NANO-TECHNOLOGY: NEW NANOMATERIALS FOR RADIOACTIVE WASTE CLEAN-UP IN WATER

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ABSTRACT

Nanotechnology is the science and technology of precisely manipulating the structure of matter at the molecular level. The term nanotechnology embraces many different fields and specialties, including engineering, chemistry, electronics, and medicine, among others, but all are concerned with bringing existing technologies down to a very small scale, measured in nanometers A nanometer a billionth of a meter is about the size of six carbon atoms in a row. Today, as in the past, most industrial products are created by pushing piles of millions of atoms together by mixing, grinding, heating a very imprecise process. However, scientists can now pick up individual atoms to assemble them into simple structures or cause specific chemical reactions. Propellers have been attached to molecular motors, and electricity has been conducted through nanowires. Nanotubes made of carbon are being investigated for a variety of industrial and research purposes. In the future, nanotechnology may be able to harness the forces that operate at the scale of the nanometer, such as the van der Waals force, as well as changes in the quantum states of particles, for new engineering purposes.

Radioactive waste that contains radioactive material is hazardous to human health and the environment, and is regulated by government agencies in order to protect human health and the environment. Among the many applications of nanotechnology that have environmental implications, remediation of contaminated groundwater using nanoparticles containing zero-valent iron (nZVI) is one of the most prominent examples of a rapidly emerging technology with considerable potential benefits.

This paper will covers the strength of Nanotechnology that helps to clean drinking water. Technology has long been important in providing clean drinking water and irrigation for food crops. Water is a scarce resource, and for many countries — particularly those in the Middle East — supplies already fall short of demand, since with the pressures of climate change and population growth, water will become even scarcer, especially in developing regions.

***Keywords**: Nanotechnology, Radioactive waste, Nanotubes.*

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INTRODUCTION

Radioactive wastes are wastes that contain radioactive material. Radioactive wastes are usually by-products of nuclear power generation and other applications of nuclear fission or nuclear technology, such as research and medicine. Radioactive waste is hazardous to human health and the environment, and is regulated by government agencies in order to protect human health and the environment.

Radioactivity diminishes over time, so waste is typically isolated and stored for a period of time until it no longer poses a hazard. The period of time waste must be stored depends on the type of waste. Low-level waste with low levels of radioactivity per mass or volume (such as some common medical or industrial radioactive wastes) may need to be stored for only hours, days, or months, while high-level wastes (such as spent nuclear fuel or by-products of nuclear reprocessing) must be stored for thousands of years. Current major approaches to managing radioactive waste have been segregation and storage for short-lived wastes, near-surface disposal for low and some intermediate level wastes, and deep burial or transmutation for the long-lived, high-level wastes.

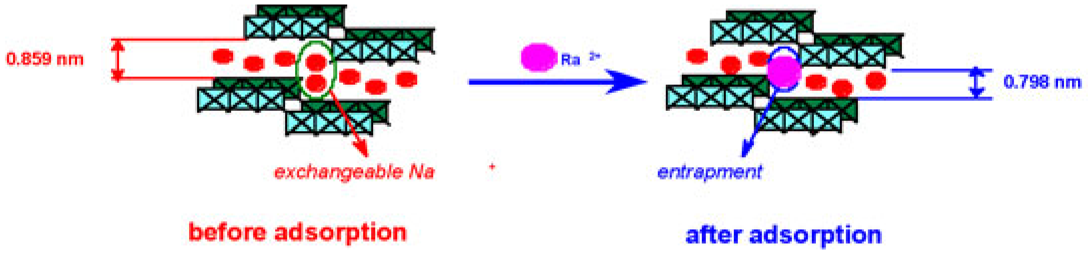
A summary of the amounts of radioactive wastes and management approaches for most developed countries are presented and reviewed periodically as part of the International Atomic Energy Agency (IAEA) Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management

