face multiple challenges. Current technologies are reaching their limits in meeting increasingly stringent water quality standards and dealing with emerging contaminants such as pharmaceuticals, personal care products, and viruses. Centralized treatment and distribution systems allow little flexibility in response to changing demand for water quality or quantity, let alone differential water quality needs. The aging water infrastructure is responsible for significant energy consumption, water loss, and secondary contamination while the utilities lag behind in much needed replacements or upgrades.^{2,3} Meanwhile, rapid population growth puts 700 million people below the water stress threshold of 1700 m³/(person year), and this population is predicted to increase to 3 billion by 2025.4 Reuse of wastewater is becoming a necessity in many regions—sometimes as a source of potable water but our wastewater collection and water supply systems are not designed to accommodate this need. Clearly, separate, centralized water and wastewater systems are no longer the solution to a sustainable urban water supply.

Although existing infrastructure contributes inertia against a paradigm shift, these immense challenges call for a change toward integrated management of water and wastewater with a decentralized, differential treatment and reuse paradigm where water and wastewater are treated to the quality dictated by the intended use. Accordingly, new technologies that provide high efficiency, multiple-functionality, and high flexibility in system size and configuration are needed. Nanotechnology possesses all these features and, thus, may offer leapfrogging opportunities in this transformation. Significant research has been done on individual nanotechnology-enabled treatment processes, many of which show improved performance over conventional technologies. However, the potential and limitation of nanotechnology as an integral component of a water supply system has not been articulated. In this review, we summarize recent research and development of nanotechnology-enabled water and wastewater treatment processes, and we address an important question: When and where does it make sense to use nanotechnology to enable sustainable water management?

The "when" involves the timeline when nanotechnology is expected to be implemented in water and wastewater systems, as well as the occasion (e.g., new installations versus retrofits), scale, and treatment goals for which nanotechnology should be considered. The "where" deals with the geographical location of the water supply system; the size, density, and socioeconomic status of the population served; and the location within a treatment train where nanotechnology could be incorporated. On the basis of these analyses, we offer a vision of future integrated water treatment and reuse systems.

2. Application of Nanotechnology for Water **Treatment and Reuse**

Nanotechnology is actively pursued to both enhance the performance of existing treatment processes and develop new processes. Nanomaterial properties desirable for water and wastewater applications include high surface area for adsorption, high activity for (photo)catalysis, antimicrobial properties for disinfection and biofouling control, superparamagnetism for particle separation, and other unique optical and electronic properties that find use in novel treatment processes and sensors for water quality monitoring. The applications discussed below are all in the stage of laboratory research with noted exceptions that are being field tested.

2.1. Adsorption. Nanoadsorbents offer significant improvements over conventional adsorbents with their extremely high specific surface area, short intraparticle diffusion distance, and tunable pore size and surface chemistry. High specific surface area is mainly responsible for their high adsorption capacity. Furthermore, the high surface energy and size dependent surface structure at the nanoscale may create highly active adsorption sites,5 resulting in higher surface-area-normalized adsorption capacity. The surface of many nanomaterials can be functionalized to target specific contaminants, achieving high selectivity. Porous nanomaterials (e.g., electrospun activated carbon nanofibers) have tunable pore size and structure to allow control of adsorption kinetics. Nanoadsorbents can be readily integrated into existing treatment processes such as slurry reactors, filters, or adsorbers (e.g., by coating filter media or loading into porous granules).

Carbon nanotubes (CNTs) are being explored as substitutes for activated carbon, as they effectively remove both organic and metal contaminants. The available binding sites (e.g., external surfaces and grooves in the bundles) and contaminant—CNT interactions (e.g., hydrophobic, π – π bonding, hydrogen bonding, covalent bonding, and electrostatic interactions) control organic contaminant adsorption on CNTs.⁶ Binding sites on CNTs are more available than those on activated carbon, which contains inaccessible pores, especially for bulky molecules such as tetracycline.⁷ Their π electron rich surface can serve as either electron donor or acceptor for many polar aromatics such as nitroaromatics and phenols.⁸ While hydrophobic graphitic surfaces are the main sites for organic adsorption, metal ions adsorb primarily on surface functional groups, which can be reversed by pH adjustment, enabling reuse.⁹ Limited by the high prices of CNTs, current research has focused on contaminants not effectively removed by existing technologies (e.g., antibiotics and polar aromatics), or for sample preconcentration. Graphite oxide nanosheets, which can potentially be produced at low cost by exfoliating graphite, have emerged as another alternative nanoadsorbent for metal and organic contaminants.¹⁰

Metal oxide nanomaterials, such as nanomagnetite and nano-TiO₂, are effective, affordable adsorbents for heavy metals and radionuclides. Their surface structure can be manipulated to maximize active adsorption sites such as corners, edges, vacancies, and high energy crystallographic facets. 5,11,12 In addition, nanomagnetite possesses unique superparamagnetic properties that allow easy separation from water in a weak magnetic field.¹³ Such magnetic properties enable a new class of core-shell structure nanoparticles: the shell provides desired functionality while the magnetic core allows easy particle separation. Another promising design of core-shell nanomaterials consists of a shell chemically tailored for rapid, selective adsorption and a reactive core for degradation of adsorbed contaminants (e.g., laccase-carrying electrospun nanofibers).¹⁴ Specialty nanoadsorbents can also be designed using amphiphilic dendrimers with specific binding sites.¹⁵

2.2. Sensing and Monitoring. Water quality monitoring is challenging due to extremely low concentrations of micropollutants, high complexity of water and wastewater matrices, and lack of low-cost, rapid pathogen detection methods. Rapid detection of microorganisms is also central to diagnosis-based disinfection or biofilm control, in which treatment decisions are made on the basis of the information from advanced sensors to provide high-efficiency, responsive (on-demand), and targeted treatment.

