Environmental Science
Nano

SOURCE WATER

MACROSCALE SYSTEM

NANOSCALE MATERIALS

DRINKING WATER

NANOTECHNOLOGY-ENABLED WATER TREATMENT

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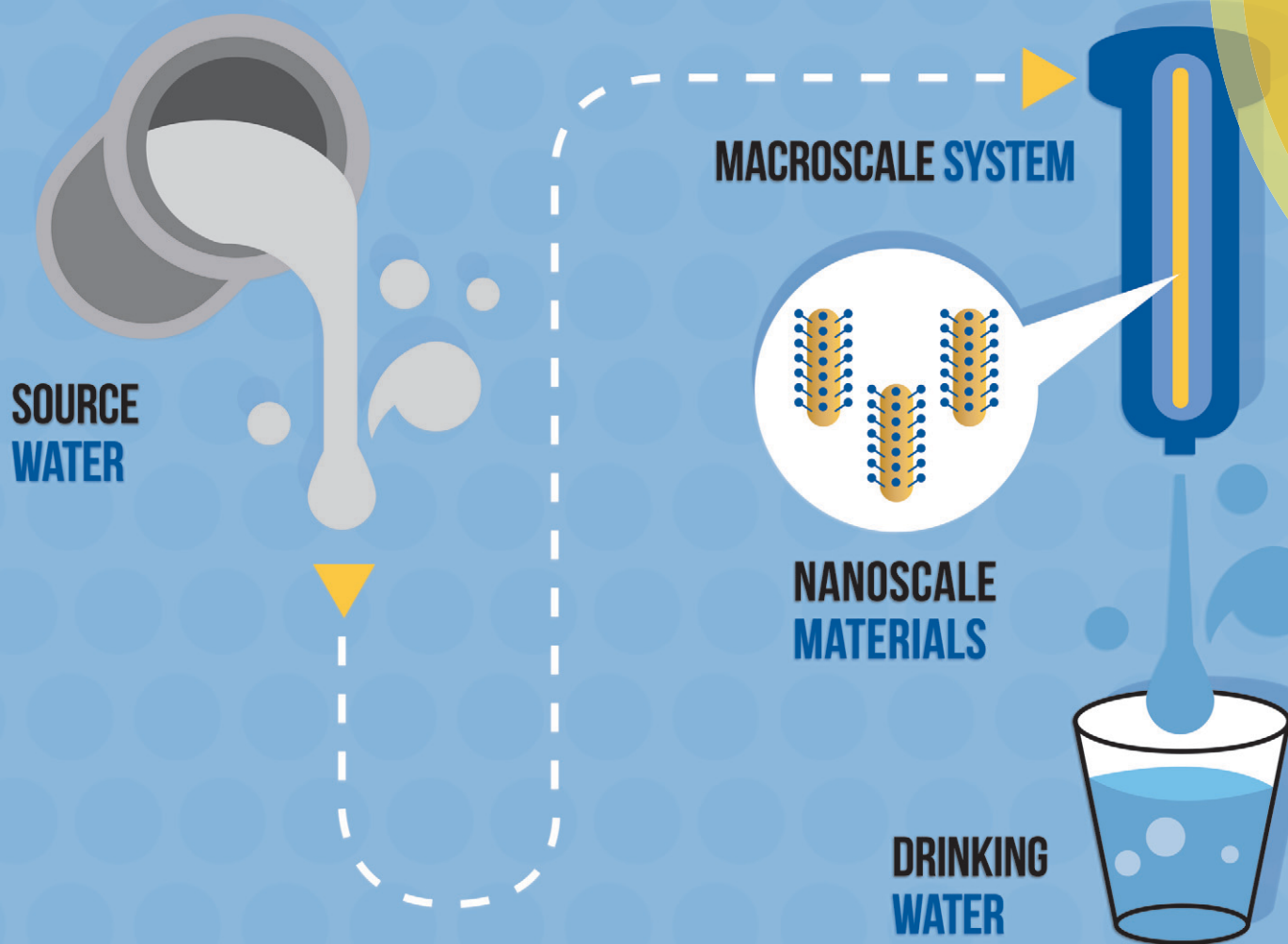
PERSPECTIVE
Paul Westerhoff *et al.*
Overcoming implementation barriers for nanotechnology in drinking water treatment

175 YEARS

PERSPECTIVE

Overcoming implementation barriers for nanotechnology in drinking water treatment

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Nanotechnology enabled water treatment is a promising approach to enhance the effectiveness and efficiency of purifying water in many areas of the world. Nanotechnology offers significant opportunities to revolutionize approaches towards drinking water treatment by enhancing the multifunctionality and versatility of treatment systems while reducing reliance on stoichiometric chemical addition (thus minimizing associated waste streams), shrinking large facilities with relatively long hydraulic contact times and minimizing energy intensive processes. The unique material properties that emerge at the nano-scale enable solutions to treat pollutants in water for which existing technologies are inefficient or ineffective. This perspective describes the rationale, opportunities and barriers for translating this nascent technology from promising bench-scale discoveries to full-scale commercialization and production of safe drinking water.

Nano impact

The unique properties that arise at the nano-scale (magnetism, high surface area, selective surface reactivity, surface catalysis, rapid ion delivery, photocatalysis, plasmonic resonance, dielectric properties, electrical conductivity, super hydrophobicity, strength, *etc.*) can be used to purify drinking water. While discoveries of these processes are reported in the literature, actual products and processes have been slow to mature beyond the bench-scale into larger-scale, constructed systems or consumer point of use devices for purifying drinking water. This perspective article helps identify barriers that can be overcome to enable nanotechnology for water treatment.