- [Nanowerk Spotlight] Radioactive material is toxic because it creates ions – by stripping away electrons from atoms – when it reacts with biological molecules. These ions can form free radicals, which damage proteins, membranes, and nucleic acids. Free radicals damage components of the cells' membranes, proteins or genetic material by "oxidizing" them – the same chemical reaction that causes iron to rust. This is called "oxidative stress". Many forms of cancer are thought to be the result of reactions between free radicals and DNA, resulting in mutations that can adversely affect the cell cycle and potentially lead to malignancy.
- Nanotechnology has provided numerous constructs that reduce oxidative damage in engineering applications with great efficiency. As a new research report shows, nanotechnology applications could also help to remediate radioactive contamination at the source, by removing radioactive ions from the environment.
- Environmental contamination with radioactive ions that originate from the processing of uranium or the leakage of nuclear reactors is a potential serious

health threat because it can leach into groundwater and contaminate drinking water supplies for large population areas. The key issue in developing technologies for the removal of radioactive ions from the environment – mainly from wastewater – and their subsequent safe disposal is to devise materials which are able to absorb radioactive ions irreversibly, selectively, efficiently, and in large quantities from contaminated water.

- "Natural inorganic cation exchange materials, such as clays and zeolites, have been extensively studied and used in the removal of radioactive ions from water via ion exchange and are subsequently disposed of in a safe way" Dr. Huai Yong Zhu explains to Nanowerk. "However, synthetic inorganic cation exchange materials – such as synthetic micas, g-zirconium phosphate, niobate molecular sieves, and titanate – have been found to be far superior to natural materials in terms of selectivity for the removal of radioactive cations from water. Radioactive cations are preferentially exchanged with sodium ions or protons in the synthetic material. More importantly, a structural collapse of the exchange materials occurs after the ion exchange proceeds to a certain extent, thereby forming a stable solid with the radioactive cations being permanently trapped inside. Hence, the immobilized radioactive cations can be disposed safely."
- Zhu, an Associate Professor in the School of Physical & Chemical Sciences at the Queensland University of Technology in Brisbane, Australia, points out that this phenomenon – that the uptake of large, radioactive cations eventually triggers the trapping of the cations – by itself represents a desirable property for any material to be used in decontamination of water from radioactive cations.
- "Generally, ion exchange materials exhibiting a layered structure are less stable than those with 3D crystal structures and the collapse of the layers can take place under moderate conditions" says Zhu. "Then again, it has also been found that nanoparticles of inorganic solids readily react with other species or are quickly converted to other crystal phases under moderate conditions, and thus are substantially less stable than the corresponding bulk material."
- Based on this, Zhu and his colleagues from Queensland University of Technology and Dr. Xue Ping Gao from the Institute of New Energy Material Chemistry at Nankai University in Tianjin, PR China, focused their search for potential

candidates for intelligent absorbents on nanoparticles of inorganic ion exchange materials with a layered structure.



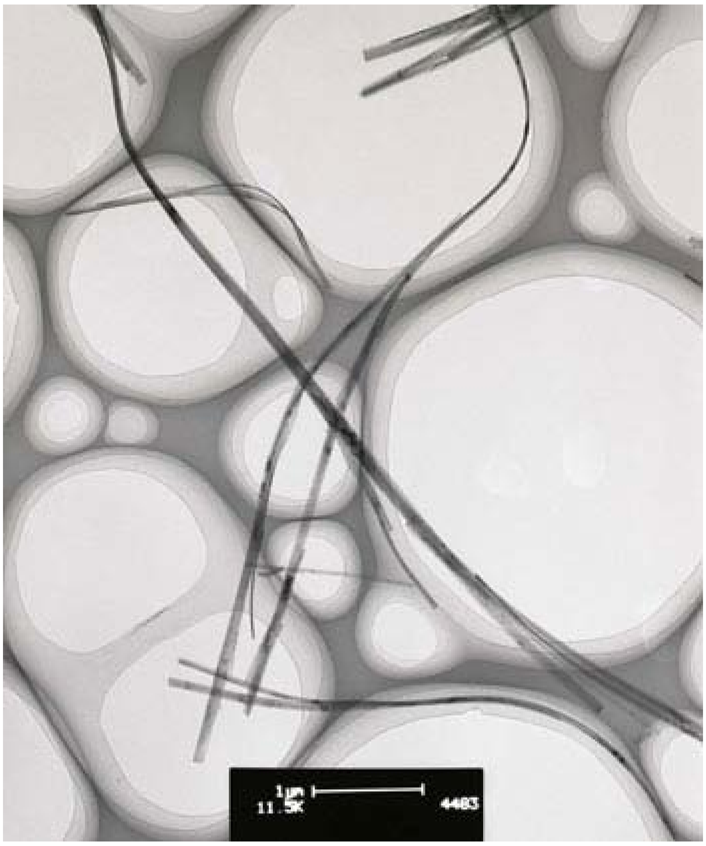
Scheme for the removal of the radioactive ions through ion exchange and structure deformation. (Image: Dr. Zhu)

In a recent paper in *Advanced Material*, the scientists describe the use of titanate nanofibers as intelligent absorbents for the removal of radioactive ions from water.