Effective integration of nanomaterials and recognition agents (e.g., antibodies, aptamers, carbohydrates, and antimicrobial peptides) could yield fast, sensitive, and selective sensors for microbial detection. Nanomaterials can improve sensor sensitivity and speed and achieve multiplex target detection utilizing their unique electrochemical, optical, or magnetic properties. Magnetic nanoparticles and CNTs are explored for sample concentration and purification. Quantum dots (QDs), dye-doped nanoparticles, noble metal nanoparticles, and CNTs are widely used in nanosensor

research. QDs have wide absorption bands but narrow and stable fluorescent emission spectra that vary with particle size and chemical composition, allowing multiplex target detection with one excitation source.¹⁷ Dye-doped silica and polymeric nanoparticles exhibit high luminescent intensity, as large numbers of dye molecules are confined to each nanoparticle. Stable localized surface plasmon resonances of noble metal nanoparticles (e.g., nano-Au, nano-Ag) enable optical pathogen detection based on changes in nanoparticle aggregation state or local refractive index.¹⁶ Nobel metal nanomaterials also improve surface enhanced Raman spectroscopy, achieving enhancement factors up to 10¹⁴ and single molecule detection.¹⁸ CNTs are excellent materials for electrodes and field-effect transistors. 19 Either coated on bulk electrode surfaces (randomly or vertically aligned) or as nanoelectrodes, CNTs promote analyte—sensor interactions and electron transfer. 19

2.3. Disinfection and Decontamination. While traditional disinfection practices such as chlorination and ozonation have tremendously improved public health, the challenge to provide effective disinfection without forming harmful disinfection byproducts (DBPs) calls for technological innovation. Several nanomaterials have strong antimicrobial properties, including nano-Ag, nano-ZnO, nano-TiO₂, nano-Ce₂O₄, CNTs, and fullerenes.^{20,21} These nanomaterials inactivate microorganisms by releasing toxic metal ions (e.g., Ag⁺ and Zn²⁺), compromising cell membrane integrity upon direct contact (e.g., CNTs, nC₆₀, nano-Ce₂O₄) or generating reactive oxygen species (ROS, e.g., nano-TiO2, fullerol, and aminofullerene)²⁰⁻²² with fewer tendencies to form DBPs. Nano-Ag is a common choice for point-of-use (POU) water treatment devices because of its strong and wide-spectrum antimicrobial activity and low toxicity to humans. The antimicrobial activity of nano-Ag is largely attributed to the release of Ag⁺, which attacks functional groups with high affinity for Ag⁺, e.g., thiol in proteins and phosphates in DNA.²³ Therefore, solution chemistry, such as the presence of Ag⁺ ligands (e.g., sulfides, chlorides, phosphates), plays an important role in the bioavailability and toxicity of nano-Ag.²³ Because dissolution of nano-Ag leads to its eventual depletion, release control and replenishing strategies are crucial for its long-term efficacy. Responsive polymers that change the hydration and swelling state or degrade upon changes in local chemistry (e.g., protease concentration²⁴) induced by rising microbial concentrations can potentially be used to achieve release of biocides on demand.

The fibrous structure, antibacterial activity, and conductivity of CNTs enable their use in antimicrobial filters.

The antibacterial mechanism of CNTs and some other carbon based nanomaterials (e.g., graphite, graphite oxide, graphene oxide) was proposed to involve membrane perturbation and electronic structure-dependent oxidation stress. Short, dispersed, and metallic CNTs with small diameters are more toxic. CNT filters can also be used in electrochemical processes, in which a small intermittent voltage inactivates physically trapped microorganisms through oxidation. The electric potential results in electrophoresis of viruses toward CNTs, alleviating the negative impact of natural organic matter on virus retention by the CNT filter.

An actively pursued water treatment strategy utilizes sunlight and nanophotocatalysts to degrade organic contaminants and inactivate pathogens. Research is being conducted to enhance quantum yield and photocatalyst dispersion/recovery and immobilization and to optimize photoreactor design.³⁰ Little has been done, however, to improve selectivity via targeted adsorption, which could be achieved by tailoring nanophotocatalyst surface chemistry.

TiO₂ photocatalysts effectively produce ROS, especially superoxide and hydroxyl radicals, under UV-A irradiation,³¹ which allows activation by sunlight. ROS inactivate pathogens and degrade organic contaminants with little DBP formation. Compared to its bulk form, nano-TiO₂ has much higher photocatalytic activity due to its large surface area (hence more surface reactive sites), lower volume e⁻/h⁺ recombination, and faster interfacial charge transfer. 32 However, when particle size becomes extremely small (several nanometers), photocatalytic activity decreases due to surface e⁻/h⁺ recombination. Thus, an optimum particle size exists in the nanometer scale. The activity of nano-TiO2 can be improved by maximizing the reactive facets, 11 reducing the e⁻/h⁺ recombination by noble metal doping,³³ and surface treatment to enhance contaminant adsorption. Compared to nanoparticles, TiO₂ nanotubes generally have lower e⁻/h⁺ recombination, owing to the short carrierdiffusion paths and better adsorption of contaminants.³⁴ Various dopants, including metals, dye sensitizers, narrow band gap semiconductors, and nonmetals have been tested to extend the excitation spectrum of nano-TiO₂ to the visible range through formation of impurity energy levels, electron injection, or band gap narrowing.33,35 Among them, nonmetal dopants such as nitrogen are considered most costeffective and feasible for industrial applications. 35 However, reduced UV-activity and the stability of doped TiO2 need to be addressed.35

