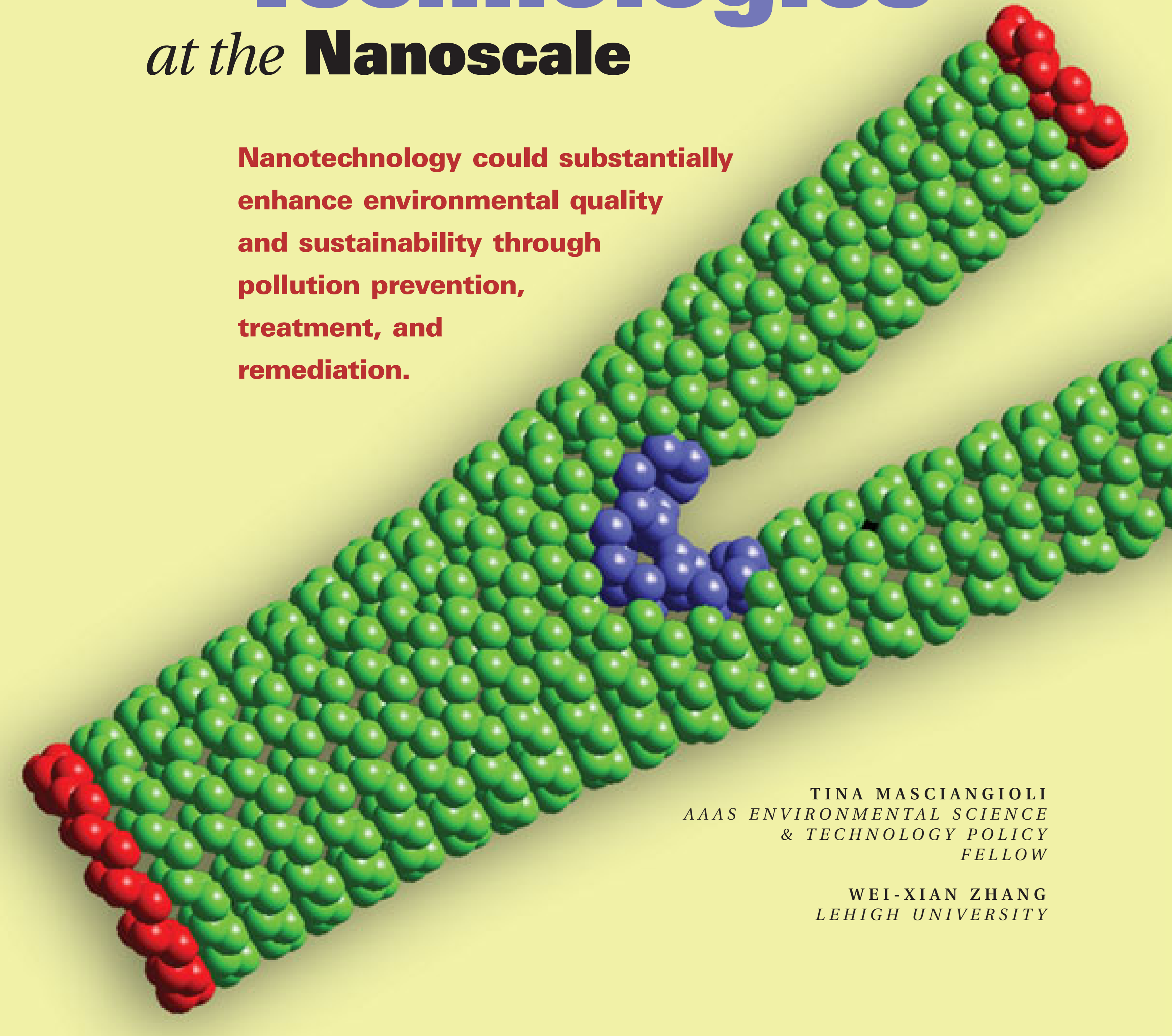
Environmental Technologies at the Nanoscale



Nanotechnology could substantially enhance environmental quality and sustainability through pollution prevention, treatment, and remediation.