The need for technology innovation

Water treatment facilities rely on several treatment stages to remove multiple contaminants, which can be chemical or microbiological. Facilities treating fresh water rivers and lakes need to remove natural and anthropogenic contaminants in addition to particulate matter, including pathogenic microbes, clay and other debris, which typically require additional processes compared with groundwater systems containing dissolved pollutants. Traditional, yet still standard practice today, drinking water treatment unit processes rely on chemical coagulants, gravity sedimentation and sand or membrane filtration to remove particulate matter from surface waters. Chemical coagulants also offer the potential to remove a few inorganic dissolved trace metals (*e.g.*, arsenic). The physical removal of pathogens is augmented by oxidants to inactivate them and prevent their replication *via* addition of chemicals (chlorine, ozone) or exposure to ultraviolet light. However, there are no disinfectants that are effective against all pathogens, and chemical disinfection can result in formation of disinfection by-products (DBPs), some of which are known human carcinogens such as chloroform. To minimize formation of harmful organic DBPs, water utilities enhance coagulation processes (*e.g.*, with higher coagulant dosages or acid/base addition to modulate pH) or add non-selective sorbents (*e.g.*, activated carbon, ion exchange) to remove natural organic matter (NOM) that can serve as DBP precursors. Despite these known challenges, innovation is generally slow in the municipal water market because of the large size, high capital cost, strict regulatory environment and need for proven technology. Advanced technologies are now even capable of converting treated sewage into drinking water that surpasses all regulatory guidelines, but high cost and operational expertise requirements will limit their implementation to augmenting net water production in large cities. Desalination

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technologies rely on energy-intensive processes such as high pressure reverse osmosis or thermal distillation. The largest desalination plants are located in coastal regions and supply water to large cities. Despite pervasive use of technology to purify drinking water, consumers have become convinced that the all-purpose tap water currently provided by municipalities may not meet their personal aesthetic or perceived health requirements, and consequentially bottled water and point-of-use treatment units (under the sink, refrigerator, *etc.*) are multi-billion dollar markets in developed and developing countries alike.

Water treatment plants (WTPs) are now efficient at producing safe water for use throughout society, where water is not only used for drinking, but also for a wide array of domestic uses (washing clothes and dishes, bathing, toilets, outdoor irrigation), commercial uses (heating, cooling towers, sanitation at restaurants, *etc.*), industrial uses (bottling facilities, manufacturing facilities, *etc.*) and other societal uses (fire fighting, water features, *etc.*). The fraction of potable water used for drinking, food preparation and washing dishes is small (<10 L per-day) compared against the net *per capita* tap water production (~200 to 500 L per-day) in developed countries. Yet in most locations, all the water is treated to the same high degree of water quality.

Despite the reports and potential of emerging technologies,[1,2] many people do not have access to municipal water supplies or water known to be in compliance with federal regulations. For example, over 40 million people in the United States rely on other sources (*e.g.*, wells) that are not regulated. Furthermore, over 84% of all water systems in the USA serve fewer than 500 people and account for 79% of all violations of federal maximum contaminant level regulations. So-called point-of-entry (POE) water treatment systems for these communities still need to meet the entire *per capita* water demand (beyond just drinking water demand), but small communities often lack capital or technical expertise to operate sophisticated water treatment systems. Many of these systems treat groundwater and face very specific water quality challenges. For example, over 3000 water utilities in the USA violate the EPA regulation for nitrate in drinking water, and others violate regulations for a limited number of organic pollutants (*e.g.*, pesticides). In emerging mega-cities and developing communities across the globe water delivery may be intermittent or require augmentation by on-site storage (including rainwater harvesting). A growing number of middle class families throughout China and India are purchasing point-of-use water treatment devices for ~$200 (US) each that include individual or combinations of processes such as activated carbon, reverse osmosis and UV-disinfection.

Simply scaling down Victorian age coagulation, sedimentation and filtration processes from municipal to community or point-of-use scale faces many challenges, from use of concentrated and hazardous chemicals to managing complex residual waste streams. As such, POU systems (and increasingly POE systems) are relying on more selective technology choices (selective sorbents, advanced separation systems or

disinfection schemes). Managing DBPs illustrates an interesting contrast between controlling their formation at large centralized WTPs (*e.g.*, through improved NOM precursor removal) and having consumers use POU devices that remove some regulated DBPs (*e.g.*, trihalomethanes by sorption to activated carbon) but may not remove unregulated DBPs (*e.g.*, nitrosamines). The POU marketplace (>$20 billion annually) can rapidly incorporate new technologies because of its high sales volume, lower capital cost, small scale and relatively rapid turnover of replacement parts (*i.e.*, change out of sorption systems may be once every three months or every few thousand liters). Innovation and technology turnover in the larger and more fiscally conservative municipal water treatment plants have been much slower. Examples of innovation do exist. For example, although used for decades in the wastewater industry, consideration of low-pressure ultraviolet irradiation for microbial inactivation in drinking water was not seriously considered until both a major outbreak of waterborne illness in the USA and tightening regulations on inorganic and organic DBPs spurred on research, technology validation and sensors. 20 years later, regulatory acceptance of UV light for primary drinking water disinfection was common. This long cycle time in innovation is becoming a recognized barrier for investment and rapid innovation in the municipal-level drinking water sector.

We postulate that the POU marketplace offers a very good opportunity for development and implementation of novel technology because of its growing customer demand, competitiveness among industrial companies, relatively rapid product turn-over, willingness to innovate technologies, and relatively low per unit capital costs. Furthermore, residential POU systems offer the opportunity to innovate new water management approaches, from complete in-home wastewater reclamation and reuse to increased rainwater harvesting to treatment and use of brackish or saline groundwater. In some locations across the rural western USA, especially on native American lands, rural communities must haul water over 10 miles because local well water is too saline. Developing low-energy POU technologies to purify the local saline water could reduce the need to haul water. Innovations in the POU marketplace can and will impact larger and more capital intensive municipal water treatment facilities by validating technologies. Early adaptors of new technology will likely include larger progressive municipalities or utilities facing few options because of existing technology limitations or limited access to alternative water sources.

