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Convergence of Nanotechnology and Microbiology: Emerging Opportunities for Water Disinfection, Microbial Control, and Integrated Urban Water Management

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"Water, water everywhere, nor any drop to drink."

Samuel Taylor Coleridge

The Rime of the Ancient Mariner

Abstract

The extraordinary size-dependent properties of some nanomaterials (e.g., highly specific surface area, photosensitivity, catalytic and antimicrobial activity, electrochemical, optical and magnetic properties, and/or tunable pore size and surface chemistry) offer leapfrogging opportunities to develop next-generation applications for drinking water disinfection and safer wastewater reuse (e.g., photocatalytically-enhanced disinfection, biofouling-resistant membranes, biofilm- and corrosion-resistant surfaces, and sensors for pathogen detection).

The modular, multifunctional, and high-efficiency processes enabled by nanotechnology can be broadly applicable in both industrialized and developing countries, by enabling the retrofitting of aging infrastructure and the development of high-performance, low-maintenance point-of-use (POU) devices that facilitate differential water treatment and reuse.

Widespread dissemination of nanotechnology in water treatment will require overcoming the relatively high costs of manufactured nanomaterials (e.g., by enabling their reuse and avoiding diminishing returns of ultra-high material purity) and mitigating unintended risks to the public and environmental health (e.g., by immobilizing nanoparticles to minimize unintended release).

The convergence of nanotechnology with environmental microbiology is a fertile interdisciplinary research area that could expand the limits of technology, enhance global health through safer water reuse, serve as an innovative ecosystem to nurture intellectual

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entrepreneurs, and contribute towards sustainable and integrated urban water management.

Clean Water: A Limiting Factor for Public, Environmental, and Economic Health

No other resource is as universally necessary for life as is water; its safety and availability is a grand challenge inextricably linked to global health, energy production, and economic competitiveness. While a myriad of water contaminants can cause disease, by far the greatest waterborne threat arises from microorganisms such as pathogenic viruses, bacteria, and protozoa. Overcoming this challenge is becoming increasingly difficult as the demand for safer water grows with the world's population and climate change threatens to take away a large fraction of already scarce freshwater. The United Nation's Intergovernmental Panel on Climate Change recently stated that, "Water and its availability and quality will be the main pressures on, and issues for, societies and the environment under climate change" (Bates et al., 2008). Furthermore, aging water treatment and distribution systems in many cities cannot ensure reliable disinfection; in fact, some systems serve as incidental sources of microbial diseases.

Traditional solutions to microbial control have not been able to keep up with the increasing complexity, new barriers, and renewed relevance of this problem. While chlorination and ozonation of drinking water have had a significant beneficial impact on public health (e.g., water disinfection is largely responsible for increased life expectancies in the United States from 49 to 78 years in the twentieth century) (Shrestha, 2006), they produce carcinogenic disinfection byproducts (DBPs), such as trihalomethanes, haloamides, halonitriles, and bromate. Furthermore, current microbial control approaches have limited efficacy to address problems of an aging water infrastructure in which microbial infiltration, biofilm formation, and biofouling are more common (Figure 1), and are increasingly ineffective to treat a growing number of resistant microorganisms.

Figure 1. Waterborne infectious diseases are the leading cause of death on a global basis. Biofouling is a health hazard that promotes microbial-induced corrosion, impairs water's taste and odor, and contributes to energy (head) loss during water flow and filtration. (a) Children in Lesotho gather water; (b) pipe biofouling (http://netldev.netl.doe.gov/ research/coal/energy-systems/combustion/water-and-energy-interface/pp-mgmt/non-traditional-sources/nalco); (c) membrane fouling (www.usbr.gov/research/AWT/fouling.html and www.sandia.gov/cfd-water/membranes.htm), and (d) broken sewage pipe (www.epa.gov/nrmrl/wswrd/research.html).

In fact, 106 outbreaks and 5,024 recent cases of illness in the U.S. were attributed to waterborne pathogens in public water systems (Yoder et al., 2008), while each year 39-million Americans suffer infections from waterborne pathogens, leading to productivity losses on the order of $20 billion (Reynolds et al., 2008). The problem is more pronounced in developing nations. Although adoption of the Millennium Development Goals has resulted in significant progress, almost 1-billion people still lack access to safe water (Hutton and Haller, 2004) and diarrhea causes about 2-million infant deaths every year (UNICEF/WHO, 2009).

Microbes in water can also cause major problems for industry. Such contamination exacerbates corrosion and biofouling, both of which can significantly increase the cost and complexity of many critical operations. For example, the annual costs of biocorrosion to the oil and gas (O&G) industry exceed $2 billion (Koch et al., 2001), excluding externalities associated with the increased risk of accidental releases. Furthermore, sulfate-reducing bacteria in well bores and O&G fields sour hydrocarbon reservoirs due to the generation of hydrogen sulfide (H_2S). These sulfides also can precipitate as biogenic minerals in pipelines and drilling fluids (Figure 2), leading to flow obstruction, interruptions in extraction processes, and higher water requirements for O&G extraction (currently about 10 barrels of water per barrel of crude oil produced, and 5-million gallons per hydrofracking well). Conventional biocides are only marginally effective in addressing this problem, as they have low specificity to sulfate-reducing bacteria. Thus, current microbial control practice relies on high dosage that leads to undesirable reactions with chemicals used in drilling and refining, and leave significant residuals that pose substantial environmental risks.

Overall, the importance of enhancing water disinfection and microbial control cannot be overstated. The challenge to efficiently disinfect without forming harmful DBPs, and the growing demand for retrofitting aging water infrastructure and developing distributed POU water treatment and reuse systems, underscore the need for new technologies and water management approaches that provide practical solutions for clean water.