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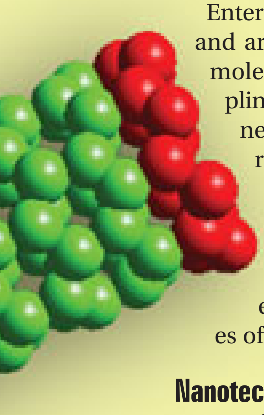
Maintaining and improving soil, water, and air quality represent some of the most formidable challenges facing global society in the 21st century. Pollutants from such diverse sources as oil and chemical spills, pesticide and fertilizer runoff, abandoned industrial and mining sites, and airborne gaseous and particulate matter from automobiles exacerbate the situation on a daily basis. Detecting and treating existing contaminants and preventing new pollution are among the challenges. The aggregate financial burden for improving air, water, and soil quality is truly staggering (*1*). In light of these enormous and complex challenges, it is perhaps ironic that one prospective solution is diminutive in size but immensely powerful in capacity.



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Enter nanotechnology—the revolutionary science and art of manipulating matter at the atomic or molecular scale that has cut across such disciplines as chemistry, physics, biology, and engineering (*2*). Despite a largely unproven track record in the environmental arena, nanotechnology offers great promise for delivering new and improved environmental technologies. However, proliferation of nanotechnology could also lead to new environmental problems, such as new classes of toxins or related environmental hazards.

Nanotechnology overview

Nanotechnology refers broadly to using materials and structures with nanoscale dimensions, usually ranging from 1 to 100 nanometers (nm). Perhaps, without realizing it, we already encounter some likeness of nanotechnology in daily life. For example, proteinaceous molecules in living organisms from bacteria to beetles to humans serve as "molecular motors" to drive everything from flagellar motion to muscle flexion. Nanometer-sized particles have been developed to improve the mechanical properties of tires, initiate photographic film development, and serve as vital catalysts in the petrochemical industry.

To some extent, environmental scientists and engineers are already working with nanoscale structures (*3*). Natural weathering of minerals, such as iron oxides and silicates, and microorganisms, such as bacteria and algae, produce nanoscale colloids, which include dispersions of nanosized-particles in media with special properties that can be important in the fate, transport, transformation, and bioavailability of environmentally harmful substances. Anthropogenic and natural colloids of solids, liquids, and gases in liquids (sols, emulsions, and foams, respectively), and solids and liquids in gases (smokes and fogs, respectively) are commonly encountered in the environment.

However, nanotechnology is not just about the size of very small things. More important, it is about structure and the ability to work—observe, manipulate, and build—at the atomic or molecular level. This results in materials and systems that often exhibit novel and significantly changed physical, chemical, and biological properties due to their size and structure. These new properties, which we will elaborate on later in this article, include improved catalysis (*4*), tunable wavelength sensing ability (*5*), and increased mechanical strength (*6*).