"The novelty of our project is that the adsorption of bivalent toxic radioactive cations by the nanofibers finally induces structure collapse and deformation of the nanofibers, which permanently locks in the toxic radioactive cations," Zhu explains. "The permanent entrapment prevents the radioactive cations to be released from the adsorbents and assures that they can be safely disposed. Furthermore, the titanate nanofiber can selectively remove the radioactive ions in the presence of plentiful competitive ions."

It has been know for years that titanate solids possess a layered structure and exchangeable sodium ions. Also, titanate materials are stable to radiation, chemicals, and thermal as well as mechanical stress, so that they make an ideal carrier for radioactive ions.

Zhu points out that titanate nanofibers have a much larger capacity to take up the bivalent toxic radioactive cations, and they can do it much faster than other materials. "The most important finding by us is the nanofibers can trap the toxic radioactive cations permanently" he says.



Transmission electron microscopy image of the titanate nanofibers.

(Image: Dr. Zhu)

The property of these nanofibers to permanently trapping radioactive cations makes them an ideal absorbent to remove them from contaminated water, while the used sorbents can be disposed safely without having to risk a release of the absorbed cations from the absorbents which may cause secondary contamination.

The scientists also mention that the titanate nanofibers possess a number of additional **Advantages** for practical application in the removal of radioactive cations:

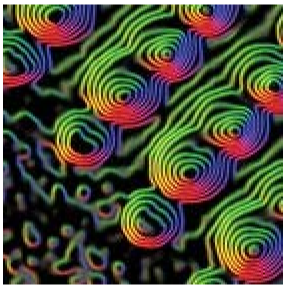
The synthesis of phase pure titanate nanofibers with a small and uniform particle size can be achieved in large quantities from abundant raw materials, such as titanium dioxide minerals, using simple and cost-effective processes.

- The fabrication costs of nanofibers are much lower than that of titanate whiskers which are prepared by pyro-synthesis at high temperatures.
- Titanate nanofiber sorbents can be readily dispersed into solutions because the fibers do not aggregate as much as clays and zeolites.
- Moreover, the absorbents can be separated from any liquid after the absorption simply by filtration, sedimentation, or centrifugation due to their fibril morphology.

- Absorption of radioactive ions by the fibers is very prompt. The amount absorbed within the first 24 hours is approximately 80% of the final equilibrium capacity.

Zhu and his team are now working on developing inorganic adsorbents with meta-stable structures for irreversible ion exchange. Such a structure will be useful for removal toxic ions in water. They are also making efforts to improve the selectivity and increase the capacity of the materials so that they can be used for treatment of radioactive wastes on an industrial scale and produce waste solids suitable for long-term storage and disposal.