Promulgation of new regulations (*e.g.*, lowering arsenic or DBP MCLs) has also spurred innovation and adoption of technologies. Smaller rural communities relying on POE systems often have the most limitations on alternative water sources, but they must also meet increasingly stringent drinking water regulations. Therefore, POE systems will also likely become early adopters of new technologies. This was demonstrated in the USA after tightening regulation on arsenic in drinking water disproportionately affected small groundwater-reliant communities, and several new sorption

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technologies using selective nano-structured sorbents of iron or titanium dioxide were rapidly developed, approved by regulators and are now widely used. Because of these social, technology and regulatory drivers, consumers and even some small communities are increasing reliant on POU systems to help meet the growing demand for high quality drinking water.

Why nanotechnology?

While nanotechnology is not the only approach to innovate POU technologies, it does offer the opportunity to decrease the size and cost of POU systems and improve their pollutant selectivity. This enhances flexibility to match treated water quality to the intended use, resulting in more effective use of treatment capacity. Nanotechnology also offers the opportunity to mediate reactions and processes where chemical or reactor based technology counterparts simply do not exist. Excellent review articles describe how the novel properties of nanoparticles, nanomaterials or nanoscale processes can be incorporated into water treatment processes.[2–14] For example: iron nanoparticles can sorb arsenic and be removed in magnetic fields; titanium dioxide nanoparticles can be photocatalytic to produce powerful oxidants (HO radicals) or selectively transfer electrons to water pollutants (e.g., nitrate) to reduce them to innocuous by-products; platinum series metal nanoparticles with high surface area can transform chlorinated organics to innocuous by-products; high surface area nano-silver can release silver ions to disinfect membrane surfaces and prevent biofouling sunlight photolysis of fullerenes produces reactive oxygen species capable of inactivating virus and some bacteria; low friction and narrow pore diameter carbon nanotubes can be used to separate H_2O from salt ions; and unique aspect ratio of graphene oxide can create anti-fouling bacterial surfaces.

Most nanotechnology research for water treatment applications remains on the bench-top where a single process is often demonstrated in very simple water matrices rather than complex real-world waters that contain low levels of multiple pollutants in the presence of competing ions, foulants (iron, silica, etc.), particulates, and NOM. There are few examples of integrated intentionally nano-enabled commercialized water treatment systems. While some known examples exist, other examples new to the market are slow to disclose their precise unique nano-material. Building on the previously mentioned, successful commercialization of nano-sorbents for arsenic treatment is an interesting example. Arsenic treatment in the USA largely impacted POE systems where groundwater was the source for a publically owned water distribution systems.[15,16] Although decades of research showed the ability to synthesize nano- to micron-iron (hydr)oxides and titanium dioxide (rutile, anatase and amorphous phases) that readily complex arsenate ion on the sorbent surface, there were few commercially-available media that could be readily placed into packed beds and operate for long periods of time without leaching metals or leading to excessive head loss. The

regulation spurred innovation to create iron-, titanium and other metal oxide based nano-structured and agglomerated nanoparticle based sorbents for arsenic removal. In one case, nano-scale iron (hydr)oxide was produced in situ within macroporous ion exchange beads.[17–21] The spherical beads embedded with irregularly shaped nano-iron could be easily placed in packed bed columns and operated at hydraulic loading rates consistent with practical experience. Design consultants, tank/pump equipment manufacturers and regulators could easily understand technology principles, thereby leading to rapid adoption. A second nano-adsorbent also entered the market for use in a packed bed configuration, presumably for the same reasons including operational ease. This product involved nano-scale titanium dioxide sintered together into a highly porous aggregate, which could be milled and sieved to a size commensurate with the required hydraulic conditions in packed bed systems. Other metal oxide media entered the marketplace, and after a variety of testing, those that became commercially viable also received certification of claims by the National Sanitation Foundation International (NSF International). This certification is essential for all materials and systems used in municipal water supplies and are commonly advertised on POU devices. All these metal oxide materials in packed beds potentially underwent some "attrition" during use (normal operations or backwashing to waste), where release of nanoparticles could occur. The NSF International certification centered on claims that the system removed arsenic and did not release any contaminants that potentially violate EPA pollutant regulations. There was no special regulation that required monitoring or and unique concern about iron or titanium nanoparticle release from the systems. It would appear that the benefit of addressing challenging problems (i.e., human health risk benefits of reducing arsenic levels in drinking water) outweigh concerns about potential hazards or public perception about adopting nanotechnology for water purification, even though the potential release of nanoparticles was not rigorously tested. Thus, there are examples of deployed systems that are nano-enabled and accepted by the public and regulatory agencies, and these successful stories show one route of technology development in response to various drivers. This path depends upon regulatory drivers, takes significant time and does not represent a pro-active technology leadership route for technology innovation. Now, around the globe there are hundreds of examples of nanotechnology based solutions to water quality challenges that have been discovered, but few nanotechnologies have yet to be integrated into functional drinking water treatment systems.

Approaches towards nano-enabled water treatment systems

In the context of this perspectives article, a system is defined as a single module or series of modules that removes pollutants and produces clean drinking water that meets regulatory requirements and consumer aesthetic and perceived safety expectations. A module may consist of an existing reactor

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platform (*e.g.*, packed bed, polymeric membrane, gravity sedimentation system, *etc.*) or a new reactor design platform necessary for deploying nanotechnology. Nanotechnology refers to the use of pre-synthesized objects, or *in situ* production of objects, with at least one dimension below 100 nm. We do not consider the use of polymers or sorbents simply having pores below 100 nm as nanotechnology because many examples of these are already in use today for water purification (*e.g.*, ion exchange resins, granular activated carbon, nanofiltration and reverse osmosis). Five overarching science questions will be addressed that could guide the safe development of nano-enabled water treatment systems:

1. Which novel nano-properties could be used for water purification?

2. What features of new reactor designs are required to enable use of nano-scale properties?

3. Does embedding or attaching nanomaterials into scaffolding decrease their unique functionality?

4. How can we harness solar energy directly to reduce costs of water purification?

5. What safety concerns must be addressed to commercialize nano-enabled water technologies?

Which novel nano-properties could be used for water purification?