Fullerenes and CNTs are also photosensitive and can generate ROS in water.^{20,22,36} When activated by visible

light, aminofullerenes and fullerol produce singlet oxygen ($^{1}O_{2}$), which has high selectivity toward contaminants containing electron-rich moieties, allowing their degradation in water with less interference from background organics (e.g., wastewater).²²

2.4. Membrane Nanotechnology and Fouling Control. Membrane technology is a key component of an integrated water treatment and reuse paradigm. It removes a wide range of contaminants, allows use of nonconventional water sources (e.g., brackish water, seawater, and wastewater), provides a high level of automation, and requires little land and chemical use, and the modular configuration is adaptive to various system scales. The performance of a membrane system largely depends on the membrane material, which bears an inherent trade-off between solvent permeation and solute rejection. Three membrane nanotechnologies have shown promise in overcoming such a trade-off: aligned CNTs, biomimetic membranes, and thin film nanocomposite (TFNC) membranes.

Both aligned CNT and biomimetic membranes utilize nanochannels (CNTs and protein channels called aquaporins, respectively) that allow water molecules to pass in a single file with exceptional permeation rates, 3 orders of magnitude greater than the Hagen-Poiseuille equation prediction in the case of CNTs.³⁷ The selectivity for water is achieved by CNT diameter and chemistry of the nanotube opening,³⁸ or the unique hourglass shape, size, and chemical structure of aquaporins.³⁹ Incorporation of vertically aligned CNTs and aquaporins into membrane matrices, even at a low percentage (0.03% CNT surface porosity⁴⁰ or 0.005 mol % of Aquaporin Z⁴¹) could provide flux exceeding that of current commercial seawater reverse osmosis (RO) membranes. The higher flux may not significantly improve the energy consumption of seawater desalination by RO,⁴² but it can greatly reduce the footprint and cost of wastewater treatment by RO, whose theoretical energy consumption is much lower. High rejection of salts and small contaminant molecules remains challenging for aligned CNT membranes due to the lack of nanotubes with uniform subnanometer diameters; and the opening gating either is susceptible to charge screening or reduces the membrane permeability.

Another key barrier for both technologies is the scale-up of the membrane fabrication; alignment of CNTs and production of aquaporins are very challenging at large scale. Continuous high-yield chemical vapor deposition⁴³ and postmanufacture alignment using a magnetic field⁴⁴ have been explored for fabrication of aligned CNT membranes. In addition to water channels, biological membranes also

provide examples of selective ion channels. A proposed strategy is to pull the ions out of product water with highly selective ion channels/pumps.⁴⁵ The size, hydrophobicity, tunable surface chemistry, and electronic properties of CNTs make them good substrates for biomimetic water and ion channels.

TFNC membranes comprise nanozeolites in the polyamide active layer of thin film composite membranes. The enhanced permeability was attributed to small, hydrophilic pores of zeolites that create preferential paths for water while excluding hydrated ions, ⁴⁶ and possibly defects at the zeolite-polyamide interface. Nanozeolites can also serve as carriers for antimicrobial agents; e.g., Ag⁺, whose release and regeneration can be realized through ion exchange. The TFNC technology has reached the early stage of commercialization (www.nanoh2o.com).

Much research has been devoted to developing reactive membranes, often comprising nano-TiO $_2$, to simultaneously separate and degrade contaminants as well as reduce membrane fouling. Nano-TiO $_2$ has been incorporated into both polymeric and ceramic membranes, although long-term exposure to UV light and ROS could potentially damage polymeric membranes. 47

Another important application of nanomaterials is fouling control of membranes and other surfaces in water treatment, storage, and distribution systems. Various nanomaterials, including nano-Ag, nano-TiO₂, nanoalumina, and (unaligned) CNTs, have been incorporated into polymeric membranes via surface self-assembly or addition to the membrane casting solution,⁴⁰ requiring minimum changes in current industrial manufacturing processes. Surface immobilization through covalent bonding, however, is more preferable, as it maximizes nanomaterial utilization and minimizes interference with the membrane chemistry.⁴⁸ The resulting nanocomposite membranes have enhanced fouling resistance due to surface hydrophilicity or antimicrobial activity of the nanomaterial. An alternative approach is to employ fouling resistant surface morphologies, a strategy used by marine animals (e.g., sharks) and plants (e.g., lotus leaves).49

2.5. Groundwater Remediation. Nanozero valent iron (nZVI) and bimetallic nanoparticles have been used for *in situ* reductive treatment of groundwater contaminated with oxidized pollutants such as chlorinated solvents and pesticides, nitrate, and hexavalent chromium.^{50,51} Compared to their bulk counterparts, these nanoreductants have higher surface area and reactivity. nZVI and bimetallic nanoparticles have been successfully field tested in over 44