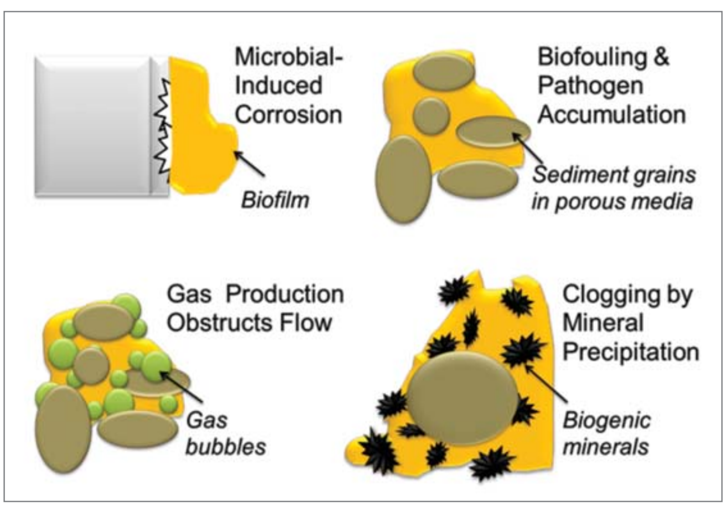

Figure 2. Some microbial processes of concern to the O&G industry.

Convergence of Nanotechnology and Microbiology as a Synergistic Interdisciplinary Area

The most intellectually stimulating and technologically productive areas of research often occur at the interstices between disciplines. Such interdisciplinary research has great potential to generate new products and services; enhance human capacity, economic competitiveness, and social achievements; and enable sustainable development (Roco and Bainbridge, 2003). Synergistic convergence between scientific and engineering disciplines has brought about tremendous advances in generative technologies with great intrinsic value that also transform or generate new disciplines. An early related example of a generative technology was the invention of the microscope by Antonie van Leeuwenhoek, who observed living “animalcules” (bacteria) in 1683 and stimulated the emergence of microbiology as a new science. A more recent example is the emergence of nanotechnology, which is defined by the National Nanotechnology Initiative as “the understanding and control of matter at the nanoscale, at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications.” Interest in nanotechnology boomed after the discovery of buckminsterfullerene in 1985 by Noble Laureates Richard Smalley, Robert Curl, and Harry Kroto (Kroto et al., 1985). Credit should also be given to Richard Feynman for his inspiring 1959 talk, “There’s Plenty of Room at the Bottom,” Norio Taniguchi for coining the term “nanotechnology” in 1974, and Eric Drexler, who popularized the theme with his 1986 book, “Engines of Creation: The Coming Era of Nanotechnology.”

Nanotechnology has had a transformative impact on numerous disciplines, including surface science, organic chemistry, molecular biology, semiconductor physics, and microfabrication. Similarly, the convergence of nanotechnology with environmental microbiology would likely result in an interdisciplinary field with great potential for meaningful disruptive innovation. This convergence could expand the limits of water technologies and enhance industrial competitiveness in the emerging markets of global health, microbial

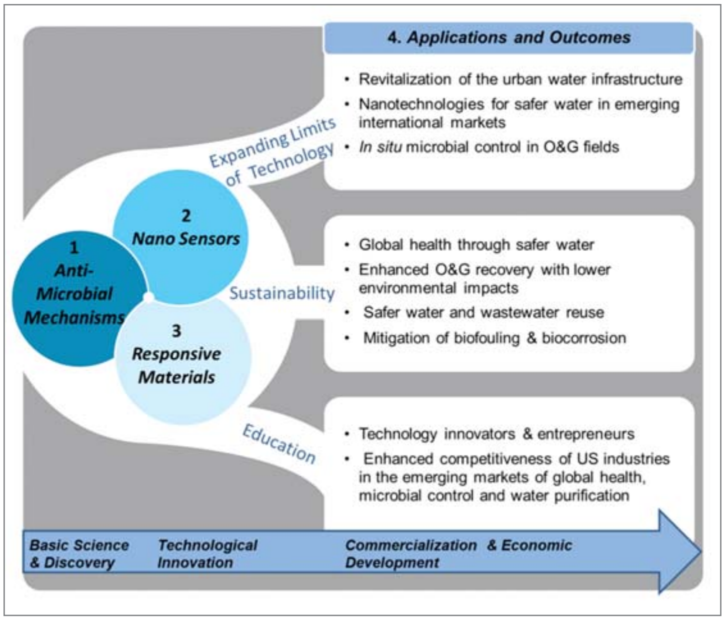

Figure 3. Operational vision and potential outcomes of nanotechnology-enabled water disinfection and microbial control.

control, and water purification, as well as contribute to water security (and, thus, energy and food security) and to sustainable development (Figure 3). This convergence could stimulate an ecosystem of innovation for multiple stakeholders – from academic researchers to practitioners and users, and from start-ups to small firms and global companies — that would translate fundamental research to technological innovation with broad commercialization and dissemination potential.

How Can Nanotechnology Make a Difference in Water Treatment?

Nanotechnology can enable both safer and sustainable solutions for clean water by both enhancing the performance of existing treatment processes and developing new (modular) processes. For microbial control, the overarching goal is to develop antimicrobial systems that sense and selectively target waterborne pathogens for safer water disinfection, diagnosis of pathogenic disease, and mitigation of biofouling and biocorrosion in a manner that is eco-responsible, broadly accessible, and practical. Previous research suggests a great potential for nanotechnology-enabled microbial control (Li et al., 2008). Nanotechnology can address emerging disinfection challenges, help restore and improve aging water infrastructure, mitigate the large water footprint of O&G extraction (e.g., by reducing the abandonment of biofouled production wells and the overdosing of biocides), and provide opportunities to develop leading-edge technologies that enhance industrial competitiveness in the global market of water management (see Figure 3). This prospect is timely because 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.