Nanomaterials offer engineers a unique array of properties difficult or inefficient to obtain using traditional chemicals or bulk materials (Table 1). Rather than adding bulk chemicals to the entire flow stream, the localized surface reactions allow treatment at targeted locations, greatly enhancing treatment efficiency. Example applications include, among many others, localized reactions can achieve disinfection at surfaces to prevent biofouling by adding nano silver or graphitic materials,[22–26] disinfection based upon nano-material shapes,[27] heating for thermal distillation or oxidation/regeneration of organic pollutants on surfaces,[28,29] selective sorption of trace organic or inorganic pollutants.[30] Many nanomaterials have catalytic properties. Potable drinking water systems currently do not apply catalytic processes, and nanotechnology enables the use of both low cost catalysts (*e.g.*, titanium dioxide activated by light[31–33]) as well as higher value catalysts (*e.g.*, palladium, platinum, or gold activated by hydrogen peroxide) to degrade oxo-anions or chlorinated organics.[2,34–38]

The large surface area provided by nano-structures has already been incorporated into many sorbents (*e.g.*, granular activated carbon for organics removal or granular ferric (hydr)oxides for arsenic removal), but these materials are traditionally produced in "top-down" processes that involve synthesizing micron to millimeter sized materials and crushing—and potentially re-agglomerating—them into pellet-sized media for use in packed bed treatment systems. Nanotechnology allows for "bottom-up" design of sorbents, where morphology, pore sizes and surface composition can be

Table 1 Examples nanomaterial applications for drinking water treatment

Nanoscale property	Opportunities in water purification systems	Comparison with current technology for drinking water treatment
Magnetism	Separation of small reactive particles used as catalysts or sorbents	Replaces gravity separation or high pressure filtration
High surface area & selective surface reactivity	High ratio of reactive atoms on the outside of nanomaterials relative to their total mass improves unit efficiency; achieves highly selective sorption of singular or multiple contaminants	High surface area can be attained using nano-porous materials but have internal mass transport limitations; high surface area materials can be precipitated *in situ* by continuous addition of chemicals (*e.g.*, alum)
Surface catalysis	Allows for multiple elements to be placed in close proximity; allows use of small quantities of costly elements	Catalysis is not currently used in drinking water treatment
Ion delivery	Localized deposition of anti-bacterial nanomaterials to prevent biofouling	Practices chemical disinfection of the entire water body rather than localized surface release of anti-bacterial agents
Photocatalysis	New materials allow for controlled production of different reactive oxygen species or aqueous electrons	Titanium dioxide with low-pressure Hg lamps are only commercialized technology
Photo-thermal	Super-heating *via* light to enable solar membrane distillation	Thermal membrane distillation heats entire body of water rather than localized surface heating
Dielectric properties	Heating induced by microwaves for self-cleaning surfaces or regeneration of sorbents	Self cleaning surfaces are not currently available, and reactivation of granular activated carbon occurs *ex situ* to packed beds in large gas fired kilns
Electrically conductive	Functionalized MWCNT electrodes in capacitive deionization processes	Metallic electrodes have low adsorption capacity compared with MWCNTs
Super hydrophobic	Controlling hydrophobicity of surfaces with graphene can reduce biofouling or improve membrane flux	A narrow range of polymers exist to modulate hydrophobicity of membrane or other surfaces
Strength	Electrospinning of nanofibers offers new opportunities to synthesize polymers and metal (hydr)oxide composites	Hydraulically rigid ion exchange beds, activated carbon agglomerates or other porous sorbents are used in packed beds; thin film polymeric membranes are supported on more rigid supports; cationic polymers added to strengthen metal hydroxide flocs

controlled, and then materials can be used directly or agglomerated into pellet-sized media. Specific surface area may not be the key determinant for adsorption within the nano-range; instead, available surface area based on the number of reactive sites is a more important characteristic, as shown for selenium ion sorption to nano-hematite.[30] The prior example of agglomerated nano-TiO_2 media for arsenic removal is one example. Zeolites, which have been explored for trace organic removal in potable water treatment systems,[39,40] have potential to be integrated into other reactor designs that benefit from their molecular sieve properties. Thus, differences between "top-down" and "bottom-up" material preparation is one important aspect of nano-technology. In some cases, the economics of manufacturing bottom-up products have limited adoption of some water treatment products, but the nanotechnology revolution is moving such synthesis processes from custom design to bulk scale manufacturing.

What features of new reactor designs are required to enable use of nano-scale properties?

Two basic process design approaches can be taken to utilize nanoparticles. First, nanoparticles can be freely dispersed in bulk water much like a chemical additive would be, with the difference being that a method must be in place to recover the added nanoparticles. For example, the Purifics PhotoCat® system uses ~1 g L^{-1} TiO_2 photocatalyst slurry through banks of low-pressure mercury lamps (~254 nm), and it is then recovered by a ceramic membrane for recirculation and reuse.[41] Purified water permeates through the membrane, and a high cross-flow velocity prevents membrane fouling. The ceramic membrane resists abrasion by the TiO_2 slurry. While the primary TiO_2 nanoparticles are small (~20 nm), the common catalyst material (P25 – TiO_2) is larger and photo-aggregates such that under normal operation the concentration of titanium in the permeate is below most ICP-MS detection limits of 2 to 10 μg L^{-1}.[41] This system type has been shown to remove trace organics, hexavalent chromium, DBP precursors, virus and *Cryptosporidium*.[42–44] Other types of membranes have been used to retain and recycle particle slurries (*e.g.*, the Cristal process® combines filtration membranes and powdered activated carbon), but this has not been applied to nanoparticles. Instead of recirculating particles, other processes build up porous layers of iron oxide, PAC or silica particles on membrane surfaces to prevent accumulation of foulants directly at the membrane surface.[45] Another example is magnetite core nanoparticles, which could be removed from flowing water using magnetic technology.[46–50] While research exists on such reactors, no water treatment magnetic separation reactors are currently commercially available. In these examples, it is advantageous to separate, recover and reuse nanoparticles, which differs from the single use application of traditional chemicals. There may be applications where solely nanoparticle removal is appropriate. For example, the template assisted nucleation (TAN) process produces calcite nanoparticles on the surface

of beads in a supersaturated solution of calcium carbonate, and hydraulic forces in a fluidized bed release the nanoparticles into solution.[51] Applying this technology in cooling towers suggests that the nanoparticles cause less, or easier to clean, scale formation on heat exchange systems, and similar approaches might be replacements for chemical intensive lime softening processes prior to membrane filtration, thus avoiding formation, separation and dewatering of sludges.

