

Nanotechnology: a source of answers to the global clean water challenge

● Nanotechnology offers an exciting range of potential applications in providing water treatment. **QILIN LI, MASON B TOMSON, MICHAEL WONG, and PEDRO JJ ALVAREZ** review the progress being made.

Ensuring access to inexpensive and clean sources of water is emerging as one of the greatest global challenges of this century. More than five million people die every year from water-related diseases, and more than one billion people suffer without access to safe water for their basic needs.

We cannot overestimate the importance of clean water to the health of a population and the economy. In the US, for example, life expectancy has increased from 48 to 76 over the past 100 years, primarily by properly treating water. Unfortunately, the amount of readily-accessible water is decreasing due to over-exploitation of water resources, a disposal mentality, global climate change and increasing pollution from emerging contaminants, while demand for water is rising due to the growth of the world's population and mega-urbanisation.

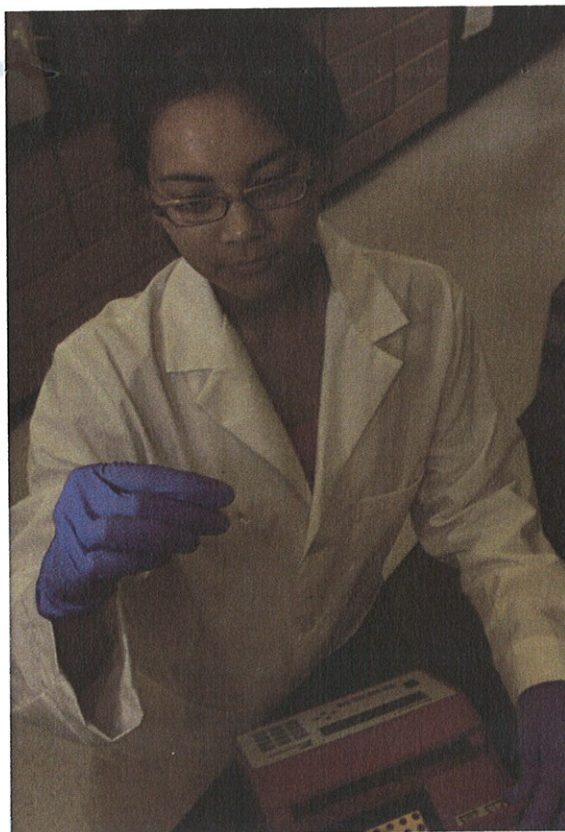
Most current approaches to water treatment are relatively old, dating back to the Victorian era. They are materials-intensive, have a large footprint and cannot always meet the increasingly-stringent water quality standards of industrialised nations, especially given the large number of emerging contaminants and antibiotic-resistant pathogens found in source waters. Moreover, conventional methods of disinfection such as chlorination, chloramination and ozonation can produce harmful disinfection byproducts from reactions with various constituents of natural waters, requiring a trade-off between adequate disinfection and minimising harmful byproduct formation.

Another great challenge faced by existing treatment technologies is that drinking water distribution systems in many large cities are nearing the end of their lifespan and cannot meet the demand from a growing population.

Deterioration of water quality in ageing and leaky distribution systems compromises drinking water safety. Water shortages in many parts of the world are promoting the use of alternative water sources such as wastewater and seawater, which require treatment performance beyond that which conventional methods can provide.

This situation calls for new ideas and immediate action on sustainable water management and technology. One promising alternative is a distributed water reuse and treatment paradigm to remove concerns about degradation of water quality within distribution networks, alleviate dependence on

Delina Lyon, a doctoral student, working in Pedro Alvarez's laboratory. Credit: Jeff Fitlow, Courtesy of Rice University.



major system infrastructure, and exploit alternative water sources such as recycled 'new water' for potable use. Many scientists and engineers working in the field of water treatment see nanotechnology as a major part of the solution for restoring the world's clean water resources. Initial successes suggest unlimited opportunities afforded by more advanced composite nanomaterials.

Why nanotechnology?

Nanotechnology is the understanding and control of matter, working atom by atom at a scale of 1 to 100 nanometres, to create larger structures with new molecular organisation, novel properties and functions. By virtue of their size – a human hair is about 80,000 nanometres thick – nanomaterials have many possible advantages that can be exploited for new or improved treatment processes, such as their large surface-to-volume ratio, high reactivity, photosensitivity, and unique properties that allow easy separation. Such properties include superparamagnetism, which allows nanoparticles to temporarily form large agglomerates that can be easily separated from water in a low magnetic field. Removal of the external magnetic field reverses the process, resulting in disaggregation, so that the nanoparticles can be reused. Researchers are finding that nanotechnology can be used in water monitoring, treatment and reuse systems that target a wide variety of water pollutants in ways that are affordable and easy to operate.