Nanotechnology can also contribute to integrated urban water and wastewater management by enabling a distributed and differential water treatment and reuse paradigm where water and wastewater are treated locally to the level required by the intended use (Figure 4). This would minimize water quality degradation within aging distribution networks, alleviate dependence on large and centralized system infrastructure (e.g., use only basic treatment near the source water to enhance distribution, and complement it by tailored POU treatment), exploit alternative water sources (e.g., recycled wastewater or stormwater) for potable, agricultural, or industrial use, and decrease energy requirements for treating and moving water (Qu et al., 2012). This vision represents an important paradigm shift for urban systems with extensive (centralized) water infrastructure because:

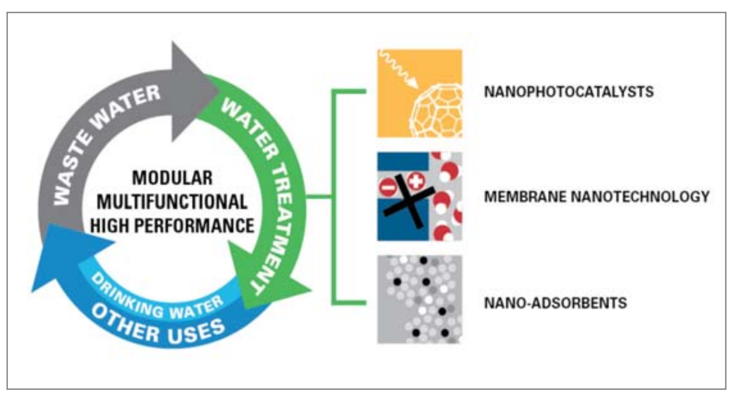

Figure 4. Nanotechnology-enabled integrated urban water management (Qu et al., 2012).

- Centralized treatment and distribution systems allow little flexibility in response to changing demand for water quality or quantity, let alone differential water quality needs (we do not need to use drinking water to flush toilets or irrigate lawns).
- Our separate wastewater collection and water supply systems are not designed to accommodate the growing need for wastewater reuse.
- Aging water infrastructure is also responsible for significant energy consumption, water loss, and secondary contamination at a time when the need is growing to produce higher quality water using less energy and with lower treatment costs.

This paradigm of distributed and differential treatment and reuse is also appropriate for emergency response following catastrophic events, as well as for developing countries, where building extensive (centralized) systems in regions lacking water and wastewater infrastructure is often beyond their economic possibilities. In all of these cases, the high performance and large functional variety of engineered nanomaterials, as well as their ability to enhance treatment efficiency at relatively low additive ratios, can facilitate the development of modular units that can be added or removed to meet different treatment and reuse goals at the POU.

Which Nanomaterials Have Antimicrobial Properties and How Do They Work?

Many manufactured nanoparticles can inactivate microbial cells using a wide variety of antimicrobial mechanisms (Figure 5). Some nanoparticles interact directly with microbial cells to disrupt the integrity of the cell membrane (e.g., carbon nanotubes) and interrupt respiration and energy transduction (e.g., fullerenes and ceric oxide [CeO_2]). Other nanoparticles act indirectly by producing secondary products that serve as disinfection agents (e.g., reactive oxygen species [ROS] generated by titanium dioxide [TiO_2] or dissolved metal ions released by silver nanoparticles [AgNPs]).

The most widely used antimicrobial nanoparticles are AgNPs, which are used in a wide variety of microbial control applications,

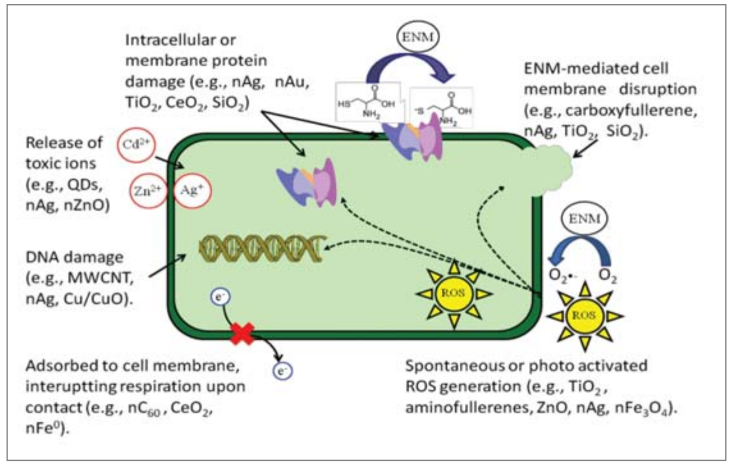

Figure 5. Antimicrobial mechanisms exerted by various manufactured nanoparticles (Li et al., 2008).

from disinfecting medical devices and home appliances to water treatment. Silver was a prevalent antibiotic before the advent of penicillin. The silver ions (Ag^+) that are released from AgNPs interact with thiol groups in proteins, which can inactivate respiratory enzymes or create oxidative stress associated with intracellular ROS generation. One elusive question has been whether the AgNPs exert "particle-specific" antimicrobial activity upon contacting cells, beyond the known antimicrobial activity of released Ag^+. Recently, we found that Ag^+ is the determinant molecular toxicant. Direct particle-specific biological effects were ruled out by observing a lack of toxicity of AgNPs when synthesized and tested under strictly anaerobic conditions that preclude silver (Ag[0]) oxidation and Ag^+ release. Furthermore, the toxicity of various AgNPs (of different coatings and sizes) accurately followed the dose-response pattern of bacteria exposed to Ag^+ (added as silver nitrate [$AgNO_3$]) (Xiu et al., 2012). Therefore, AgNP morphological properties known to affect antimicrobial activity are indirect effectors that mainly influence Ag^+ release. This suggests that antibacterial activity could be controlled by modulating Ag^+ release, possibly through the manipulation of oxygen availability, particle size, shape, and/or type of coating. Furthermore, Ag^+ is more susceptible than AgNPs to binding by common natural ligands, such as chloride, phosphate, sulfide, and natural organic matter, which decreases its bioavailability. Thus, AgNPs may serve as a more bioavailable vehicle for effective delivery of Ag^+ to the bacteria.