The second basic design approach is to embed nanoparticles into macroscale hierarchical structures. This would include nanoparticle coatings on membranes; glass fiber filters or packed bed media; precipitation of nanomaterials within pores of ion exchange, activated carbon or other macroporous sorbents; attachment of nanomaterials to reactor surfaces; agglomeration of individual nanoparticles into pellets or porous ceramics (ceramic filters, carbon block); or integration of pre-formed nanoparticles into polymers as they are casted into membranes, fibers or other structures. Several arsenic treatment media fall into this second basic design approach. Hybrid ion exchange media contain iron (hydr)oxide precipitated nanoparticles within pores of ion exchange beads and are commercially available for drinking water treatment. The engineered nanoparticles are initiated with sorption of permanganate in the beads before adding iron salts, resulting in formation of iron nanoparticles within the media. During operation, there is no release of iron nanoparticles from the media. Other media are commercially produced by sintering and re-agglomerating TiO_2 using inorganic or organic binders. Fig. 1 shows additional techniques yet to be commercialized for integrating functional nanomaterials into hierarchical structures suitable for use in reactors.

Does embedding or attaching nanomaterials into scaffolding decrease their unique functionality?

Adding freely dispersed nanoparticles to water will almost certainly require energy (magnetic, pressure) to separate them from flowing water. While nanoparticle slurries have advantages associated with high particle concentrations and pollutant diffusion mass transfer limitations, the risk of nanoparticles in finished drinking water may necessitate attaching or embedding nanoparticles into macroporous hierarchical structures (*i.e.*, scaffolding). Scaffolding may be inert polymers or other materials or may be active structures themselves (*e.g.*, activated carbon, ion exchange polymers, *etc.*). Scaffolding nanoparticles may overcome barriers associated with nanoparticle release, but it may also result in new barriers associated with mass transport and/or the ability to apply external stimuli (*e.g.*, light) to nanomaterials. While scaffolding nanoparticles may result in a loss of active surface for pollutant reactions, some evidence exists suggests that immobilizing nanoparticles may enhance performance by preventing agglomeration of nanoparticles in slurry-form and by maintaining highly accessible surface area.[52]
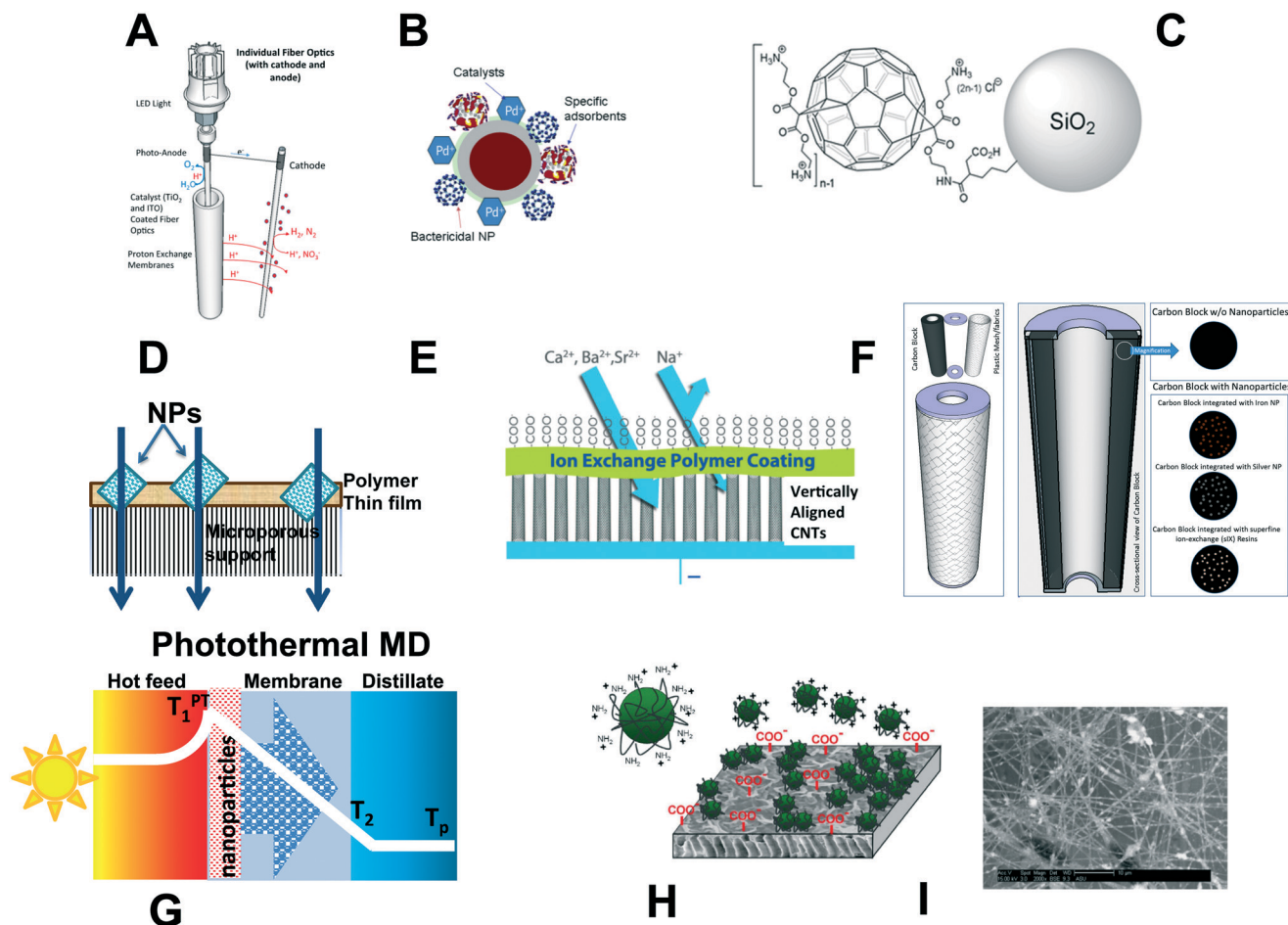
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Fig. 1 Example techniques to embed nanomaterials into hierarchical structures for enable purification of drinking water. A) LED launching light into a fiber optic coated with nano-catalysts combined with a membrane and photo-electric cathode; B) nanoparticle decorated surface on a super paramagnet magnetite core; C) amine functionalize fullerene covalently bound on silica to attract and photoactively inactivate virus *via* ROS production; D) mixed matrix membrane with nano-zeolites embedded in a non-permeable polymer thin film; E) conducting MWCNTs into a capacitive deionization system; F) homogeneous distribution of multiple highly selective for sorption nanoparticles embedded within carbon block; G) embedded carbon nanoparticles in an electrospun layer above a hydrophobic membrane to generate solar drive water vapor production; H) super-hydrophilic or antimicrobial functionalized nanoparticles deposited on the surface of conventional polymeric membranes; I) nanoparticles (white regions) imaged in a network of polymeric electrospun fibers.