Nanotechnology used in membrane filtration systems

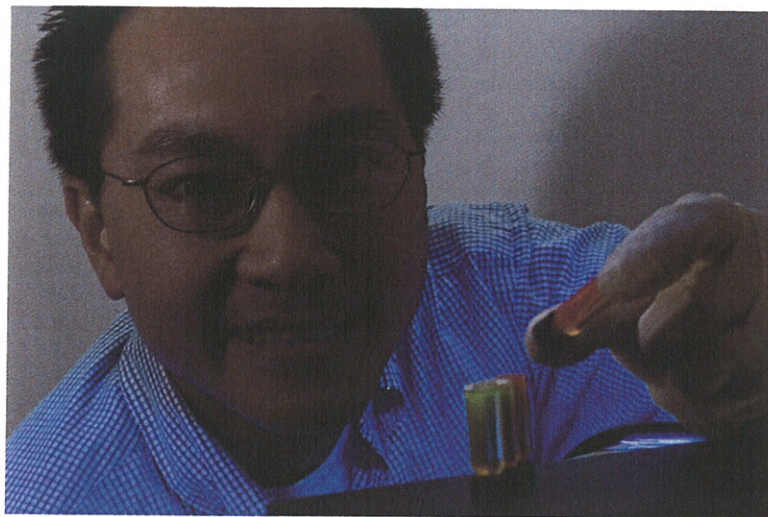
Applications for membrane technology are growing rapidly, and it is becoming a core water treatment method. With the aggravating water shortage problems being experienced around the world, particularly in coastal cities where saline intrusion is an increasing concern and fresh water is becoming a luxury, the need for brackish groundwater and seawater desalination, as well as direct or indirect potable reuse of wastewater, is increasing rapidly. This requires high-efficiency membrane systems. In addition, with a growing world population, bringing water from distant locations is becoming increasingly untenable. Smaller, distributed systems – portable units containing filtration membranes – are being proposed to serve hotels, small villages or neighbourhoods.

However, membranes can become clogged, or fouled, over time – through scaling, by particulate or dissolved organic matter, or from bacterial

contamination – which reduces their effectiveness. Fouling poses the biggest obstacle to their broader application. In addition, the wide variety of contaminants in water and the diversity of their properties usually means a need for multiple stages of treatment, making the treatment system quite complex. The challenge is to produce better, cheaper, longer-lasting filters with easily-tunable selectivity.

Nanotechnology provides us with an opportunity to develop fouling resistant, multifunctional membranes that target a wide range of contaminants. For example, when irradiated by UV light, titanium dioxide (TiO_2) is a bactericide that can degrade a wide range of organic contaminants. By incorporating such photocatalytic and antimicrobial nanoparticles into water treatment membranes, we can develop nanocomposite membranes that reduce membrane fouling and at the same time remove contaminants that

Michael Wong, with vials of Quantum Dots (nanoscale sensors). Credit: Jeff Fitlow, Courtesy of Rice University.



'The world's water supplies are facing new threats; affordable, advanced technologies could make a difference for millions of people around the world.'

Grand Challenges for Engineering, National Academy of Engineering of the National Academies, February 2008.

are too small to be retained by membranes [1, 2].

Nanomaterials are also being used to develop cost effective, highly selective membranes with higher permeability for water purification and desalination. The usual procedure for removing salt from water is reverse osmosis – a physical separation process in which pretreated source water is delivered at high pressure through a semi-permeable polymeric membrane.

New research using membranes made with vertically-aligned carbon nanotubes – extremely narrow, hollow cylinders consisting entirely of carbon atoms – as pores has shown potential to dramatically improve reverse osmosis technology [3, 4]. Because they have an extremely smooth interior, the tiny hollow carbon cylinders allow water to flow more rapidly. Consequently, these carbon nanotube membranes can be ten times more permeable than existing membranes and therefore do not need as much pressure to push water through them.

Although salt rejection has not been demonstrated for these nanotube membranes, researchers expect that it can be achieved using carbon nanotubes of very small diameters. This improvement can potentially reduce

the energy costs of the RO step of desalination by up to 75%. Carbon nanotubes can also be used to make filtration membranes of easily tunable pore sizes by varying the spacing between the individual tubes, which allows selective removal of pollutants based on their sizes. Because these tiny carbon tubes are also highly elastic, mechanical compression and release can be used to reversibly tune the pore size of nanotube membranes [5].

In addition, filters made of nanotubes are effective at removing bacteria such as *Escherichia coli* and *Staphylococcus aureus*, as well as viruses such as *Poliovirus sabin 1* from contaminated water. The filters are easily cleaned using ultrasonication (high intensity acoustic energy) and autoclaving (a high pressure method of heating liquids above boiling point for sterilisation).