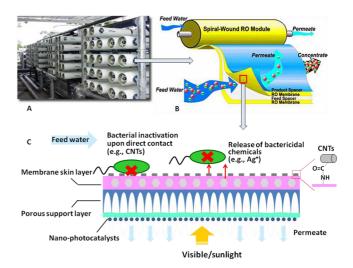


FIGURE 1. Nanotechnology-enabled multifunctional membrane system. (A) RO membrane water treatment system; (B) spiral-wound RO membrane module (www.water-technology.net); (C) conceptual multifunctional membrane. Antimicrobial nanomaterials coated on a membrane surface or impregnated in a membrane matrix can inactivate microorganisms upon contact or by releasing biocides, preventing biofouling. Nanophotocatalysts utilize photons to further disinfect and decontaminate permeate water.

remediation sites.⁵¹ However, nZVI tends to aggregate and lose its mobility and reactivity. Surface coating with organic polymers can enhance nZVI delivery but lower reactivity.⁵²

2.6. Multifunctional Processes. Advances in functional nanomaterials and their convergence with conventional technologies open up opportunities in designing nanotechnology-enabled multifunctional processes capable of performing multiple tasks—e.g., water disinfection, decontamination, and separation—in one reactor. Multifunctional systems can enhance the overall performance by creating synergy, avoiding redundancy, simplifying operation, and reducing the system footprint and cost. Nanomaterials are uniquely suitable for multifunctional systems, since nanomaterials of different functions can be easily assembled together, even on very small carriers such as nanofibers.

In addition to magnetic nanoparticles, membranes are a good and extensively studied platform for multifunctional devices (Figure 1). Recently, electrospun nanofiber-based multifunctional devices have been proposed as a solution for low cost water treatment.⁵³ Electrospinning is a simple and inexpensive method to make ultrafine nonwoven fibers using a variety of materials.⁵⁴ The resulting nanofiber filters (Figure 2) possess high specific surface area, tunable pore size, and high porosity. Treatment functions beyond filtration can be added by surface coating or blending nanoparticle precursors in spinning solutions. Also, conventional sol–gel precursor solutions can be used to form ceramic

nanofibers.⁵⁴ These features make electrospun nanofibers an excellent platform for multifunctional filters. Although not yet reported, it is expected that nanofibers of different functionalities can be assembled in layers/cartridges, allowing optimization/regeneration of each functionality separately.

3. Barriers

While nanotechnology holds significant promise for enabling water treatment and wastewater reuse, significant barriers stand between some of these promises and their delivery. Issues such as cost effectiveness, potential nanomaterial toxicity, and social acceptability must be addressed.

3.1. Cost and Performance. Broad acceptance of novel water and wastewater treatment nanotechnologies depends on both their performance and affordability. In developing countries, water treatment often only covers the most basic needs (e.g., disinfection), while the developed world uses more advanced technologies to remove a wider spectrum

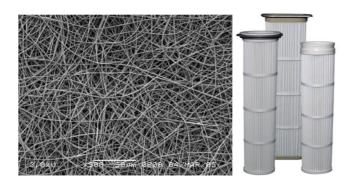


FIGURE 2. SEM image (left) of electrospun nanofibers and photo (right, Donaldson Company, Inc.) of electrospun nanofiber bag filters.

of pollutants. However, in both scenarios, the need to treat increasingly complex contaminant mixtures and produce higher quality water at lower cost is pushing the boundaries of current treatment paradigms. Most nanotechnology-based treatment options are high-performance—enabling more efficient treatment—but their costs are currently high (Figure 3). This represents a significant but not insurmountable barrier.

A considerable fraction of the nanomaterial production cost is related to separation and purification. Prices of researchgrade nanomaterials (with high purity and uniform reproducible properties) have remained relatively constant over the past decade (Figure 4), and they are unlikely to drop significantly without increased demand and production scale-up. Yet, the feasibility of using nanomaterials for water treatment can be enhanced by producing nanomaterials of lower purity. For example, aminofullerene photocatalysts⁵⁵ made with fullerene soot rather than ultrapure C_{60} (a cost savings of \sim 90%) exhibit a minimal (<10%) loss of effectiveness (unpublished results). Furthermore, longterm reusability of nanomaterials enhances their cost-effectiveness. Encouraging examples include photocatalysts that retain activity through multiple reuse cycles, 55 and regeneration of nanoadsorbents⁵⁶ and magnetically separable multifunctional nanomaterials. 13

3.2. Unintended Consequences. There are many precedents of beneficial water treatment technologies that have had unintended detrimental consequences. One example is disinfection with chlorine, which contributed to a near doubling of life expectancy in the developed world⁵⁷ but was later found to produce carcinogenic byproducts

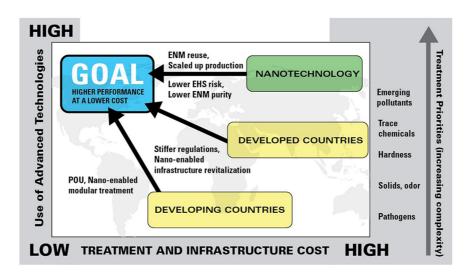


FIGURE 3. Conceptual improvements to water treatment through nanotechnology. Arrows represent specific strategies or drivers that can enhance performance and/or decrease costs through use of nanotechnology.