NANOTECHNOLOGY FOR CLEAN WATER: FACTS AND FIGURES



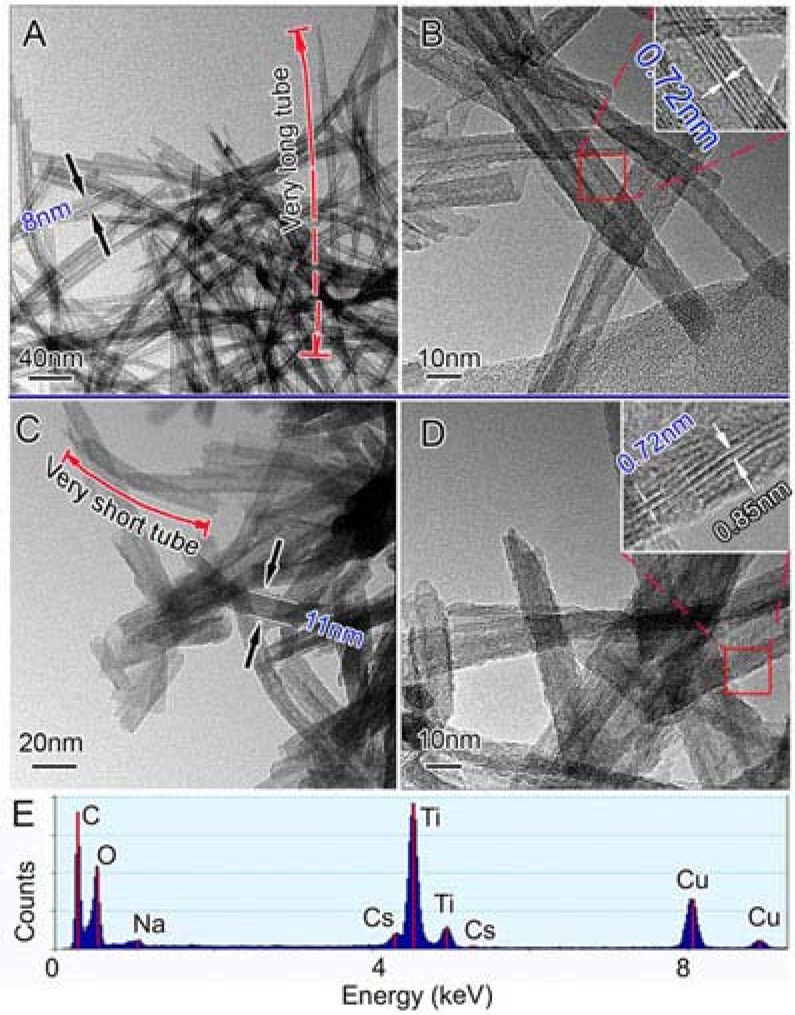
Magnetic fields around nickel nanoparticles

New nanomaterials for radioactive waste clean-up in water
(*Nanowerk Spotlight*) Back in 2008 we reported on nanotechnology solution for radioactive waste cleanup, specifically the use of titanate nanofibers as absorbents for the removal of radioactive ions from water. Now, the same group that developed these nanomaterials reports in a new study that the unique structural properties of titanate nanotubes and nanofibers make them superior materials for removal of radioactive cesium and iodine ions in water.
Radioactive cesium and iodine ions are products of uranium fission and can be easily dissolved in water during an accident at a nuclear reactor like the one in Fukushima earlier this year. The fear is that these fission products could get into the groundwater and could make their way into the food chain.
As we reported in our previous *Nanowerk Spotlight* mentioned above, natural inorganic cation exchange materials, such as clays and zeolites, have been extensively studied and used in the removal of radioactive ions from water via ion exchange and are subsequently disposed of in a safe way. However, synthetic inorganic cation exchange materials – such as synthetic micas, g-zirconium phosphate, niobate molecular sieves, and titanate – have been found to be far superior to natural materials in terms of selectivity for the removal of

radioactive cations from water. Radioactive cations are preferentially exchanged with sodium ions or protons in the synthetic material. More importantly, a structural collapse of the exchange materials occurs after the ion exchange proceeds to a certain extent, thereby forming a stable solid with the radioactive cations being permanently trapped inside. Hence, the immobilized radioactive cations can be disposed safely.

"Based on our earlier work, we have now demonstrated a potentially cost-effective method to remediate cesium and iodine ions from contaminated water by using the unique chemistry of titanate nanotubes and nanofibers to chemisorb these ions," HuaiYong Zhu, a professor of chemistry at the Queensland University of Technology, tells Nanowerk.