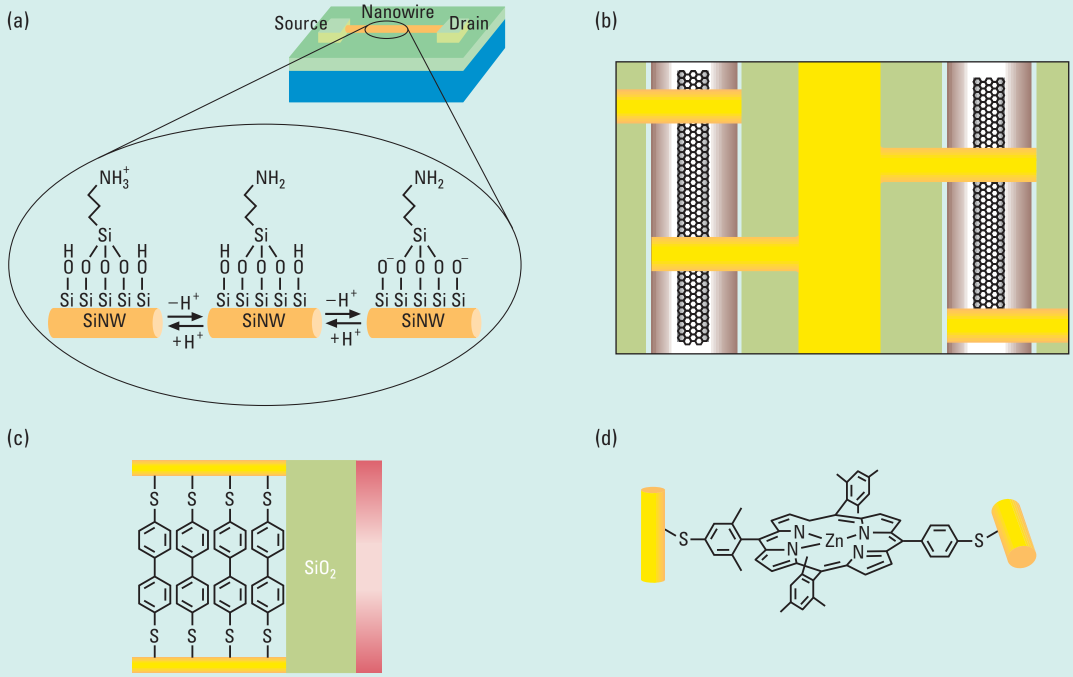
The basic structures of nanotechnology include nanoparticles or nanocrystals, nanolayers, and nanotubes. These nanostructures differ in how they are made and how their atoms and molecules are ordered. A nanoparticle—a collection of tens to thousands of atoms measuring about 1–100 nm in aggregate diameter—is the most basic structure in nanotechnology. Such nanoparticles are created atom by atom, so the size, and often the shape, of a particle is controlled by experimental conditions. These particles can also be described as nanocrystals because the atoms within the particle are highly ordered, or crystalline.

Nanostructures, such as those shown in Figure 1, are often arranged or self-assembled into highly ordered layers arising from hydrogen bonding, dipolar forces, hydrophilic or hydrophobic interactions, gravity, and other forces (*7*). Many naturally occurring biological structures, like membranes, vesicles,

FIGURE 1

Nanostructures

(a) Silicon nanowires that detect pH, (b) carbon nanotubes, (c) small organic molecules, and (d) biomolecules are examples of nanoscale materials, devices, and circuits that could be used for pollutant sensinng, prevention, and treatment.



Source: Figure 1a was adapted with permission from Reference (*28*), and Figures 1b–d were adapted with permission from Reference (*37*).

and DNA, form because of such self-assembly. Repeating structures with a tailored periodicity are essential in many applications of nanotechnology, such as photonics, catalysts, and membranes. Understanding and building nanostructures through self-assembly is the core of the nanotechnology creation process (*8*).

The extraordinary mechanical, electronic, and chemical characteristics of nanostructures called carbon nanotubes, which were discovered by Sumio Iijima in 1991, have captured the imagination of scientists and engineers (*9*). As shown in Figure 2, nanotubes generally consist of hexagonal lattices of carbon atoms arranged spirally to form concentric cylinders (*10*). The tubes are nearly perfect crystals and thinner than graphite whiskers. Single-wall nanotubes (SWNTs) have a diameter of approximately 1.4 nm, and multiwall nanotubes (MWNTs) consist of between 2 and 30 concentric tubes that form an outer diameter of 30–50 nm. Nanotubes range in length from a few tens of nanometers to several micrometers.

Nanotubes have characteristics that lead to various applications (*11*). For example, nanotubes are stronger than steel but very flexible and lightweight, which makes them a suitable material for both superstrong cable and tips for scanning probe microscopes. In addition to the remarkable mechanical properties, nanotubes could potentially replace copper as an electrical conductor or, with a small change in structure, replace silicon as a semiconductor. Nanotubes also transfer heat better than any other known material.