Another well studied and widely available inorganic nanomaterial is TiO_2, which has great potential to enhance the photodisinfection of both water and air. The antibacterial effect of TiO_2 involves ROS production (e.g., hydroxyl radicals) when the nanoparticles are illuminated by ultraviolet (UV-A) light (320 to 400 nanometers [nm]). UV-A is a minor component of visible light, and sunlight is generally not very effective in activating TiO_2 for photocatalytic disinfection. Nevertheless, the doping of TiO_2 with common elements (e.g., nitrogen [N], sulfur [S], and boron [B]) can enable activation by sunlight, thereby enabling its use in remote locations without electricity. Nobel metals can also improve the photosensitivity of sunlight-irradiated TiO_2 and increase its photocatalytic activity under UV irradiation. The enhancement is related to improved electron-hole separation and/or an increase in surface area for light adsorption.

Zinc oxide [ZnO] nanoparticles also exhibit antimicrobial properties, although they are more commonly used to absorb UV light in sunscreens, coatings, and paints. Several mechanisms have been postulated to explain the antibacterial activity of ZnO. Similar to AgNPs, the dissolution and release of metal ions (i.e., zinc cation [Zn^{2+}]) is an important mechanism. Apparently, Zn^{2+} binds to bacterial cell membranes, promotes disorganization of the phospholipids, and retards microbial growth. ZnO is also photosensitive and generates hydrogen peroxide, which has antimicrobial properties.

Fullerenes, which are organic nanoparticles made up of sp2-hybridized carbon atoms in the form of a hallow sphere, ellipsoid, or tube (such as buckminsterfullerene [C_{60}] and C_{70} fullerene) also have potential for use in water disinfection. Fullerenes are also photosensitive and generate singlet oxygen when irradiated by sunlight (Figure 6).

Singlet oxygen is a weaker disinfectant than the hydroxyl radical produced by TiO_2, which has higher oxidation potential. However, singlet oxygen is a more selective (electrophilic) ROS and is less susceptible to scavenging by non-target background organic matter.

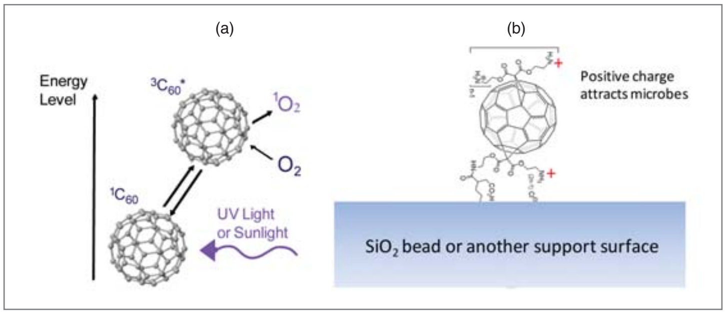

Figure 6. Light excites C_{60} to triplet state (a) and energy transfer between $^3C_{60}*$ and molecular oxygen gives rise to singlet oxygen ($^1O_2$), an antimicrobial reactive oxygen species. Fullerenes can be derivatized to enhance disinfection (b) and immobilized onto a surface to facilitate reuse.

One limiting factor about fullerenes is their extremely low solubility, which limits their accessibility to reactions in water. However, fullerenes can be made water soluble by derivatization. For example, hydroxylated C_{60} (fullerol) forms stable suspensions in water and exhibits enough photochemical activity for disinfection. Aminofullerene derivatives (see Figure 6) are more effective for photodisinfection (their positive charge attracts negatively-charged bacteria and viruses for more effective disinfection) and are more amenable to immobilization than fullerol (Lee et al., 2010). Immobilization precludes dense nanoparticle clustering and the associated triplet-triplet annihilation that hinders ROS generation. C_{60} can also cluster and form stable aqueous suspensions, termed nC_{60}, which lack photosensitivity (due to triplet-triplet annihilation), but exhibit a broad spectrum antibacterial activity. This is exerted by direct oxidation of critical cell components, such as membrane proteins involved in electron transport phosphorylation (Lyon et al., 2008). As is the case with nanoparticles that need direct contact to kill microbes, the coating of nC_{60} by natural organic matter in water significantly hinders bioavailability and antimicrobial activity (Li et al., 2008). Similar to TiO_2, ROS production by fullerenes has the collateral benefit of degrading a wide variety of recalcitrant micropollutants (Lee et al., 2011). However, fullerenes are currently much more expensive and are not as readily available as TiO_2, which is a more established photo-oxidant.

Carbon nanotubes (CNTs) represent a special class of fullerenes with antimicrobial properties. Their antibacterial activity is attributed to a physical interaction in which CNTs pierce cells (Mauter and Elimelech, 2008). Thus, CNTs may inhibit microbial attachment and biofilm formation on surfaces. Single-walled CNTs are more toxic to bacteria than multi-walled CNTs, and could be coated and immobilized onto filters to endow them with antibacterial properties. Additionally, multi-walled CNTs could be made into hollow fibers or bundled to pack filters with antimicrobial and antiviral properties. CNTs offer desirable properties, such as high mechanical strength, heat resistance, and easy cleaning. However, their tendency for aggregation, stabilization by dissolved natural organic matter, and bioavailability need to be considered to ensure effective antimicrobial applications.

Naturally occurring antibacterial macromolecules, such as chitosan (obtained from chitin in arthropod shells), could also be useful in water disinfection. Chitosan can be made into nanoparticles with broad disinfection capabilities. The antimicrobial mechanisms of (positively-charged) chitosan likely involve its interaction with negatively-charged cell membranes, causing an increase in membrane permeability, osmotic stress, and rupture and leakage of intracellular components. Chitosan is not an effective disinfectant at pH>6, when its amino groups are unprotonated (i.e., uncharged). Another postulated antimicrobial mechanism for chitosan involves its ability to chelate trace metals, thus inhibiting some enzyme activities (Rabea et al., 2003).

Emerging Nanotechnology-Enabled Disinfection and Microbial Control Applications

In addition to the antimicrobial activities described above, many nanomaterials exhibit desirable properties for water and wastewater treatment (Table 1). These include highly specific surface area for adsorption (with the potential for tunable surface chemistry to enhance selectivity), very high catalytic activity to destroy recalcitrant pollutants, superparamagnetism for particle separation and reuse, and optical and electronic properties that are useful to develop selective sensors for water quality monitoring. Furthermore, unlike conventional chemical disinfectants, antimicrobial nanomaterials are generally weaker oxidants and do not produce harmful DBPs.