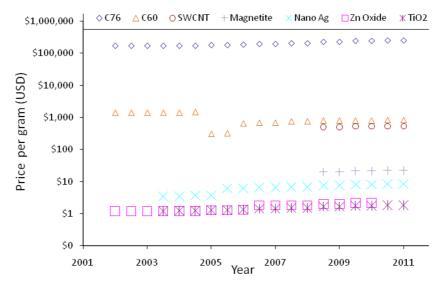


FIGURE 4. Nanomaterial price by year (not adjusted for inflation). Data represents research-grade nanomaterials; commercially available nanomaterials can be much less expensive. (Data from Sigma Aldrich.)

(e.g., trihalomethanes and *N*-nitrosodimethylamine). This underscores the need to understand and mitigate potential hazards associated with the use of nanomaterials in water treatment.

The potential toxicity of nanomaterials is often associated with the same properties that make them useful. Thus, toxicity depends on the molecular structure of nanomaterial constituents (which generally dictates the toxicity end points) as well as the size (which affects uptake). Shape-dependent toxicity has been reported for silver nanoparticles^{58,59} and CNTs;^{25,27} however, it is unclear whether such observations reflect the presence of highly reactive surface sites formed only at the nanoscale or shape-related differences in bioavailability, uptake, and bioaccumulation potential.⁶⁰

Risk assessment for many nanomaterials can benefit from the extensive toxicological database available for their bulk counterparts and shared constituents. However, allotropic nanomaterials such as fullerenes and CNTs do not have bulk counterparts, which precludes such comparisons and suggests the need for more careful toxicity studies. In a broad prospective, risk assessment should consider every stage in the life cycle of nanomaterials.⁶¹

Minimizing risks to public and environmental health could be achieved by curtailing potential exposure through nanoparticle immobilization onto reactor surfaces or support media. This may have the ancillary benefit of reduced nanoparticle aggregation and improved activity. For nanoparticles that release toxic metals (e.g., nano-Ag and metallic QDs), it is important to control their dissolution,

e.g., by using stabilizing coatings or optimizing nanoparticle shape and size. Depending on the application scenario, barrier technologies (e.g., membranes and magnetic separation) may be used to recover nanoparticle and prevent their release. Risk minimization should also consider the design of safer nanomaterials using constituents that are inherently nonhazardous. A significant challenge facing this strategy is to reduce toxicity without stifling nanomaterial performance.

4. Outlook for the Future

Nanotechnology provides leapfrogging opportunities to develop next-generation water supply systems. In the developed world, near-term applications include solving problems with existing treatment processes (e.g., DBPs, emerging contaminants, and membrane fouling) through system retrofitting. Many nanotechnologies can enhance treatment capabilities and efficiency with minimum alterations to the existing infrastructure, enabling the use of nonconventional water sources such as wastewater for different reuse scenarios (Figure 5). Nanotechnology-enabled POU systems can polish tap water for drinking or other high-end use, alleviating the risk associated with secondary contamination in the distribution system. In developing countries, nanotechnology would enable POU systems that are easy to operate, maintain, and replace, and can be tailored to specific treatment needs with minimal use of electricity or chemicals.

In the future, nanotechnology will likely play an important role in reshaping water supply systems to be more sustainable and smarter (i.e., differentiating and responding to changes in available water resources, and water quality

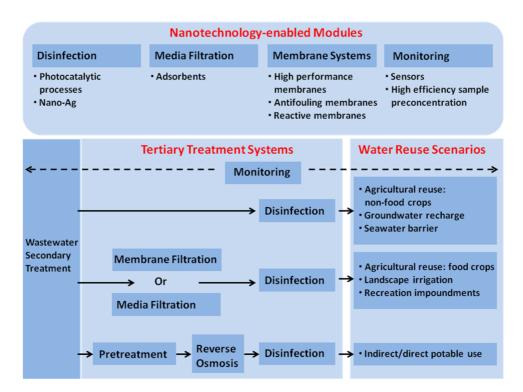


FIGURE 5. Wastewater tertiary treatment systems with nanotechnology-enabled modular design for differential water reuse scenarios. These nanotechnology-enabled modules can be similarly applied for drinking water treatment.

and quantity requirements). This will most likely be achieved by centralized basic treatment (e.g., suspended solids removal) near the source water, complemented by differential treatment and water reuse at the point of use (residential communities, farms, industries, etc). The large variety of nanomaterials makes it possible to have modular units for different treatment goals, which allow easy control of functionality and capacity by plugging in or pulling out modules. As the same treatment schemes for differential reuse of wastewater (Figure 5) can be applied to treat natural water to varying quality, local combined water treatment and reuse can be realized. Furthermore, future nanotechnologyenabled systems might function on-demand by detecting contaminants in real time and triggering corresponding treatment when needed.

Nanotechnology will not be universally applicable. Feasible niches in the near future will likely include POU devices and locations or occasions that require high treatment efficiency, a small footprint, and easy operation, such as the following (1) heavily populated arid regions needing high performance water treatment and reuse; (2) remote, small public water systems with challenging source waters; (3) crisis management/disaster response situations where POU treatment systems offer a stopgap until damaged infrastructure recovers; (4) personal water supply devices

that utilize any source water; and groundwater cleanup and in situ remediation of recalcitrant contaminants.

Ensuring reliable access to clean and affordable water is one of the greatest global challenges of this century. Overcoming this challenge will require new water resource management approaches and technological reform. Current water treatment and reuse systems will need to be bolstered and new systems installed to meet increasing demands for clean water. Nanotechnology will likely play a critical role, not only supplementing and enhancing existing processes, but also facilitating the transformation of water supply systems toward a distributed differential treatment paradigm that integrates wastewater reuse with energy neutral operations, lower residuals production, and safer water quality.