Anti-microbial nanoparticles for disinfection and microbial control

Over five million people die every year from infectious waterborne diseases.

This issue is made worse by natural catastrophes such as earthquakes and flooding following hurricanes, which interrupt water treatment. Biofilm formation in water distribution and storage systems and industrial cooling facilities also compromises water quality, greatly increases the cost of maintaining these systems and hinders efficient water conservation.

Current disinfection and microbial control often relies on chemical oxidants such as free chlorine, chloramines and ozone. These agents, while effective at killing bacteria and inactivating viruses, do not work well against cyst-forming parasites that cause severe diarrhoea, such as *Giardia* and *Cryptosporidium*. In addition, when reacting with different constituents of natural water these disinfectants often produce harmful byproducts, many of which are carcinogens.

One area of nanotechnology research centres on the use of

nanoparticles with anti-microbial properties to filter out and destroy microbial pathogens [6]. Several natural and engineered nanomaterials are known to have antibacterial properties and can be used as disinfecting agents. We have already mentioned TiO_2 , and commercial water purification systems based on TiO_2 photocatalysis already exist. Silver is another such agent, and is the most commonly used nanomaterial for microbial control. Currently, there are over 100 consumer products that contain silver nanoparticles as an antimicrobial agent, including point-of-use water purification units.

Finally, certain types of fullerenes, such as carbon nanotubes (also mentioned above) and photosensitive fullerenols have potential as antimicrobials [7, 8]. These nanomaterials have the potential to enhance existing disinfection technologies such as UV inactivation of viruses and solar disinfection of bacteria, as well as to reduce bio-fouling during membrane filtration.

In addition, the growing demand for decentralised water treatment systems makes this option an attractive one to pursue. In the future, high-performance, small-scale or point-of-use systems incorporating antimicrobial nanomaterials may enhance community water systems and can be used for emergency response for contaminated water produced during natural disasters.

Nanotechnology for removing arsenic and other heavy metals

The toxicity of certain heavy metals, such as lead, mercury and arsenic, is well-known. According to the World Health Organization, arsenic contamination of drinking water – especially well water – affects tens of millions of people in more than 20 countries around the world, including areas of the US. Mercury exposure is now a public health problem in almost every part of the world. Lead poisoning of water often

occurs when lead in older plumbing leaches into the water supply.

Numerous studies have reported the high efficiency of nanomaterials in removing arsenic and other heavy metals by adsorption. One of the most promising developments is a process called Nano Rust. The Nano Rust particles attract heavy metals such as arsenic, and even some radionuclides. Because they are superparamagnetic, when put in a weak magnetic field such as that created by a computer hard drive, the magnetic interaction that takes place between the Nano Rust particles (one tenth the size of a human cell) separates them from water, taking the adsorbed contaminants with them. The process can easily reduce the amount of arsenic in water to levels well below the EPA's threshold for US drinking water [9].

Reactive and catalytic nanoparticles for contaminant removal

The contamination of groundwater, which is the source of most drinking water, is a serious health concern. Over the years, groundwater has been contaminated by a wide variety of toxic chemicals used in industry. The two most prevalent in the US and other industrialised countries are trichloroethene (TCE) and perchloroethene (PCE). These chlorinated compounds are found in an estimated 5000 contaminated sites on the US government's Superfund National Priorities List. TCE was once widely used as a solvent to degrease metal parts in a number of industries and PCE as a dry cleaning fluid. They are among the most hazardous pollutants around, having been found to cause liver and kidney damage, impaired pregnancies and cancer. New technologies use bimetallic nanoparticles of gold and palladium as catalysts to break down the undesired contaminants – a process that is much faster and more effective than existing technologies [10].

Nano-sensors for water quality monitoring

Nanoscale sensors are being widely researched for use in both health and environmental applications. They are smaller, less expensive and more accurate than larger sensors and, due to their tiny size, are much more easily incorporated into the environment, giving them a wider range of sensing applications.

The nanosensors currently being studied are carbon nanotubes, quantum dots and nanoshells. Quantum dots are tiny semiconductor nanocrystals – each far less than a millionth of an inch in diameter – that radiate brilliant colors when exposed to UV light. They can be used in bio-labeling bacteria such as

E. coli for quick detection of water-borne pathogens. Nanoshells usually consist of a non-conducting core such as glass or silicon dioxide and a bi-compatible metal surface layer such as gold. Depending on the ratio between the size of the core and the thickness of the surface layer, nanoshells absorb light in different wavelength ranges, which can be utilised to detect chemical and biological analytes.