Table 1. Opportunities for Engineered Nanomaterials (ENMs) in Water Treatment and Reuse (Brame et al., 2011)

Desirable ENM Properties	Examples of ENM-Enabled Technologies	References
Large surface area to volume ratio	Superior sorbents with high, irreversible adsorption capacity (e.g., nanomagnetite to remove arsenic and other heavy metals) and reactants (Nanoscale Zero Valent Iron [NZVI])	Mayo et al., 2007
Enhanced catalytic properties	Hypercatalysts for advanced oxidation (TiO2 and fullerene-based photocatalysts) and reduction processes (palladium/gold) to treat residual pesticides and other priority pollutants	Hoffman et al., 1995; Nutt et al., 2005
Antimicrobial properties	Disinfection without harmful byproducts (e.g., enhanced solar and UV disinfection by TiO2 and derivatized fullerenes)	Lee et al., 2009; Yang et al., 2009
Multi-functionality (antibiotic, catalytic, etc.)	Fouling-resistant (self-cleaning), multi-functional filtration membranes that inactivate virus and destroy organic contaminants	Zodrow et al., 2009
Self-assembly on surfaces	Surface structures that decrease bacterial adhesion, biofilm formation, and corrosion of water distribution and storage systems	Nelet al., 2009
High conductivity	Novel electrodes for capacitive deionization (electro-sorption) and low-cost, energy-efficient desalination of high salinity water	Oren, 2007
Fluorescence	Sensitive sensors to detect pathogens and other priority pollutants	Bogue, 2009

Most nanotechnology-enabled applications are at an early stage of development. One promising application is nano-photocatalyst-enabled solar or UV disinfection. This approach could be easily implemented to augment or retrofit existing UV disinfection systems, with the added benefit that the generated ROS can also target co-occurring recalcitrant micro-pollutants, such as endocrine disruptors and other trace priority pollutants. Similar to solar disinfection (SODIS), nano-enabled photodisinfection is also amenable for deployment as POU devices at the household level in areas lacking water infrastructure (Figure 7).

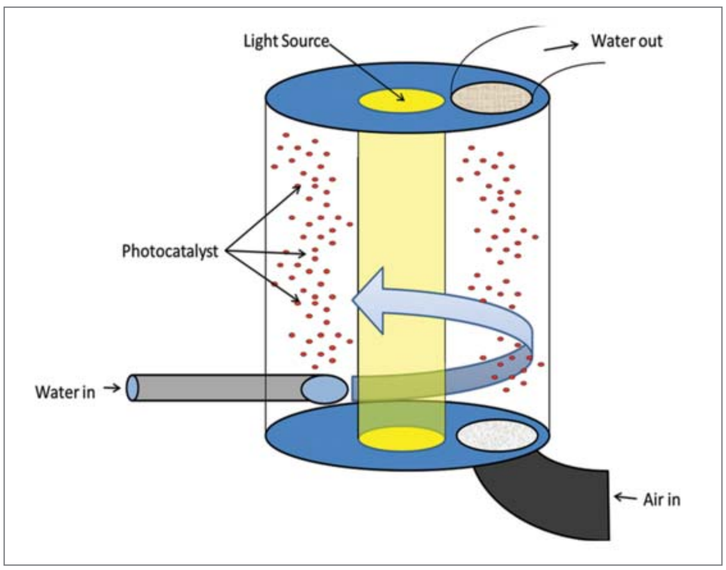

Figure 7. POU fluidized bed reactor using suspended nano-photocataliysts (e.g., TiO2 nanoparticles immobilized onto sand particles) to enhance UV or solar disinfection. The photocatalystis retained by an outlet screen.

Another approach that is already being used in commercial products such, as textiles and plastic containers, is the incorporation of anti-microbial nanoparticles such as AgNPs. Amtiomicrobial nanoparticles can be used in personal devices, as well as inantimicrobial surface coatings, to mitigate biofilm formation and secondary contamination in water storage and distribution systems. Biofilms in water distribution systems are very difficult to eradicate by traditional disinfectants, which just kill microbes in the outer layers. Antimicrobial coatings might be more effective in mitigating biofilm formation and the establishment of associated pathogenic reservoirs. Antimicrobial coatings could include elements that quench quorum sensing to interfere with cell-to-cell communication and hinder the coordination of metabolic functions associated with cell attachment, as well as D-aminoacids, which induce natural signals for biofilm disassembly and for inhibition of protein accumulation in the matrix to discourage biofilm growth (Hochbaum et al., 2011).

The combination of nanoparticle surface assembly, advanced photolithography, and novel nano-template based methods could be used to create surface patterns that inhibit bacterial adhesion and delay biofilm formation (Ma et al., 2011). This approach is used by marine organisms (dolphins and sharks) and plants (lotus leaf) to prevent microbial adhesion.

Nanomaterials used to inhibit biofilm formation could have the collateral benefit of mitigating microbial-induced corrosion of the water infrastructure. In addition, thin (nano-sized) grapheme coatings could be spread over by chemical vapor deposition to prevent oxygen diffusion and mitigate electrochemical corrosion (Prasai et al., 2012). Some nanocomposites with high electrical conductivity also show promise for inhibiting corrosion, including polyaniline/zinc nanocomposite film (Olad et al., 2011) and nano-TiO_2 in nickel coatings (Aal, 2008).

Nanotechnology could also help develop biofouling-resistant, multifunctional membranes. Membrane systems are widely used for desalination and the potable reuse of wastewater. However, the long-term feasibility of membrane systems is jeopardized by biofouling, which significantly increases energy requirements. The incorporation of functional (e.g., adsorptive, [photo] catalytic and antimicrobial) nanomaterials into membranes offers an opportunity to prevent fouling and achieve multiple treatment goals in a single step. For example, UV-irradiated TiO_2 can be incorporated to degrade a wide range of organic contaminants, including major membrane foulants such as natural organic matter, and both CNTs and AgNPs could inhibit bacterial adhesion and growth on membrane surfaces (Figure 8).