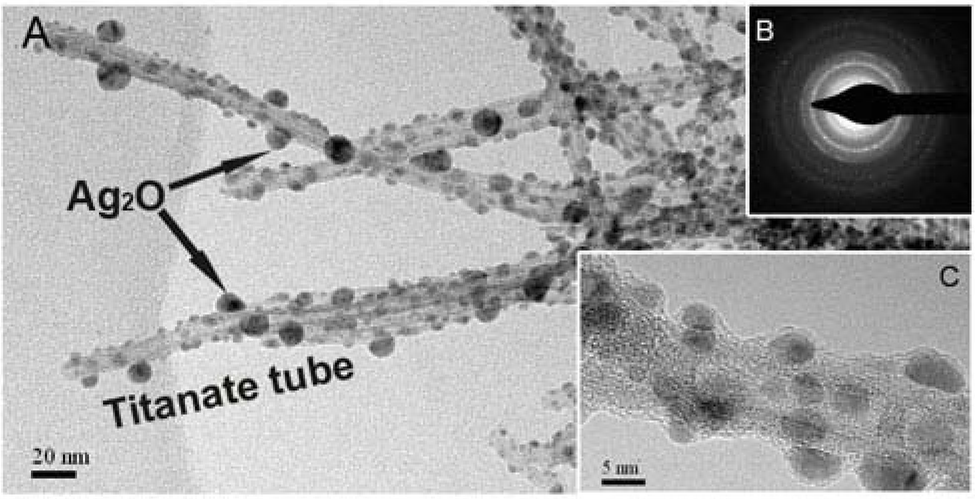
The team, which reported their findings in the September 20, 2011 online edition of *Angewandte Chemie International Edition* also found that the new sorbents can not only take up these ions but efficiently trap them for safe disposal because of their unique structural and chemical features.



PTEM micrographs of the tubular sorbents before and after entrapment of cesium ions. Panel A and B are the TEM images of the initial T3NT. Inset in panel B is a HRTEM image of the selected area in panel B. Panel C and D are the TEM images of the nanotubes after adsorption of cesium ions (Cs-T3NT). Inset in panel D is a HRTEM image of the selected area in panel D, in which tube walls with two different interlayer distances are connected by a trapezoid neck. Panel E is the EDS analysis of Cs-T3NT. (Reprinted with permission from Wiley-VCH Verlag)

"The sorbents take up cesium ions via an exchange with sodium ions in the nanostructures; the rapid uptake of cesium ions eventually triggers a phase transition of the titanate and traps the cesium ions inside permanently for safe disposal," explains Zhu. "This is because the fibers and tubes consist of negatively charged thin layers – as thin as two oxygen atoms – and phase transition of the layers with low rigidity can be readily induced."

In order to capture and immobilize iodine ions from water, the researchers anchored silver oxide nanocrystals on the external surfaces of titanate nanotubes and nanofibers by chemical bonds owing to their crystallographic similarity. These composites can efficiently capture iodine ions forming silver iodine precipitate on the titanates.



Silver oxide nanocrystals anchored sodium titanate nanotubes (Ag_2O-NT). (A) Typical TEM image depicting the abundant silver oxide nanocrystals (~5-10 nm) coated on titanate nanotubes. (B)The selected area Electron Diffraction Pattern (EDP) of the nanotubes. (C) HRTEM image of a single nanotube and the anchored silver oxide nanocrystals. (Reprinted with permission from Wiley-VCH Verlag)

Zhu explains that this work introduces three new concepts:

1) Utilizing ion exchange to uptake cesium ions; which eventually triggers a phase transition of the titanate trapping the ions inside permanently for safe disposal.
2) To attach silver oxide nanocrystals to the external surface of the nanostructures via coherent interface between the crystal and the substrate, for silver oxide nanocrystals to capture iodine ions efficiently. It is impractical to use fine silver oxide powder directly for the removal of iodine anions because the separation of the used silver oxide particles from water will be extremely difficult and costly, and aggregation of the fine nanocrystals also substantially reduces the removal efficiency.
3) The new adsorbents can be readily dispersed in liquid and easily separated after purification for safe disposal due to their one-dimensional morphology; and the adsorption beds loaded with the adsorbents can permit high flux. This significantly enhances the adsorption efficiency and reduces the separation costs. Furthermore, the titanate nanofibers and nanotubes can be easily synthesized from titanium compounds including titanium dioxide at low cost.
Given that there are hundreds of nuclear power stations over the world, and hundreds more in planning, developing efficient adsorbents is of great significance for the nuclear industry, not to mention our environment. Even if all these nuclear power plants will be shut down eventually, the necessary clean-up work will still have to be done.
"The adsorbent of titanate nanofibers and nanotubes not only can be produced from titanium dioxide at low cost, but the ability to tailor these structural features to enhance uptake and trapping of ions can be exploited for further development of new and selective adsorbents for the removal of other toxic cations and anions that may be found in groundwater or wastewater," says Zhu.