We are grateful to the Korea Institute of Science and Technology for partial funding. Special thanks are due to Donald Soward for graphical support.

BIOGRAPHICAL INFORMATION

Xiaolei Qu is a Ph.D. student in the Department of Civil and Environmental Engineering at Rice University. He received his B.S. and M.S. in Environmental Science from Nanjing University, researching sorption mechanisms of organic chemicals. His current

research focuses on the environmental impact of carbon based nanomaterials.

Jonathon Brame is a graduate student at Rice University pursuing a Ph.D. in Environmental Engineering researching nanotechnology applications for water treatment, remediation, and reuse. He received his B.S. in physics from Brigham Young University, where he studied nanomaterial applications in collaboration with NASA Goddard Space Flight Center.

Qilin Li is an Associate Professor of Civil and Environmental Engineering at Rice University. She received her B.S. in Environmental Engineering from Tsinghua University and her M.S. and Ph.D. degrees in Environmental Engineering from the University of Illinois at Urbana—Champaign. Her research focuses on advanced technologies for water treatment and reuse, environmental fate and transport of nanomaterials, and sustainable water infrastructure.

Pedro J. J. Alvarez is the George R. Brown Professor and Chair of Civil and Environmental Engineering at Rice University. He graduated as a Civil Engineer at McGill University and got M.S. and Ph.D. degrees in Environmental Engineering from the University of Michigan. Alvarez is a fellow of AAAS, ASCE, IWA, and WEF, and conducts research on environmental nanotechnology (implications and applications), bioremediation, the fate and transport of toxic chemicals, and the water footprint of biofuels.

FOOTNOTES

*Corresponding authors: (0.L.) phone, (713)348-2046; fax, (713)348-5268; e-mail, qilin.li@rice.edu. (P.J.J.A.) phone, (713)348-5903; e-mail, alvarez@rice.edu. The authors declare no competing financial interest.

REFERENCES

- 1 WHO. UNICEF "Progress on sanitation and drinking-water 2010 update"; WHO/UNICEF: 2010.
- 2 Committee on Public Water Supply Distribution Systems: Assessing and Reducing Risks, National Research Council. *Drinking Water Distribution Systems: Assessing and Reducing Risks*; The National Academies Press: 2006.
- 3 EPA. The Clean Water and Drinking Water Infrastructure Gap Analysis, U.S. EPA Office of Water: 2002.
- 4 Alcamo, J.; Henrichs, T.; Rosch, T. World Water in 2025: Global modeling and scenario analysis for the World Commission on Water for the 21st Century; 2000.
- 5 Auffan, M.; Rose, J.; Proux, O.; Borschneck, D.; Masion, A.; Chaurand, P.; Hazemann, J. L.; Chaneac, C.; Jolivet, J. P.; Wiesner, M. R.; Van Geen, A.; Bottero, J. Y. Enhanced adsorption of arsenic onto maghemites nanoparticles: As(III) as a probe of the surface structure and heterogeneity. *Langmuir* 2008, *24*, 3215–3222.
- 6 Yang, K.; Xing, B. S. Adsorption of Organic Compounds by Carbon Nanomaterials in Aqueous Phase: Polaryi Theory and Its Application. Chem. Rev. 2010, 110, 5989–6008.
- 7 Ji, L.; Chen, W.; Duan, L.; Zhu, D. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. *Environ. Sci. Technol.* 2009, 43, 2322–2327.
- Pan, B.; Xing, B. S. Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes. Environ. Sci. Technol. 2008, 42, 9005–9013.
- 9 Rao, G. P.; Lu, C.; Su, F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Sep. Purif. Technol. 2007, 58, 224–231.
- 10 Gao, W.; Majumder, M.; Alemany, L. B.; Narayanan, T. N.; Ibarra, M. A.; Pradhan, B. K.; Ajayan, P. M. Engineered Graphite Oxide Materials for Application in Water Purification. ACS Appl. Mater. Interfaces 2011, 3, 1821–1826.
- 11 Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. Anatase TiO(2) single crystals with a large percentage of reactive facets. *Nature* **2008**, 453, 638–U4.
- 12 Roduner, E. Size matters: why nanomaterials are different. Chem. Soc. Rev. 2006, 35, 583–592.
- 13 Yavuz, C. T.; Mayo, J. T.; Yu, W. W.; Prakash, A.; Falkner, J. C.; Yean, S.; Cong, L. L.; Shipley, H. J.; Kan, A.; Tomson, M.; Natelson, D.; Colvin, V. L. Low-field magnetic separation of monodisperse Fe₃O₄ nanocrystals. *Science* 2006, *314*, 964–967.