Researchers are exploring the use of nanotubes in drug delivery and medical diagnostic applications. Several different companies in the United States, Japan, and Europe are testing production of nanotubes on a pilot scale. However, at several hundred dollars per gram, nanotubes are still too expensive for most applications.

Pollution prevention

Pollution prevention refers to "source reduction" and other practices that efficiently use raw materials, energy, water, or other resources to reduce or eliminate creation of waste. This strategy also includes using less toxic and renewable reagents and processing materials, where possible, and the production of more environmentally benign manufactured products. Nanotechnology could play a key role in pollution prevention technologies. For example, nanotechnology-based home lighting could reduce energy consumption by an estimated 10% in the United States, saving $100 billion annually and reducing carbon emissions by 200 million tons per year (*12*).

Nanostructured catalysts, for example, can make chemical manufacturing more efficient by providing higher selectivity for desired reaction products (*13*). For example, aluminosilicate molecular sieves (zeolites) are porous crystalline solids with well-defined structures widely used for separations and catalysis. Nanometer-sized zeolites (10–100 nm) are being developed to selectively oxidize hydrocarbons, such as toluene to benzaldehyde (*14*). Using nanostructured zeolites makes this example more environmentally benign for two reasons. First, the oxidation reaction is initiated by visible light, which reduces energy consumption. Second, using visible light accesses low-energy reaction pathways that help eliminate wasteful secondary photoreactions and increase the yield of the desired product. In this study, selectivity for benzaldehyde using the nanostructures was 87%, compared to less than 35% for the same reaction with conventional zeolite material.

Assembling nanostructures from biopolymers or bio-inspired materials is an example of an environmentally benign approach to fabricating microelectronics. According to recent calculations, 1.7 kg of fossil fuel and chemicals and 32 kg of water are required to produce a single 2-gram, 32-megabyte microchip (*15*). Biomolecular nanolithography represents a "bottom-up" approach to replace current semiconductor chip production methods (*16*). Nanoscale metal particles on a biopolymer (poly-L-lysine) template or scaffold are stretched out on a surface into well-defined chip architectures, such as lines and grids, at room temperature. Biodegradable materials like poly-L-lysine are used for construction of these structures.

Nanotechnology applications could also help create benign substances that replace currently used toxic materials. For example, nontoxic, energy-efficient computer monitors are replacing those made of cathode ray tubes (CRT), which contain many toxic materials (*17*). Newer liquid crystalline displays are smaller, do not contain lead, and consume less power than CRT computer monitors (*17*). Using carbon nanotubes in computer displays may further diminish the environmental impacts by eliminating toxic heavy metals and drastically reducing material and energy use requirements, while providing enhanced performance for consumer needs. Field emission displays (FEDs) that use carbon nanotubes are the latest development in display technology and may be commercially available from several manufacturers within the next year (*18*). Although the toxicity of carbon nanotubes is largely unknown, the amount of carbon nanotubes used in FEDs is quite small (0.5 g/monitor) compared to the kilograms of lead in CRTs (*17*).