NANOTECHNOLOGY COULD HELP GIVE MILLIONS CLEAN DRINKING WATER:

Technology has long been important in providing clean drinking water and irrigation for food crops. Indeed, people have had water technology for thousands of years — the Romans were using aqueducts as conduits for drinking wateraround 300BC. But making modern technology accessible and affordable to the global poor is a daunting task. Can nanotechnology perform better than previous technologies?

Water is a scarce resource, and for many countries — particularly those in the Middle East — supplies already fall short of demand. With the pressures of climate change and population growth, water will become even scarcer, especially in developing regions. Moreover, in these regions, what water is available is often unsafe to drink (see Table 1).

884 million	people lack access to safe water supplies — approximately one in eight people
6 kilometres	is the average distance African and Asian women walk to fetch water
3.6 million	people die each year from water-related diseases
98 per cent	of water-related deaths occur in the developing world
84 per cent	of water-related deaths are in children ages 0–14
43 per cent	of water-related deaths are due to diarrhoea
65 million	People are at risk of arsenic poisoning in the Bangladesh, India and Nepal area

Table 1: Key Water Facts

The quest to ensure that all people have access to clean drinking water is now enshrined in the UN's Millennium Development Goals, which aim to halve the proportion of people without sustainable access to safe drinking water by 2015. According to the World Water Assessment Programme, that will mean improving water supplies for 1.5 billion people.

But how to achieve this? Economics or technology have often driven approaches to providing water for poor communities. The economics route might typically centre on the importance of regulations, institutions and open markets. The technology approach might focus on designing a water pump, filter systems or novel applications, for example, of nanotechnology

NANOTECHNOLOGY'S POTENTIAL:

Unlike other technologies, which have often sprung directly from a particular scientific discipline, nanotechnology spans a wide spectrum of science. Essentially, it is defined by the scale it operates at. Nanoscience and nanotechnology involve studying and working with matter on an ultrasmall scale. One nanometre is one-millionth of a millimetre and a single human hair is around 80,000 nanometres in width. This kind of scale is difficult for us to visualise but if the distance between the Sun and the Earth were one metre then a nanometre would be the size of a football pitch.

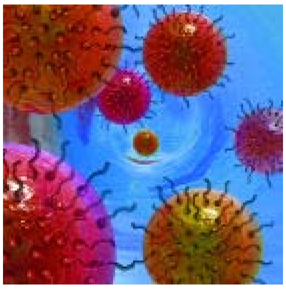
The nanoscale deals with the smallest parts of matter that we can manipulate. Operating at the nanoscale makes assembling atoms and molecules to exact specifications easier. Rather like building a model from Lego bricks, we might envisage creating new materials or modifying existing ones. In applications like water filtration this means materials can be tailored, or tuned, to filter out heavy metals and biological toxins.

Materials at the nanoscale often have different optical or electrical properties from the same material at the micro or macroscale. For example, nano titanium oxide is a more effective catalyst than microscale titanium oxide. And it can be used in water treatment to degrade organic pollutants. But in other cases, manufactured nanoparticles' small size may make the material more toxic than normal.

Nanotechnology can solve the technical challenge of removing salt from water

Nano catalysts, magnets and detectors

Nanocatalysts and magnetic nanoparticles are other examples of how nanotechnology could make heavily polluted water fit for drinking, sanitation and irrigation. Nanocatalysts owe their better catalytic properties to their nanosize or to being modified at the nanoscale. They can chemically degrade pollutants instead of simply moving them somewhere else, including pollutants for which existing technologies are inefficient or prohibitively expensive. Researchers at the Indian Institute of Science, in Bangalore, have used nano titanium dioxide for this very purpose. Magnetic nanoparticles have large surface areas relative to their volume and can easily bind with chemicals. In water treatment applications, they can be used to bind with contaminants — such as arsenic or oil — and then be removed using a magnet. Several companies are commercialising such technologies and researchers are frequently publishing new discoveries in this area.