- 14 Dai, Y.; Yin, L.; Niu, J. Laccase-Carrying Electrospun Fibrous Membranes for Adsorption and Degradation of PAHs in Shoal Soils. Environ. Sci. Technol. 2011, 45, 10611–10618.
- 15 Theron, J.; Walker, J. A.; Cloete, T. E. Nanotechnology and water treatment: Applications and emerging opportunities. Crit. Rev. Microbiol. 2008, 34, 43–69.
- 16 Vikesland, P. J.; Wigginton, K. R. Nanomaterial Enabled Biosensors for Pathogen Monitoring—A Review. Environ. Sci. Technol. 2010, 44, 3656–3669.
- 17 Wu, X. Y.; Liu, H. J.; Liu, J. Q.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N. F.; Peale, F.; Bruchez, M. P. Immunofluorescent labeling of cancer marker Her2 and other cellular targets with semiconductor quantum dots. *Nat. Biotechnol.* 2003, *21*, 41–46.
- 18 Nie, S.; Emory, S. R. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. Science 1997, 275, 1102–1106.
- 19 Yang, W. R.; Ratinac, K. R.; Ringer, S. P.; Thordarson, P.; Gooding, J. J.; Braet, F. Carbon Nanomaterials in Biosensors: Should You Use Nanotubes or Graphene? *Angew. Chem., Int. Ed.* **2010**, *49*, 2114–2138.
- 20 Li, Q. L.; Mahendra, S.; Lyon, D. Y.; Brunet, L.; Liga, M. V.; Li, D.; Alvarez, P. J. J. Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Res.* 2008, 42, 4591–4602.
- 21 Klaine, S. J.; Alvarez, P. J. J.; Batley, G. E.; Fernandes, T. F.; Handy, R. D.; Lyon, D. Y.; Mahendra, S.; McLaughlin, M. J.; Lead, J. R. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* **2008**, *27*, 1825–1851.
- 22 Lee, J.; Hong, S.; Mackeyev, Y.; Lee, C.; Chung, E.; Wilson, L. J.; Kim, J. H.; Alvarez, P. J. J. Photosensitized Oxidation of Emerging Organic Pollutants by Tetrakis C(60) Aminofullerene-Derivatized Silica under Visible Light Irradiation. *Environ. Sci. Technol.* 2011, 45, 10598–10604.
- 23 Xiu, Z. M.; Ma, J.; Alvarez, P. J. J. Differential Effect of Common Ligands and Molecular Oxygen on Antimicrobial Activity of Silver Nanoparticles versus Silver Ions. *Environ. Sci. Technol.* **2011**, *45*, 9003–9008.
- 24 West, J. L.; Hubbell, J. A. Polymeric biomaterials with degradation sites for proteases involved in cell migration. *Macromolecules* 1999, 32, 241–244.
- 25 Vecitis, C. D.; Zodrow, K. R.; Kang, S.; Elimelech, M. Electronic-Structure-Dependent Bacterial Cytotoxicity of Single-Walled Carbon Nanotubes. ACS Nano 2010, 4, 5471– 5479.
- 26 Liu, S. B.; Zeng, T. H.; Hofmann, M.; Burcombe, E.; Wei, J.; Jiang, R. R.; Kong, J.; Chen, Y. Antibacterial Activity of Graphite, Graphite Oxide, Graphene Oxide, and Reduced Graphene Oxide: Membrane and Oxidative Stress. ACS Nano 2011, 5, 6971–6980.
- 27 Kang, S.; Mauter, M. S.; Elimelech, M. Physicochemical determinants of multiwalled carbon nanotube bacterial cytotoxicity. *Environ. Sci. Technol.* 2008, 42, 7528–7534.
- 28 Vecitis, C. D.; Schnoor, M. H.; Rahaman, M. S.; Schiffman, J. D.; Elimelech, M. Electrochemical Multiwalled Carbon Nanotube Filter for Viral and Bacterial Removal and Inactivation. *Environ. Sci. Technol.* **2011**, *45*, 3672–3679.
- 29 Rahaman, M. S.; Vecitis, C. D.; Elimelech, M. Electrochemical Carbon-Nanotube Filter Performance towards Virus Removal and Inactivation in the Presence of Natural Organic Matter. *Environ. Sci. Technol.* 2012, 46, 1556–1564.
- 30 Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic water treatment technology: A review. Water Res. 2010, 44, 2997–3027.
- 31 Kikuchi, Y.; Sunada, K.; Iyoda, T.; Hashimoto, K.; Fujishima, A. Photocatalytic bactericidal effect of TiO₂ thin films: Dynamic view of the active oxygen species responsible for the effect. J. Photochem. Photobiol., A: Chem. 1997, 106, 51–56.
- 32 Zhang, Z. B.; Wang, C. C.; Zakaria, R.; Ying, J. Y. Role of particle size in nanocrystalline TiO₂-based photocatalysts. J. Phys. Chem. B 1998, 102, 10871–10878.
- 33 Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renewable Sustainable Energy Rev.* **2007**, *11*, 401–425.
- 34 Macak, J. M.; Zlamal, M.; Krysa, J.; Schmuki, P. Self-organized TiO₂ nanotube layers as highly efficient photocatalysts. Small 2007, 3, 300–304.
- 35 Fujishima, A.; Zhang, X. T.; Tryk, D. A. TiO(2) photocatalysis and related surface phenomena. Surf. Sci. Rep. 2008, 63, 515–582.
- 36 Chen, C. Y.; Jafvert, C. T. The role of surface functionalization in the solar light-induced production of reactive oxygen species by single-walled carbon nanotubes in water. *Carbon* 2011, 49, 5099–5106.
- 37 Holt, J. K.; Park, H. G.; Wang, Y. M.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* **2006**, *312*, 1034–1037.
- 38 Mauter, M. S.; Elimelech, M. Environmental applications of carbon-based nanomaterials. Environ. Sci. Technol. 2008, 42, 5843–5859.
- 39 de Groot, B. L.; Grubmuller, H. Water permeation across biological membranes: Mechanism and dynamics of aquaporin-1 and GlpF. *Science* **2001**, *294*, 2353–2357.
- 40 Pendergast, M. M.; Hoek, E. M. V. A review of water treatment membrane nanotechnologies. *Energy Environ. Sci.* 2011, 4, 1946–1971.
- 41 Kumar, M.; Grzelakowski, M.; Zilles, J.; Clark, M.; Meier, W. Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z. *Proc. Natl. Acad. Sci. U. S. A.* 2007, 104, 20719–20724.