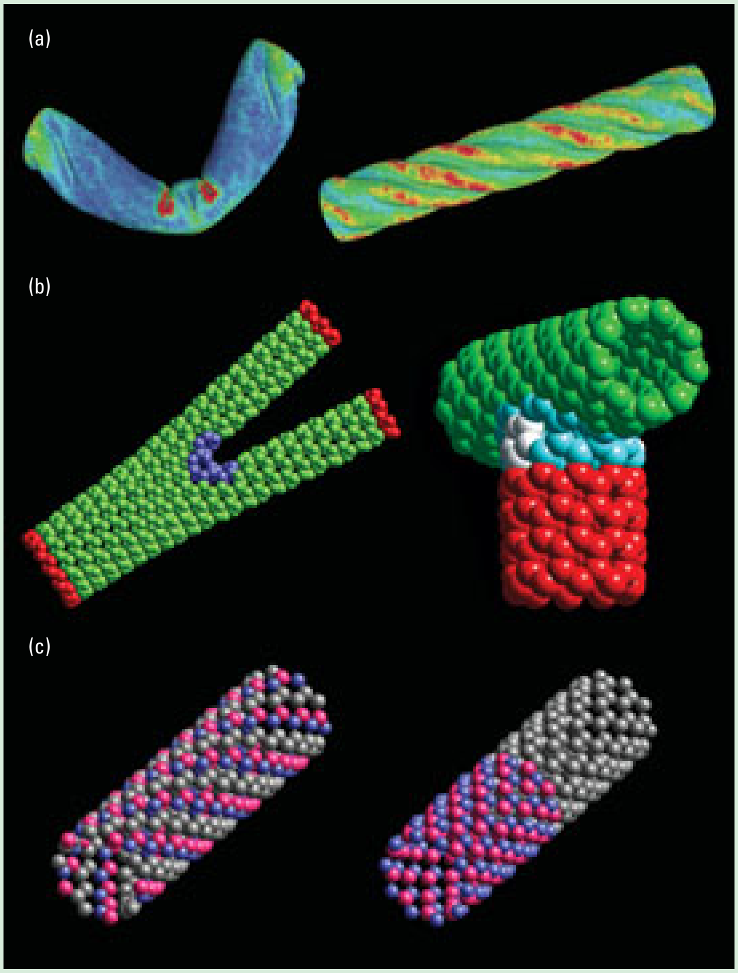
Treatment and remediation

The early impact of nanotechnology research has been mostly in remediation and end-of-pipe treatment technologies. Various reports have appeared on the use of a variety of nanoparticles for treatment and remediation of pollutants in the environment. For example, nanoparticles of various oxidants, reductants, and nutrients have been suggested as useful for promoting contaminant transformation and stimulating microbial growth, because their small size and larger surface area make them more reactive and more flexible in terms of deployment. Nanoparticles can also exhibit unique chemical reactivity not observed for larger particles because of their unusual crystal shapes and lattice order. For example, conventional methods (e.g., bioremediation and zero-valent iron) for in situ remediation of chlorinated organic solvents, such as trichlorethylene, tend to produce undesirable byprod-

FIGURE 2

Carbon nanotubes can be specialized

(a) Nanotubes are stronger than steel but very flexible and lightweight. These exceptional mechanical characteristics make them suitable as "tips" for scanning probe microscopes or enforcing fibers for nanotube–polymer composite materials. (b) Depending on the construction, nanotubes can behave like electrical conductors or semiconductors, which makes them extremely useful for nanoscale electronics applications. The electronic characteristics of carbon nanotubes are strongly coupled to the mechanical properties and provide great opportunity to develop novel electromechanical nanodevices (*11*). (c) Variations in nanotube composition allow for tuning electron transport properties over a wide range. Nanotubes can also be constructed from materials such as boron, carbon, and nitrogen (B_x-C_y-N_z) that are structurally similar to those consisting only of carbon. These heteroatomic nanotubes are expected to be insulators, unlike carbon nanotubes (*38*).



Source: Deepak Srivastava/NASA.

ucts, such as dichloroethylenes and vinyl chloride. Using nanoscale bimetallic particles essentially eliminates all the undesirable byproducts (*19, 20*).

Nanoparticles that are activated by light, such as the large band-gap semiconductors titanium dioxide (TiO_2) and zinc oxide (ZnO), continue to be studied for their ability to remove organic contaminants from various media. These particles are readily available, inexpensive, and have low toxicity (*21, 22*). Recently, ZnO nanoparticles were shown to act as both a sensor and photocatalyst for treatment of chlorinated phenols (*22*). Researchers are also quite interested in manipulating the surface of nanoparticles with organic or inorganic dyes to extend their photoresponse from UV to visible light, making them even more efficient as photocatalysts for the transformation of environmental contaminants because UV light represents only 5% of the solar spectrum (*23*).