Nanomaterials have high surface area that can enable rapid reaction kinetics, but this is only advantageous if target pollutants can readily come into contact with their surfaces. Pollutants such as arsenic need to diffuse through stagnant films and then into pores of millimeter diameter hybrid (nanoparticle) ion exchange/adsorption media. These systems are often limited by intraparticle mass transfer rates[53–57] whereas faster arsenic removal can occur when nanoparticles (5–25 nm diameter) are freely dispersed in water.[57,58] In other cases, diffusion limitations may not be between a target pollutant and a nanoparticle reactive surface. Instead, the limitation is from diffusion of ions from a nanoparticle into solution (*e.g.*, dissolution of silver ions from nano-silver for disinfection purposes). Embedding the silver nanoparticle within a low water permeability polymer limits the rate of redox-mediate dissolution of Ag^0 to Ag^+, and diffusion of Ag^+ back into solution. Proper polymer selection, surface attachment of nanoparticles, or creation of pores within polymer may all influence the mass transfer rate of Ag^+ delivery back into solution. In contrast to influencing pollutant or ion mass transport, embedded nanoparticles themselves can lead to certain types of mass transport limitations. For example, the wettability (*i.e.*, hydrophobicity) or tortuosity of pores in zeolites impregnated in non-permeability polymers influences the water flux rate through this type of new low-pressure membrane system.[59] Nano-silver particles attached to the surface of ceramic membranes reduced bacterial growth.[7,60] A final example relates to embedding pre-formed nanoparticles into electrospun polymeric fibers for the intended use of pollutant sorption. Adding metallic nanoparticles into polymer precursors produces fibers with nanoparticles well dispersed in the fiber, but the polymer coats the nanoparticles and prevents their access to pollutants in water.[61] However, use of carbon nanoparticles surprisingly produces pores that allow access by pollutants in water to sorb on these nanoparticle surfaces.[61] Alternative to this

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single-step synthesis process, fibers can undergo post-treatment after spinning and be decorated with nanoparticles on the outside of fiber.[62]

Many nano-materials of interest require external stimuli to become functional. This includes light (UV, visible, solar) for photolysis, upconverting or photothermal processes, magnetic fields for recovery of paramagnetic nanoparticles, microwaves for materials with high dielectric constants, electrical current for conductive materials, or hydrogen gas for reductive processes. Reactors containing nanomaterials that depend on external stimuli face similar mass transport limitations for molecular diffusion or water flux, and they require configurations to deliver the external stimuli. For example, solar light mediated processes require large surface areas and potentially shallow reactor depths to allow light to contact nanoparticle surfaces on the base of the reactor. Use of radial emitting low-pressure or medium-pressure mercury lamps with nano-particles coated on the internal surface of reactors have been developed,[63] but the reactors suffer from relative low masses of photocatalysts and are prone to surface fouling by inorganic ions (*e.g.*, iron).[64] Solar light concentrated with reflective mirrors or artificial light sources can be delivered into reactors *via* fiber optics. Coating high surface area fiber optics with photocatalysts induces a change in refractive index on the fibers that causes light absorption by the photocatalyst to produce reactive oxidants capable of oxidizing pollutants in the outer water phase.[65–67]

Managing light irradiation of photocatalysts is a barrier in both fixed film and slurry-based reactors. In dense slurries (*e.g.*, >1 gTiO$_2$ L^{-1}) light penetration may be <1 mm into the slurry solution, creating a small reactive zone around the light source. Decreasing the slurry concentration can increase light penetration, but may be offset by less efficient surface reactions. Slurry-based systems also have the barrier of requiring highly efficient separation of freely dispersed nano-photocatalysts in water (*e.g.*, ceramic membranes), from treated water which should not contain any nanoparticles.

Some have sought to overcome the barrier of using slurries and ceramic membranes, but creating ceramic coatings containing photo-active surfaces.[7,68] Others envision electro-spinning titanium precursors followed by calcination to produce fibers of anatase or rutile that are a few microns wide and can operate as a reactive filter when integrated with artificial light.[69,70] A second example involves a physic–chemical reductive process, which is uncommon in drinking water treatment despite the presence of many oxidized pollutants (*e.g.*, nitrate, perchlorate, MTBE, TCE). Slurry and embedded/attached catalytic nanoparticle (*e.g.*, Pd/Pt) reactor designs are discussed in the literature,[71–73] and all face barriers of effective hydrogen gas delivery through water to the catalyst surface.

How can we harness solar energy directly to reduce costs of water purification?