- 42 Elimelech, M.; Phillip, W. A. The Future of Seawater Desalination: Energy, Technology, and the Environment. *Science* **2011**, *333*, 712–717.
- 43 de Villoria, R. G.; Hart, A. J.; Wardle, B. L. Continuous High-Yield Production of Vertically Aligned Carbon Nanotubes on 2D and 3D Substrates. ACS Nano 2011, 5, 4850–4857.
- 44 Mauter, M. S.; Elimelech, M.; Osuji, C. O. Nanocomposites of Vertically Aligned Single-Walled Carbon Nanotubes by Magnetic Alignment and Polymerization of a Lyotropic Precursor. ACS Nano 2010, 4, 6651–6658.
- 45 Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. Science and technology for water purification in the coming decades. *Nature* **2008**, 452, 301–310.
- 46 Jeong, B. H.; Hoek, E. M. V.; Yan, Y. S.; Subramani, A.; Huang, X. F.; Hurwitz, G.; Ghosh, A. K.; Jawor, A. Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes. *J. Membr. Sci.* 2007, 294, 1–7.
- 47 China, S. S.; Chiang, K.; Fane, A. G. The stability of polymeric membranes in a TiO₂ photocatalysis process. *J. Membr. Sci.* 2006, *275*, 202–211.
- 48 Tiraferri, A.; Vecitis, C. D.; Elimelech, M. Covalent Binding of Single-Walled Carbon Nanotubes to Polyamide Membranes for Antimicrobial Surface Properties. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2869–2877.
- 49 Salta, M.; Wharton, J. A.; Stoodley, P.; Dennington, S. P.; Goodes, L. R.; Werwinski, S.; Mart, U.; Wood, R. J. K.; Stokes, K. R. Designing biomimetic antifouling surfaces. *Philos. Trans. R. Soc., A: Math. Phys. Eng. Sci.* **2010**, *368*, 4729–4754.
- 50 Zhang, W. X. Nanoscale iron particles for environmental remediation: An overview. J. Nanopart. Res. 2003, 5, 323–332.
- 51 Karn, B.; Kuiken, T.; Otto, M. Nanotechnology and in Situ Remediation: A Review of the Benefits and Potential Risks. *Environ. Health Perspect.* 2009, 117, 1823–1831.

- 52 Wiesner, M. R.; Lowry, G. V.; Alvarez, P.; Dionysiou, D.; Biswas, P. Assessing the risks of manufactured nanomaterials. *Environ. Sci. Technol.* **2006**, *40*, 4336–4345.
- 53 Cloete, T. E.; Kwaadsteniet, M. d.; Botes, M.; Lopez-Romero, J. M. Nanotechnology in Water Treatment Applications; Caister Academic Press: 2010.
- 54 Li, D.; Xia, Y. N. Electrospinning of nanofibers: Reinventing the wheel? Adv. Mater. 2004, 16, 1151–1170.
- 55 Lee, J.; Mackeyev, Y.; Cho, M.; Wilson, L. J.; Kim, J.-H.; Alvarez, P. J. J. C60 Aminofullerene Immobilized on Silica as a Visible-Light-Activated Photocatalyst. *Environ. Sci. Technol.* 2010, *44*, 9488–9495.
- 56 Roberts, A. P.; Mount, A. S.; Seda, B.; Souther, J.; Qiao, R.; Lin, S. J.; Ke, P. C.; Rao, A. M.; Klaine, S. J. In vivo biomodification of lipid-coated carbon nanotubes by Daphnia magna. *Environ. Sci. Technol.* **2007**, *41*, 3025–3029.
- 57 Griffiths, J.; Maguire, J.; Heggenhougen, K.; Quah, S. R. Public Health and Infectious Diseases: Elsevier: 2010.
- 58 Pal, S.; Tak, Y. K.; Song, J. M. Does the Antibacterial Activity of Silver Nanoparticles Depend on the Shape of the Nanoparticle? A Study of the Gram-Negative Bacterium Escherichia coli. *Appl. Environ. Microbiol.* 2007, 73, 1712–1720.
- 59 Navarro, E.; Piccapietra, F.; Wagner, B.; Marconi, F.; Kaegi, R.; Odzak, N.; Sigg, L.; Behra, R. Toxicity of Silver Nanoparticles to Chlamydomonas reinhardtii. *Environ. Sci. Technol.* 2008, 42, 8959–8964.
- 60 Handy, R. O. Richard Viewpoint: Formulating the Problems for Environmental Risk Assessment of Nanomaterials. *Environ. Sci. Technol.* **2007**, *41*, 5582–5588.
- 61 Eckelman, M. J.; Mauter, M. S.; Isaacs, J. A.; Elimelech, M. New Perspectives on Nanomaterial Aquatic Ecotoxicity: Production Impacts Exceed Direct Exposure Impacts for Carbon Nanotoubes. *Environ. Sci. Technol.* **2012**, *46*, 2902–2910.