Nanoparticles could provide enormous flexibility for in situ remediation as well. For example, nanoparticles are easily deployed in ex situ slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, they can be anchored onto a solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, or gaseous process streams (*24*). Direct subsurface injection of nanoscale iron particles, whether under gravity-feed or pressurized conditions, has already been shown to effectively degrade chlorinated organics, such as trichloroethylene, to environmentally benign compounds (*19*). The technology also holds great promise for immobilizing heavy metals and radionuclides.

Research has demonstrated that nanoscale, bimetallic particles, such as iron/palladium, iron/silver, or zinc/palladium, can serve as potent reductants and catalysts for a large variety of common environmental contaminants such as PCBs, organochlorine pesticides, and halogenated organic solvents (*4*). Nanoscale metallic particles reduced virtually all chlorinated hydrocarbons tested to benign hydrocarbons. Additionally, ample evidence indicates that iron-based nanoparticles can be used to reduce many other recalcitrant contaminants, including anions (perchlorate, nitrate, and dichromate), heavy metals (nickel and mercury), and radionuclides (uranium dioxide).

Nanotubes have been suggested as "a superior sorbent" for dioxins (*25*). The sorption energy of dioxin on carbon nanotubes is almost 3 times that of activated carbon. The Langmuir constant (B), a parameter characterizing the sorption affinity, is many orders of magnitude higher for nanotubes than for activated carbon. Thus, the prospect of using carbon nanotubes for air and water pollution control appears to be very favorable, but large-scale applications of nanotubes in the near future are limited by cost and availability.

Another example of environmental treatment and remediation-related application of nanomaterials includes using dendritic nanoscale chelating agents for polymer-supported ultrafiltration (PSUF) (*26*). Dendrimers are highly branched polymers with controlled composition and an architecture that consists of nanoscale features. These nanostructures can be designed to encapsulate metal ions and zero-valent metals, enabling them to dissolve in suitable media or bind to appropriate surfaces. This approach may present a means to produce a functional, cost-effective and, depending on the compound, environmentally sound material for PSUF.

Pollution sensing and detection

Rapid and precise sensors capable of detecting pollutants at the molecular level could greatly enhance our ability to protect human health and the environment. Manufacturing process control, compliance, ecosystem monitoring, and environmental decision making would be significantly improved if more sensitive and less costly techniques for contaminant detection were available. Of particular interest are remote, in situ, and continuous monitoring devices capable of yielding real-time information, and also those that can detect pollutants at very low concentration levels.

Recently, chemical sensors based on individual SWNTs have been demonstrated (*27*). Altered electrical resistance of semiconducting SWNTs through exposure to gaseous molecules, such as nitrogen dioxide or ammonia, forms the basis for these sensors. The nanotube sensors also exhibited fast responses at room temperature to the gases and a substantially higher sensitivity than existing solid-state sensors (*27*).

Boron-doped silicon nanowires (SiNWs) have been used to create highly sensitive, real-time electrically based sensors for biological and chemical species (*28*). The SiNWs could be modified in various ways to provide different functionalities. Specifically, the amine- and oxide-functionalized nanowires were used to detect changes in pH, and biotin-modified SiNWs were used to detect streptavidin in the picomolar concentration range. In addition, antigen-functionalized SiNWs showed reversible antibody binding and concentration-dependent detection in real time. Detection of the reversible binding of the metabolic indicator calcium was also demonstrated. These mechanisms could apply to de-