Nanotechnology's potential dark side

Although most of the applications of nanotechnology in water treatment are still at the research or development stage, they have great potential to offer effective, inexpensive solutions to the growing challenge of providing clean drinking water and improved health, especially in developing countries where this transformation is most needed.

Yet we must sound a cautionary note about this relatively new science. Over the years, new technologies have brought creative solutions to long-standing problems. However, new

The challenge is to produce better, cheaper, longer-lasting filters with easily-tunable selectivity.

technologies sometimes bring new problems as well. DDT, for example, was for many years one of the most widely used pesticides in the US, and Paul Müller won the 1948 Nobel Prize in medicine for using DDT to combat malaria. However its toxic nature, combined with its persistence in the environment, led to concerns about effects on fish and wildlife. Likewise, MTBE, which is used as a petrol additive to promote more complete combustion of hydrocarbons, has been found to contaminate groundwater.

So it is with nanotechnology. Beyond the initial excitement about its possibilities and the fearful science fiction scenarios about its terrible power are the more reasonable concerns about the impact of nanomaterials on health and the environment. Risk is composed of two parts, toxicity and exposure. Little is known about the health effects of nanoparticles, but even less is known about exposure and critical exposure routes, that is, the fate and transport of these materials in the environment.

Studies looking at the effects of nanomaterials have focused mainly on exposure by inhalation; very little research has been done on nanomaterials in aquatic environments. Determining the risk from nanomaterials to humans and the environment may take many years. Meanwhile, it is estimated the global nanotechnol-

ogy market will grow to around \$1 trillion over the next 10 years – larger than the total agricultural market. It is important that while we fully explore nanotechnology and its applications for water treatment, we also support research into safe practices for its use [11]. ●

Reference:

- 1 Choi H, Stathatos E and Dionysiou DD, 2007. Photocatalytic TiO₂ films and membranes for the development of efficient wastewater treatment and reuse systems. *Desalination*. 202: pp199-206.
- 2 Losito I, Amorisco A, Palmisano F and Zamboni PG, 2005. X-ray photoelectron spectroscopy characterization of composite TiO₂-poly(vinylidene fluoride) films synthesised for applications in pesticide photocatalytic degradation. *Applied Surface Science*. 240: pp180-188.
- 3 Holt JK, Park HG, Wang Y, Stadermann M, Artyukhin AB, Grigoropoulos CP, Noy A and Bakajin O, 2006. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science*. 312: pp1034-1037.
- 4 Majumder M, Chopra N, Andrews R and Hinds BJ, 2005. Enhanced flow in carbon nanotubes. *Nature*. 438: p. 44.
- 5 Li X, Zhu G, Dordick JS and Ajayan PM, 2007. Compression-modulated tunable-pore carbon-nanotube membrane filters. *Small* 3(4): pp595-599.
- 6 Li Q, Mahendra S, Lyon DY, Brunet L, Liga MV, Li D and Alvarez PJJ, 2008. Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. *Wat Res* (submitted).
- 7 Kang S, Pinaut M, Pfefferle LD and Elimelech M, 2007. Single-walled carbon nanotubes exhibit strong antimicrobial activity. *Langmuir*. 23: pp8670-8673.
- 8 Badireddy AR, Hotze EM, Chellam S, Alvarez PJJ and Wiesner MR, 2007. Inactivation of bacteriophages via photosensitization of fullerol nanoparticles. *Environmental Science & Technology*. 41: p. 6627-6632.
- 9 Yavuz CT, Mayo JT, Yu WW, Prakash A, Falkner JC, Yean S, Cong L, Shipley HJ, Kan A, Tomson M, Natelson D and Colvin VL, 2006. Low-Field Magnetic Separation of Monodisperse Fe₃O₄ Nanocrystals. *Science*. 314(5801): pp964 - 967.
- 10 Wong MS, Alvarez PJJ, Fang YL, Akpinar N, Nutt MO and Heck KH, 2008. Cleaner water using bimetallic nanoparticle catalysts. *Journal Chem Technol Biotechnol*. (In press).
- 11 Wiesner MR, Lowry GY, Alvarez PJJ, Dionysiou D and Biswas P, 2006. Assessing the risks of manufactured nanomaterials. *Environment Science Technology*. (14): p. 4337-4445.

About the authors

Qilin Li is Assistant Professor of Civil and Environmental Engineering, Mason B Tomson is Professor of Engineering, Michael S Wong is Associate Professor in Chemical Engineering and Assistant Professor in Chemistry, and Pedro JJ Alvarez is the George R Brown Professor of Engineering at Rice University. All are participating researchers with the Center for Biological and Environmental Nanotechnology at Rice (www.chen.rice.edu).