Nanorust and arsenic

CBEN/Rice University

For example, scientists at Rice University in the United States are using magnetic "nanorust" to remove arsenic from drinking water. Nanorust's large surface area means it can capture one hundred times more arsenic than larger counterparts. The team projects that 200–500 milligrams of nanorust could treat a litre of water. And it is developing a way of creating nanorust from inexpensive household items. This could significantly reduce production costs, making it a viable product for communities throughout the developing world.

As well as treating water, nanotechnology can also detect water-borne contaminants. Researchers are developing new sensor technologies that combine micro and nanofabrication to create small, portable and highly accurate sensors that can detect single cells of chemical and biochemical substances in water. Several research consortia are field testing such devices and some expect to commercialize these soon. For example, a team at Pennsylvania State University in the United States has developed a way of detecting arsenic in water by using nanowires on a silicon chip.

NANO RESEARCH IN THE DEVELOPING WORLD:

Research spending on nanotechnology in developed regions like Europe and the United States are very high as governments continue to prioritise technologies they think will underpin economic growth. And some intermediate countries, like China, are also investing heavily (see Figure 1).

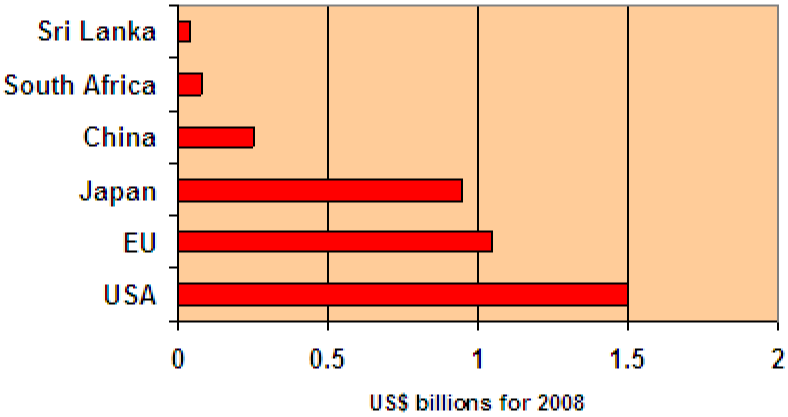


Figure 1: Research spending on nanotechnology

South Africa has developed important capabilities in nanotechnology through its National Nanotechnology Strategy, launched in 2006.It has, for example, set up innovation centres for nanoscience in two of the country's science councils. One of these includes a focus on nanoscience for water. The thrust of research here has very much been on solving local problems. The University of Stellenbosch, for example, is researching nanomembranes for water filtration.

India too has invested heavily in nanotechnology — although figures are difficult to verify, partly because investment is often a partnership between government and the private sector.

And other developing countries are increasingly seeing a need to support nanoscience, including research into how nanotechnology can help deliver clean water. Brazil, Cuba, Saudi Arabia and Sri Lanka all host nanoscience centres working on this issue. And the number of patents on nano-based inventions filed by developing country researchers is increasing rapidly.

DEVELOPMENTS FOR THE DEVELOPING WORLD:

Some interesting products are now emerging from developing countries, and other products are being developed elsewhere that are highly relevant to the needs of the South (see Table 2).

Product	**How it works**	**Importance**	**Developer**
Nanosponge for rainwater harvesting	A combination of polymers and glass nanoparticles that can be printed onto surfaces like fabrics to soak up water	Rainwater harvesting is increasingly important to countries like China, Nepal and Thailand. The nanosponge is much more efficient than traditional mist-catching nets	Massachusetts Institute of Technology, United States
Nanorust to remove arsenic	Magnetic nanoparticles of iron oxide suspended in water bind arsenic, which is then removed with a magnet	India, Bangladesh and other developing countries suffer thousands of cases of arsenic poisoning each year, linked to poisoned wells	Rice University, United States