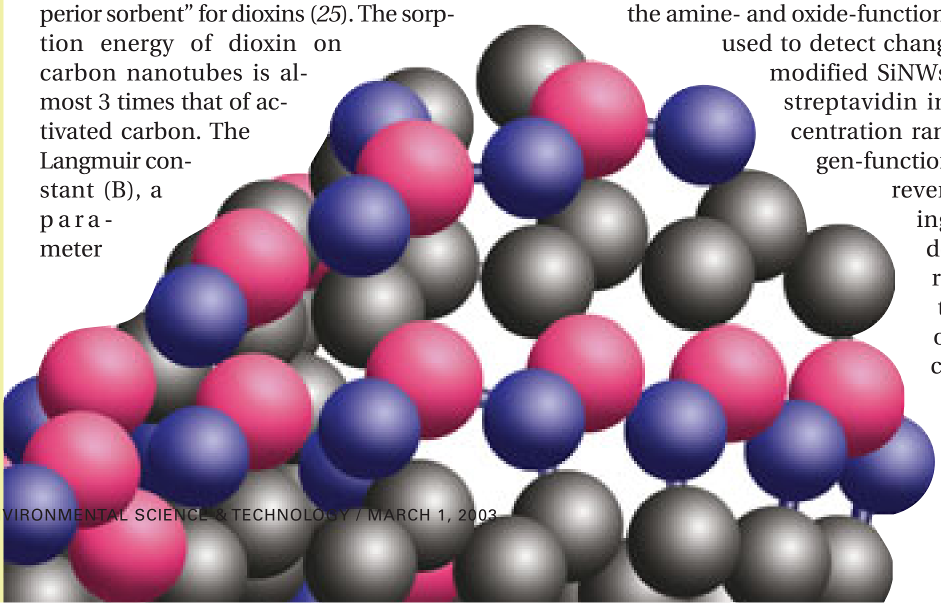
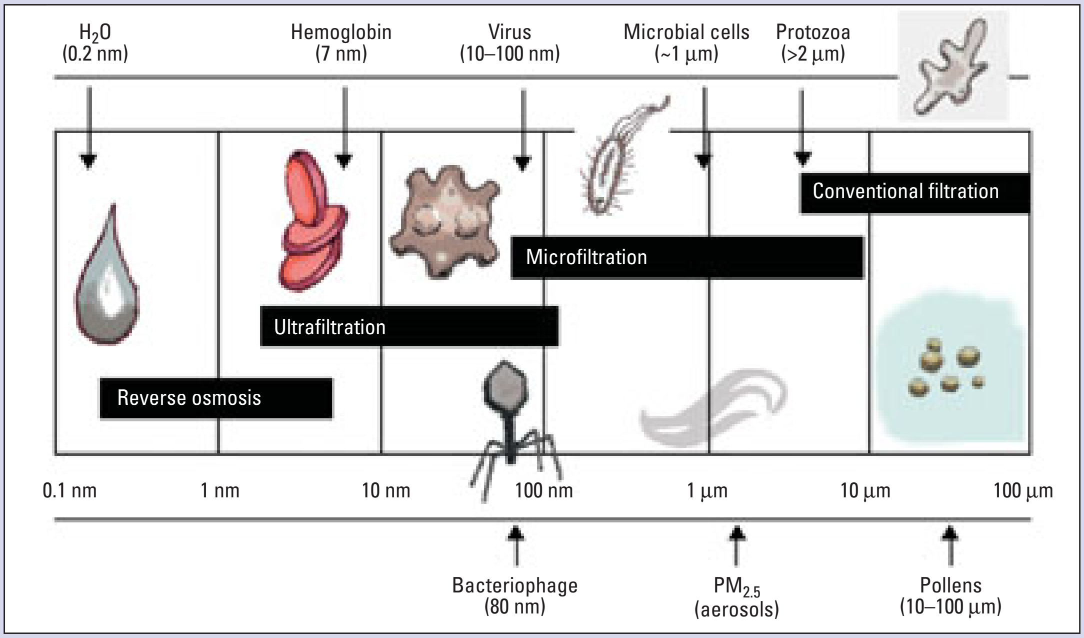


FIGURE 3

Nanotechnology could pollute many media

Because nanoscale materials are in the same size range as hemoglobin and viruses and are even smaller than common irritants, such as particulate matter (<2.5 mm) and pollen, nanomaterials could pose serious health risks. Conventional air and water treatment techniques need to be evaluated for their efficacy to treat nanoscale pollutants.



Source: Ken Raniere, Lehigh University.

tecting pathogens and chemical and biological agents in water, air, and food.