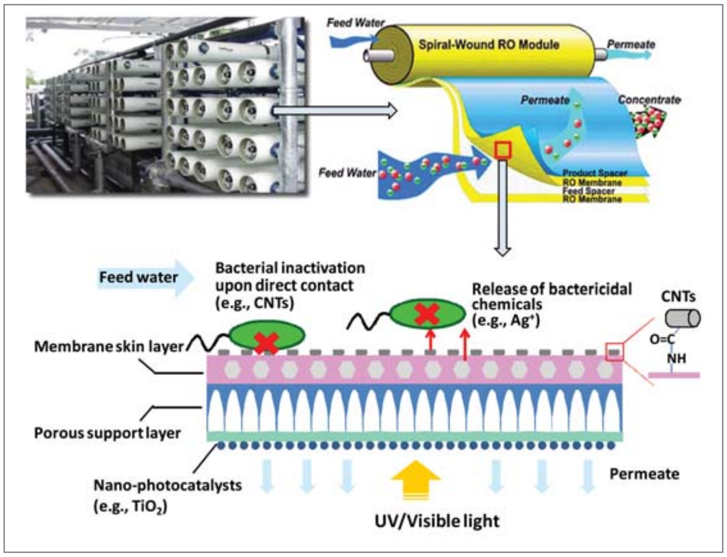

Figure 8. Detail of nanotechnology-enhanced multifunctional membranes for water treatment (Qu et al., 2012).

In theory, nanotechnology could also enhance *in situ* control of sulfate reducing bacteria (colorfully referred often as an industrial venereal disease) in oil and gas reservoirs and associated pipelines, while avoiding the adverse environmental impacts associated with flooding with generic biocides. For example, bacteriophages (phages) are nanosized viruses (25 to 100 nm) that infect and replicate within bacteria, eventually causing cell lysis and the release of more phages. Thus, phages represent a highly selective, natural, and self-propagating (nano-sized) biocide. Because phages are species-specific, the potential for off-target kill is minimal. However, isolating and preparing appropriate phage cocktails to target the dominant (site-specific) sulfate-reducing bacteria species will be a major challenge. Another challenge is ensuring adequate phage transport through porous media, which would be hindered by filtration. Phage delivery could be enhanced by preparing phage nano-composites with a size and surface chemistry that minimizes capture by the porous media. Filtration theory and empirical evidence suggests that particle retention is lowest when the particle is sufficiently large to preclude deposition onto porous media surfaces by Brownian motion and is sufficiently small to avoid straining. Thus, phages can be incorporated into particles with a size selected for minimum removal by filtration (usually on the order of 1 micrometer [µm]). Control of surface charge and hydrophobicity of the phage nano-composites can also be exploited to enhance colloidal stability in high-salinity and elevated-temperature conditions and, perhaps, also to modulate the range of phage transport.

Implementation Barriers

While nanotechnology holds significant possibilities to enable water treatment and integrated urban water management, several potential barriers exist for widespread implementation. These include concerns about nanomaterial costs, potential toxicity, and social acceptability.

Cost and performance are critical factors for the broad acceptance of novel water and wastewater treatment nanotechnologies. In developing countries, water treatment often only covers the most basic needs, such as disinfection, when available. In contrast, industrialized nations tend to use more advanced technologies to remove a wider spectrum of emerging pollutants. However, in both scenarios, there is a need to treat increasingly complex pollutant mixtures and supply higher quality water at lower cost (Figure 9), which is pushing the boundaries of current treatment approaches. The proposed nanotechnology-based treatment options are high-performance, enabling more efficient treatment. However, the

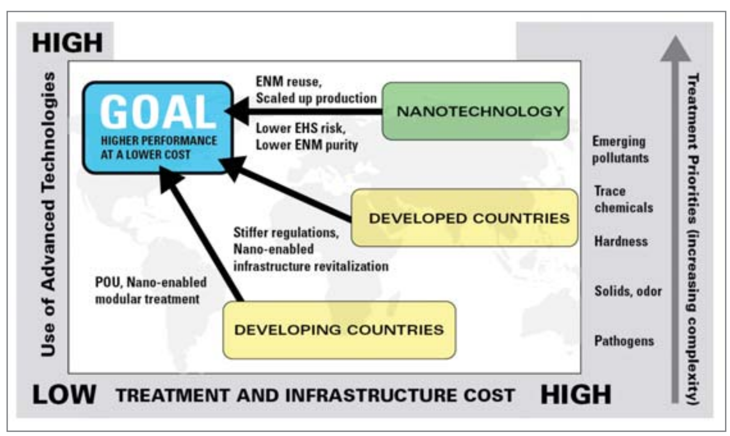

Figure 9. Conceptual improvements to water treatment through nanotechnology. The arrows represent specific strategies or drivers that can enhance performance and/or decrease costs through the use of nanotechnology (Qu et al., 2012).

relatively high costs of nanomaterials represent a significant (but, perhaps, only temporary) implementation barrier.

Nanomaterial prices are unlikely to decrease significantly without a large increase in demand to favor economies of scale. Nevertheless, the cost of nanomaterial synthesis is generally small compared to that incurred by separation and purification steps, due to high energy and chemical requirements of the latter. This suggests an opportunity to decrease costs by using nanomaterials of lower purity. In collaboration with Lon Wilson's lab at Rice University, we showed that aminofullerene photocatalysts synthesized from fullerene soot rather than research-grade C_{60} as starting material exhibited a minimal (<10 percent) loss of photoactivity while reducing the total cost by about 90 percent. Thus, understanding and managing the tradeoffs between nanomaterial purity and performance is important to reduce costs and increase nanomaterial demand to trigger manufacturer interest in scaling up production, which creates a feedback loop that further decreases costs. Another cost reduction strategy is to facilitate nanomaterial reuse, such as immobilizing photocatalysts that retain high activity after multiple reuse cycles, and iron-containing nanoadsorbents (e.g., nano-magnetite for arsenic removal), which can be separated magnetically and regenerated. Reuse decreases nanomaterial costs per volume of water treated, which is a more relevant feasibility metric than the price of nanomaterials per gram.