Desalination membrane	A combination of polymers and nanoparticles that draws in water ions and repels dissolved salts	Already on the market, this membrane enables desalination with lower energy costs than reverse osmosis	University of California, Los Angeles and NanoH2O
Nanofiltration membrane	Membrane made up of polymers with a pore size ranging from 0.1 to 10nm	Field tested to treat drinking water in China and desalinate water in Iran, using this membrane requires less energy than reverse osmosis	Saehan Industries, Korea
Nanomesh waterstick	A straw-like filtration device that uses carbon nanotubes placed on a flexible, porous, material	The waterstick cleans as you drink. Doctors in Africa are using a prototype and the final product will be made available at an affordable cost in developing countries	Seldon Laboratories, United States
World filter	Filter using a nanofibre layer, made up of polymers, resins, ceramic and other materials, that removes contaminants	Designed specifically for household or community-level use in developing countries. The filters are effective, easy to use and require no	KX Industries, United States

		maintenance	
Pesticide filter	Filter using nanosilver to adsorb and then degrade three pesticides commonly found in Indian water supplies	Pesticides are often found in developing country water supplies. This pesticide filter could provide a typical Indian household with 6000 litres of clean water over one year	Indian Institute of Technology in Chennai, India, and Eureka Forbes Limited, India

Table 2: Nano-based products relevant to developing countries seeking to improve water supplies

RISKS AND OPPORTUNITIES:

Any assessment of future markets for nanotechnology-based water treatments must take account of both the risks and opportunities.

Some researchers claim that investigations into the ethical, legal and social implications of nanotechnology are lagging behind the science. They quote the low number of citations on such topics in the literature and the fact that, in the United States at least, not all available research funds are being used. For example, the US National Nanotechnology Initiative allocated US$16–28 million to research on nanotechnology's broader social implications — but spent less than half that amount.

And the generally lower scientific capacity in developing countries means it is likely that effective regulation of the ethics and risks of nanotechnologies will lag behind the developed world. Yet there are signs that the ethics of using nanotechnology for clean water are being discussed.

Some researchers have called for more research on the potential health and environmental risks of using nanotechnology for water treatment. For example, there are concerns that the enhanced reactivity of nanoparticles makes them more toxic. Their small size also means they could be hard to contain, so could more easily escape into the environment and potentially damage aquatic life. The full effects of exposure to nanomaterials — from handling them at water treatment plants or drinking them in treated water — are as yet unknown.

But we can make a distinction, in terms of risk assessment, between active and passive nanoparticles. Passive particles, such as a coating, are likely to present no more or less a risk than other manufacturing processes. But active nanoparticles that can move around the environment lead to risks associated with control and containment.

So can nanotechnologies really help solve water problems in developing countries? There are two positive signs that they will. First, water professionals and scientists are increasingly including local communities in dialogues to understand the problems with, and opportunities for, applying nanotechnology to water improvements.

Second, since the commercialization of nanotechnology is at an early stage, we can hope that such discussions — between researchers, communities and industry — will encourage scientists and businesses to develop appropriate business models to exploit their inventions.

CONCLUSION:

A range of water treatment devices that incorporate nanotechnology are already on the market, with others either close to market launch or in the process of being developed.

Nanofiltration membranes are already widely applied to remove dissolved salts and micro-pollutants, soften water and treat wastewater. The membranes act as a physical barrier, capturing particles and microorganisms bigger than their pores, and selectively rejecting substances. Nanotechnology is expected to further improve membrane technology and also drive down the prohibitively high costs of desalination — getting fresh water from salty water.

Researchers are developing new classes of nanoporous materials that are more effective than conventional filters. For example, a study in South Africa has shown than nanofiltration membranes can produce safe drinking water from brackish groundwater. And a team of Indian and US scientists have developed carbon nanotube filters that remove bacteria and viruses more effectively than conventional membrane filters.

Naturally occurring attapulgite clays and zeolites are also used in nanofilters. These are locally available in many places around the world and have innate nanometer-size pores. A study using attapulgite clay membranes to filter wastewater from a milk factory in Algeria has shown they can economically and effectively reduce whey and other organic matter in wastewater, making it safe to drink.

Zeolites can also be fabricated. They can be used to separate harmful organics from water and to remove heavy metal ions. Researchers at Australia's Commonwealth Scientific and

Research Organization have created a low-cost synthetic clay, hydrotalcite, that attracts arsenic, removing it from water. They have suggested a novel packaging for this product for low-income communities — a 'teabag' that can be dipped into household water supplies for about 15 minutes before drinking. And selling the used teabags back to the authorities might increase recycling and help with waste disposal of concentrated arsenic.

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