For smaller drinking water systems located off the water-grid, there is significant interest in developing solar-driven water purification processes. Photovoltaic panels convert a relatively limited portion of the solar energy spectrum into electricity, where subsequent transformation and equipment inefficiencies (*e.g.*, pumps to pressurize membranes, energy to power UV lamps, *etc.*) mean that a relatively small percentage ($<10\%$) of the solar energy is available for water purification. In contrast, direct solar-driven processes aim to capture a broader solar spectrum or modulate absorption properties of nanomaterials to utilize visible light rather than only UV light. For example, traditional membrane distillation (MD) uses petroleum or solar energy to heat water and create a temperature gradient driving force across a hydrophobic membrane for water vapor molecules to diffuse through and then condense on the back-side of the membrane.[74,75] The discovery that light absorbing black nanoparticles induce plasmonic resonance processes that generate localized heating and a new mechanism for low-temperature light-induced steam generation offers new opportunities for MD design.[28,76–78] This may lead to low-energy direct solar MD units to desalinate brackish groundwater or even seawater by immobilizing the light-absorbing nanoparticles at the surface of the MD membrane, resulting in localized solar heating that creates a large thermal gradient at the membrane surface and generates vapor that diffuses rapidly across the membrane (ref). Separately, significant progress has been made to synthesize visible light active photocatalysts or upconverting materials.[79–89] Less effort has gone into design of solar-driven photocatalytic systems, but research to date includes outdoor reactors using raceways coated with photocatalysts, solar light captured *via* reflective-concentrating surfaces and launched into fiber optics coated with photocatalysts, or direct solar irradiation in batch bottles (*e.g.*, modified SODIS).[81,90–95] Two major barriers for scale-up of direct solar driven processes are light management (delivery into reactors containing water) and the amount of solar energy (~1.4 kW m^{-2}) available for reactions.

What safety concerns exist around nano-enabled water technologies?

Any new technology potentially faces public perception and regulatory acceptance obstacles. Getting ahead of and recognizing the importance of these obstacles will be critical for the success of nano-enabled water treatment technologies. Release of nanomaterials from water treatment systems into drinking water is arguably the most pressing risk. Recalling that risk is a function of hazard and exposure, mitigating these concerns could be achieved through either of these characteristics. However, few studies on nanomaterial ingestion *via* drinking water exposures have been performed, but some papers explore the potential occurrence levels or risks of nanomaterials in surface water sources entering water treatment plants.[96–99] The public may be more concerned about the use of nanotechnology in drinking water treatment, as opposed to consumer products like textiles based upon recent social science research.[100–102]

In terms of addressing inherent hazard, safe-by-design principles of nanomaterials can be undertaken. The goal is to achieve or exceed the functional performance of current materials and the technologies they enable while minimizing inherent hazard to avoid risk to human health and the environment at all stages of the nanomaterial and water treatment unit process life cycle. This emphasizes the importance of establishing structure–property–function (SPF) and structure–property–hazard (SPH) relationships to guide the rational design of nanomaterials.[103] First and foremost, the use of elements with known human toxicity (e.g., nickel, cadmium, chromium) should be avoided. Instead, nanomaterials of benign, low-cost, and earth-abundant compositions should be used. For example, iron nanoparticles synthesized from coagulant-grade ferric chloride, which is already approved for use at water treatment plants, can be integrated into an in situ regeneration process for granular activated carbon packed beds that alleviate the need to remove, transport and thermally regenerate GAC off-site.[29,104] Next, it is important to consider that shape and aspect ratio of nanomaterials influence both treatment efficiency and potential toxicity. Although surface area is not the sole determinant of functional efficacy for nanoscale materials, the shape of nano cupric oxide (CuO) influences antimicrobial activity,[27] which could be desirable to prevent surface membrane fouling. CuO nanosheets have the highest surface reactivity, electrochemical activity and antimicrobial activity. While less active than the nanosheets, CuO nanoparticles (sphere-like shape) demonstrate enhanced reactivity compared to the bulk CuO.[27] Incorporating multi-walled carbon nanotubes (MWCNTs) into water treatment systems for sorption or electrochemical reactions may be desirable, and it has been shown that surface functionalization can influence both functional performance and bioactivity. That is, surface carboxyl groups and the redox activity of carbonyl groups promote enhanced MWCNT reactivity, both in terms of electrochemical and antimicrobial activity.[105] A few examples exist where life cycle assessment and safe by design concepts have been integrated into development of nano-enabled water treatment unit processes,[30,106] but the sheer complexity in nanomaterial properties relative to the supposedly known properties of chemical additives may lead to uncertainties in the actual benefits of nanotizing processes or products.[107] Thus, by designing nanomaterials using SPF and SPH, it is possible to utilize nanomaterials that realize the desired performance with lower potential human health risks. When this information is unknown or this strategy is not viable because those nanoparticles that provide the intended function also cause the undesirable hazard, exposure control is necessary to address safety concerns.

The first consideration with respect to exposure is to design reactors that contain nanoparticles to either completely retain nanoparticles via separation systems (e.g., magnetic separation) or physical barriers (e.g., membranes). Because complete retention/separation may be difficult, an alternative approach is to embed nanoparticles in macro-scale structures where they cannot be released into water. When designing to minimize exposure, it is essential to have validated analytical techniques to quantify nanomaterials in water at levels of relevant concern. Drinking water regulations exist for some elements used in nanomaterials (Table 2) as primary (MCL) or secondary (SMCL) maximum contaminant levels and would serve as absolute values not to exceed. Some nanomaterials that undergo dissolution (e.g., Ag^0, ZnO) have been shown generally to pose less adverse hazards than the ions they release (Ag^+, Zn^{2+}), but concern about delivery of the nanoparticles into cells and causing localized risks remains debatable. Most carbon-based engineered nanoparticles contain elemental carbon rather than organic carbon. Total organic carbon (TOC) is indirectly involved in drinking water regulations as part of the Surface Water Treatment Rule, where TOC of 1 to 6 mg L^{-1} is relevant. Some carbon-based engineered nanoparticles can be detected by liquid-TOC analytical methodologies. Turbidity is a measurement of visible light scattering and is used in drinking water regulations as a surrogate for pathogens. High concentrations of engineered nanoparticles can be detected as turbidity. Filtered drinking water turbidity must be less than 0.3 NTU in at least 95% of samples and at no time exceed 5 NTU. Surface and ground waters contain natural nanoparticles (clays, cell fragments, iron (hydr)oxides, etc.) in the 1–100 nm range and are on the order of 10^8 to 10^{12} particles per liter of 10 nm particles. Physical processes at WTPs conservatively remove >99% of particles in this size range, but clearly it would be difficult to distinguish a few engineered nanoparticles mixed in with the heterogeneous sources of natural nano-scale colloids. While a few techniques exist to count particles in the 1–100 nm size range, the drinking water industry currently only widely uses particle counters in the 1–100 μm size range, where monitoring Giardia cysts or Cryptosporium oocysts in the 4 to 20 μm range is a current focus.