Potential impacts to human or ecosystem health associated with incidental or accidental releases of nanomaterials represent another important barrier from both public acceptance and regulatory perspectives (Alvarez et al., 2009). Unintended adverse impacts are common in technological advances, including water treatment. For example, although chlorination to disinfect drinking water nearly doubled life expectancy in the United States during the 1900s, it also resulted in the accompanying production of carcinogenic DBPs (Shrestha, 2006). Currently, whereas the antimicrobial activity of many nanoparticles offer great opportunities for DBP-free microbial control in engineered systems, their incidental or accidental releases to the environment represent a potential risk to microbial ecosystem services (e.g., photosynthesis, nutrient cycling, and waste biodegradation) (Klaine et al., 2008). Therefore, it is important to take a proactive approach to assess the fate and mitigate potential risks associated with nanomaterials used in (or flowing into) water and wastewater treatment processes.

A risk assessment of nanomaterials in the environment would benefit from considering nanomaterial-microbial interactions. Microorganisms are the basis of all known ecosystems and can serve both as convenient models to study cytotoxicity mechanisms (see Figure 5), as well as sensitive sentinels to forewarn us about potential impacts to ecosystem health (Wiesner et al., 2006). Metal-based nanoparticles (e.g., AgNPs, ZnO, and TiO_2) generally have bulk counterparts (manufactured or naturally occurring) for which a toxicological database and fate and transport information likely exist. Such databases provide a valuable starting point for risk assessment, notwithstanding the likelihood that the risks posed by the nanomaterials could be different (possibly higher) than those posed by their bulk counterparts. However, bulk counterparts do not exist for some manufactured nanomaterials, such as quantum dots, fullerenes, and CNTs, which may require more careful toxicity assessments (including consideration of sublethal chronic effects).

Whereas nanomaterial toxicity is an important determinant of potential risk, so is the likelihood of exposure. Thus, the risks posed by antimicrobial nanomaterials in water treatment could be minimized by ensuring their retention in the treatment process and preventing exposure to potential (human or ecological) receptors. Barrier technologies such as membranes or magnetic separation could mitigate exposure, although it may be more cost effective to immobilize the nanomaterials onto reactor surfaces or support media. For metal-based nanoparticles that exert antimicrobial activity by releasing toxic ions (e.g., AgNPs and ZnO), immobilization would not prevent some discharge. Thus, it is important to control their dissolution rates to ensure that applicable water standards for dissolved metals are not exceeded. This could be achieved by using stabilizing polymeric coatings of appropriate thickness, or manipulating other variables that affect nanoparticle dissolution, such as size, shape, and water chemistry.

Social acceptability is also a critical consideration that requires carefully balancing economic and human dimensions while adopting a position of proactive responsibility, inclusiveness, and long-term visionary-realism. An unbalanced focus on technical innovation may pose risks to the human dimension and jeopardize the sustainability of the technology, whereas focusing too much on responsible development may generate too-restrictive regulations and approaches that delay economic and societal benefits (Roco and Bainbridge, 2003). Similarly, disregarding the need to include all stakeholders represents a wasted opportunity to integrate social and ethical issues that intersect with pertinent governmental functions (e.g., funding, regulations), and to establish mechanisms to inform and involve the public about the potential impacts of nanotechnology and dispel common misconceptions. This could lead to slower technology implementation and dissemination (and even isolationism). Finally, it is important to resist a tendency to focus on short-term economic feasibility and, rather, prioritize a longer term vision for water security (e.g., nanotechnology-enabled integrated water management) for current and future generations.

Outlook for Nanotechnology in the Water Sector

Despite potential barriers to the widespread use of nanomaterials in the water sector, nanotechnology will likely be increasingly relied upon for needed innovations in water treatment and reuse. The incorporation of nanomaterials would have a clear overall benefit when:

- Current processes fail to meet existing or upcoming requirements.
- Wastewater reuse is hindered by hazardous micro-pollutants that break through the treatment process.
- POU approaches are needed because of insufficient infrastructure.
- Nanomaterials can improve the cost-effectiveness of the treatment process at low additive ratios.

Near-term applications include upgrading and enhancing treatment capabilities without major alterations to existing infrastructure (e.g., more efficient disinfection of resistant microbes, and lower potential for DBP formation, microbial induced corrosion, and membrane fouling), while possibly enabling the use of non-conventional water sources for different reuse scenarios (Qu et al., 2012). Nanomaterials could also be incorporated in POU systems to differentially treat drinking water to higher standards, obviating concerns about secondary contamination through the distribution system. Distributed and differential treatment approaches enabled by POU devices would also be attractive for rural areas and expanding cities in developing countries lacking extensive water infrastructure, where capital investment for new infrastructure may not be feasible (see Figure 9). In such cases, nanotechnology could help develop POU systems that are tailored to site-specific needs with minimal use of electricity or imported chemicals.

The large variety of nanomaterials with different properties facilitates the use of modular units that can be adapted to different treatment goals. A modular POU approach would enhance the control of functionality and treatment capacity, since modules can be inserted or removed in response to changes in source water quality and quantity and treatment requirements. This would be particularly valuable:

- In populated arid regions needing high performance water treatment and reuse.
- For remote, small public water systems with challenging source waters.
- For locations or occasions that require high treatment efficiency, small area footprint, and easy operation (e.g., disaster response situations where POU treatment systems are needed until damaged infrastructure recovers).

Future nanotechnology-enabled systems might also be responsive, sensing microbial or chemical contaminants and triggering a response as needed (e.g., on-demand release of antimicrobial agents).

Conclusion

Ensuring reliable access to safe and affordable water is one of the greatest global challenges of the twenty-first century. President John F. Kennedy once said, "Anyone who can solve the problems of water will be worthy of two Nobel prizes – one for peace and one for science." This statement reflects the importance of reliable and affordable global access to clean water for political stability and world peace, and underscores a tremendous opportunity for engineers and scientists to contribute to world affirmation by helping achieve global water security. The consequences of ignoring this pressing need may be colorfully reflected in a Turkish proverb: "When one man drinks while another can only watch, Doomsday follows."

Addressing this challenge at multiple scales will require more than technological innovation. Novel integrated water management approaches will be needed in addition to upgrading existing water infrastructure and installing new systems. Nanotechnology will likely play a critical role in both augmenting and improving existing microbial control processes, and in enabling a transition towards less reliance on centralized treatment (e.g., use only basic treatment near the source water, such as precipitation of suspended solids) complemented by modular POU systems that permit distributed and differential water treatment and reuse. Interdisciplinary research between microbiology and nanotechnology will be particularly important to develop high performance and greener disinfection and microbial control technologies for safer, broadly accessible, and more affordable water supplies worldwide.

Many Thanks

I am extremely humbled, honored, and grateful to be the recipient of the 2012 Athalie Richardson Irvine Clarke Prize. This prestigious award is an inspiration for generosity and for making the world a better place by contributing to broader access to safe and affordable water. Thus, I thank the Irvine family, Joan Irvine Smith and Athalie R. Clarke Foundation, and the National Water Research Institute for making this award possible. I am also very grateful to Clarke Laureate Meny Elimelech for nominating me and to the Clarke Prize Executive Committee for selecting me for this great honor.

I owe this award to the privilege of having had great mentors, students, and other intellectual sparring partners. My Ph.D. advisor at the University of Michigan, Tim Vogel, and my friends and colleagues at the University of Iowa – Clarke Laureate Jerry Schnoor, Richard Valentine, and Gene Parkin – taught me by example the importance of balancing rigor with relevance and relaxation (r^3). I was also inspired by many former teachers and mentors, such as Ronnie Gehr, Clarke Laureate Walt Weber, and Linda Abriola, who gave me an insurmountable example of commitment to excellence. My gratitude is also extended to Herb Ward, Joe Hughes, and Phil Bedient for welcoming me at Rice, and to Clarke Laureate Mark Wiesner for introducing me upon my arrival to the wonderful world of Environmental Nanotechnology.

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The 2012 Clarke Prize Honoree

PEDRO J.J. ALVAREZ, PH.D., P.E., DEE

Environmental engineer Pedro J.J. Alvarez, Ph.D., P.E., DEE, the George R. Brown Professor of Engineering at Rice University in Houston, Texas, was selected as the 2012 recipient of the Athalie Richardson Irvine Clarke Prize for excellence in water because of because of global leadership and contributions to enhancing water resource sustainability through water pollution control.

With a focus on examining new technologies, his work has provided fundamental insight on a broad range of water industry challenges, but he is best known for his pioneering research in two fields: bioremediation and environmental nanotechnology.

Alvarez began his career in the mid-1980s, working on a U.S. Congress directive to evaluate environmental impacts associated with the deployment of intercontinental ballistic missiles. This experience, which focused on assessing water supplies and treatment infrastructure at U.S. Air Force bases, inspired his passion to apply science, technology, and policy to protect water resources.

He moved on to earn his Ph.D. at the University of Michigan, which is where he first began to make advancements in understanding the practice of bioremediation, a water treatment process that involves using microorganisms, such as bacteria, to remove (by consuming or breaking apart) contaminants from water supplies.

Alvarez's initial research focused on remediating groundwater aquifers impacted by hydrocarbons, organic compounds that naturally occur in oil. Fellowships and awards followed, as well as expanded research. Today, he is the author of two textbooks on bioremediation in soil and water (including the only one written in Spanish). The oil and gas company BP recently used his research to develop hydrogeology models to evaluate potential groundwater impacts from different types of biofuel blends.

Taking an interdisciplinary approach to remediation technologies, Alvarez later pioneered research on groundwater impacts associated with ethanol fuel releases, resulting in the development of guidelines for many states and the U.S. Environmental Protection Agency on the remediation and natural attenuation of groundwater impacted by leaking underground storage tanks.

He has also made significant findings in the area of phytoremediation (which uses plants to remove contaminants), such as discovering that trichloroethene (TCE), a chemical found in industrial solvents, can be taken up and transformed by plants irrigated with contaminated water. His work has earned him numerous awards from groups in both the U.S. and Latin America.

Since joining Rice University in 2004, Alvarez has taken the lead in evaluating the environmental impacts of nanotechnology, an emerging field that involves the uses of technology at the molecular level. The increased production and incorporation of nanomaterials into consumer products and applications has motivated Alvarez to study the fate, transport, and impact of a number of nanomaterials in the environment.

His unique approach includes examining both the benefits that may be produced from nanomaterials (such as using them to treat subsurface contaminants) and any possible risks these materials may later pose to human health and safety. He is also examining the response of microorganisms – essential to the food web and other natural systems – to exposure to nanomaterials. His papers on the subject of environmental implications of nanotechnology are among the most widely read and cited in the water industry.

The
ATHALIE RICHARDSON IRVINE
Clarke Prize

for Outstanding Achievement
in Water Science and Technology

The 2012 Clarke Prize Lecture, Convergence of Nanotechnology and Microbiology: Emerging Opportunities for Water Disinfection, Microbial Control, and Integrated Urban Water Managements, *by Pedro J.J. Alvarez, Ph.D., P.E., DEE, of Rice University, was presented on Friday, November 2, 2012, at the Nineteenth Annual Clarke Prize Award Ceremony and Lecture, held at the Hyatt Regency Newport Beach in Newport Beach, California.*

The National Water Research Institute (NWRI) of Fountain Valley, California, established the Clarke Prize in 1993 to recognize research accomplishments that solve real-world water problems and to highlight the importance of and need to continue funding this type of research. Dr. Alvarez was the nineteenth recipient of the prize, which includes a medallion and $50,000 award.

The Clarke Prize was named after NWRI's co-founder, the late Athalie Richardson Irvine Clarke, who was a dedicated advocate of the careful stewardship and development of our water resources. The Joan Irvine Smith and Athalie R. Clarke Foundation provide funding for this award.

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