The above regulatory frameworks provide the least restrictive potential limits for nanoparticles in water, and analyses following standard methods could be applied. More advanced techniques exist to differentiate size and concentration for some elements and nanoparticles. For example, single-particle ICP-MS methods are not yet available in commercial laboratories but have been demonstrated in research laboratories to work for many of the elements in Table 2.[108] Thermal combustion and microwave based analytical schemes can detect graphitic nanomaterials in water at concentrations between 0.01 to 0.1 mg L^{-1}, but their use remains limited to only a few research labs. Fullerenes and fullerols can be quantified using LC/MS methods.[109] To improve detection at low concentrations, techniques such as cloud point extraction and solid phase extraction can be used to preconcentrate the nanoparticles.[110–112] Third-party organizations such as NSF International certify that drinking water chemicals, coatings, etc. do not exceed maximum levels of impurities and certify treatment processes removals. Similar certifications will be a barrier for nano-enabled processes to gain industry and consumer acceptance. Of course, potential

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Table 2 Regulatory implications for elements commonly used in engineered nanoparticles

Element	Example nanomaterials containing element	Regulatory level
Aluminum	Al_2O_3	SMCL = 0.05 to 0.2 mg L^{-1}
Boron	BN	No regulatory level but included on contaminant candidate list 2 (CCL2) (<1 mg L^{-1})[a]
Cadmium	CdSe	MCL = 0.005 mg L^{-1}
Carbon	SWCNT, MWCNT, graphene, graphene oxide, C60, C_3N_4	Not directly regulated
Copper	CuO	Action level = 1.3 mg L^{-1} SMCL = 1.0 mg L^{-1}
Gold	Au^0	No regulatory level (<20 ppt)[a]
Iron	Fe_2O_3, Fe_3O_4	SMCL = 0.3 mg L^{-1}
Nickel	NiO	Regulated until 1995 with an MCL = 0.1 mg L^{-1}
Palladium	Pd^0	No regulatory level (<50 ppt)[a]
Platinum		No regulatory level (<50 ppt)[a]
Silica	SiO_2, zeolites	No regulatory level (5 to 50 mgSiO_2 L^{-1})[a]
Silver	Ag^0	SMCL = 0.1 mg L^{-1}
Titanium	TiO_2	No regulatory level (0.001 to 0.01 mg L^{-1})[a]
Vanadium	$BiVO_4$	No regulatory level but included on CCL3 (0.001 to 0.01 mg L^{-1})[a]
Zinc	ZnO	SMCL = 5 mg L^{-1}

[a] Provides commonly-occurring range in surface waters for non-regulated elements as a comparison.

concerns exist regarding proper disposal at the end of life for any residuals or devices, and it remains unclear to what extent disposal of nano-containing materials may be subject to stricter regulations than other types of wastes.[113–115] Overall, barriers for safe use of nanomaterials include both readily accessible instrumentation and selection of relevant or acceptable levels of nanoparticles in finished drinking waters.

The path forward to realize new paradigms in producing drinking water

It is important to ensure that the added benefits of using new materials or processes exceed associated risks and to ensure that any risk of new technology is dwarfed by the known risks posed by priority pollutants in drinking water. With nearly two decades of research on risks posed by engineered nanomaterials, the authors believe it should now be possible to safely use nanotechnology for water purification. However, scaled-up production of nanomaterials, system-level design, operational experience and regulatory frameworks for safe use of nano-based water treatment technologies remain in their infancy and offer a rich environment for fundamental and applied research.

Although there are few commercialized nano-enabled drinking water treatment technologies on the market today, nanotechnology holds promise for transitioning away from continuous and stoichiometric chemical dosing that is commonly practiced for municipal scale water treatment (e.g., coagulants, acids, bases) or even POU scale (e.g., NaCl for ion exchange softeners) to materials that can be activated by external, non-chemical stimuli (e.g., light, microwaves, etc.) or enable catalytic reactions that do not consume chemical re-

agents. Furthermore, nanotechnology offers the opportunity for compact design because of the high and selective surface area available at the nanoscale and the ability to integrate multiple functionalities into a single process (e.g., reactive membranes). Nanotechnologies for water treatment may remain only laboratory exercises unless a viable commercialization strategy develops to address potential unintended consequences and perceived risks. Because municipal water treatment systems are large-scale, treating tens of millions of gallons per day, they are chemical intensive and costly. Consequently cities are risk-adverse with respect to implementing new technologies directly from the bench-scale. Testbeds and field demonstrations alone are likely inadequate to convince regulators and utilities of the scalability, robustness and safety of nano-enabled drinking water systems. We believe a path to commercialization lies through niche markets initially that can readily recognize the benefits of nanotechnology. These markets could include consumer-focused under the sink systems (e.g., point of use) because of the large market segment, high level of global competition, rapid innovation cycle times (6 to 24 months), and desire for product differentiation. This application focus should improve the manufacturing capability of nanomaterials for the water sector, driving down material costs as synthesis transitions from reagent-grade materials in labs to bulk-purity materials at commercial scale. Proven successes on this scale could, over 5–10 years, provide sufficient confidence in the technology and allow scale up to municipal level drinking water treatment systems.

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