Human health and ecological diagnosis could also benefit from sensors. For instance, nanobarcodes—highly encodable and chemically diverse nanoparticles—may allow for high-level multiplexing of small sample volumes (29). Evaluating the exposure of complex systems in the environment to toxic pollutants often has such requirements for sample analysis. Nanobarcodes can greatly enhance our ability to identify the source and strength of contaminants, determine the route and mechanism of environmental fate and bioavailability, and assess the effectiveness of treatment and remediation techniques.

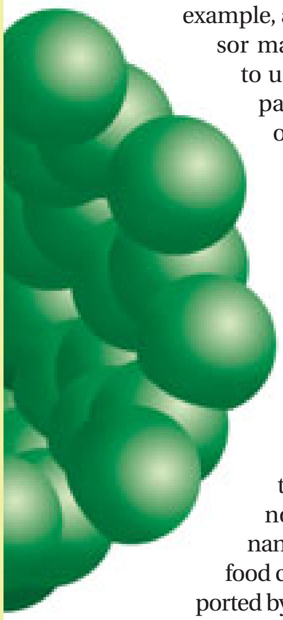
Nanotechnology pitfalls

Nanotechnology is a revolutionary scientific and engineering venture that will invariably impact the existing infrastructure of consumer goods, manufacturing methods, and materials usage. Not surprisingly, the potential benefits have dominated scientific and mass media coverage of nanotechnology. But any technology can be a double-edged sword. Environmental and safety concerns about nanotechnology only recently have been discussed in the mainstream media (*30*).

We are already witnessing some precursors of nanotechnology-associated pollution: toxic gallium arsenide used in microchips enters landfills in increasing quantities as millions of computers and cellular phones are disposed of every year. Potentially harmful effects of nanotechnology might arise as a result of the nature of nanomaterials themselves, the characteristics of the products made from them, or the aspects of the manufacturing process involved. The large surface area, crystalline structure, and reactivity of some nanoparticles, for instance, may facilitate transport of toxic materials in the environment, or the size and chemical composition of nanostructures may lead to biological harm because of the way they interact with cellular materials (*31*) (see Figure 3). For example, if nanostructures can self-assemble in the laboratory, can they replicate in the environment? If so, what will be the fate of those nanostructures and their environmental and health impacts? In addition, it is possible that nanotechnology could lead to societal changes that influence transportation, urban development, information management, and other activities of our society that directly or indirectly affect the quality of the environment. Because nanotechnology is unlikely to be the first entirely benign technology advance, there is an urgent need to evaluate the effectiveness of current water and air treatment techniques for the removal and control of potential nanoscale pollution.

The U.S. National Nanotechnology Initiative has already begun exploring the potential environmental and societal implications (*2, 32*). In the fall of 2001, Rice University opened the Center for Biological and Environmental Nanotechnology (CBEN), which is sponsored by the National Science Foundation. One of the priority areas of CBEN is to probe the behavior of nanomaterials in the environment (*33*). In 2002, the U.S. EPA announced its funding plan for external research that specifically addresses the potential beneficial applications and environmental implications of nanotechnology (*34*).

However, current federal funding for research and development in this area is inadequate. The proposed funding for studying nanoscale processes in the environment as part of the National Nanotechnology Initiative in the fiscal year 2003 budget request by the Bush administration, for example, is around $20 million out of a total investment of approximately $710 million—a mere 2.9% of the total initiative (*35*).



The responsibility to recognize and address many of the potentially adverse repercussions is in the hands of researchers and environmental professionals. As new nanoscale structures and technologies are explored and developed, are researchers considering all of the possible environmental outcomes? For example, are there more benign precursor materials or synthetic methods to use? Can we recover the nanoparticles or nanotubes for reuse or will they degrade into environmentally benign products? New nanoscale structures and other previously described environmental applications all support the prediction that nanoscale science and engineering will likely have a profound impact on science and technology (*36*). However, we must remain mindful of the potential ramifications of this technology, including the fact that nanoscale materials can enter the food chain and be absorbed or transported by water and food. Bioavailability and toxicity of newly created nanoscale materials are largely unknown. Nanotechnology is highly interdisciplinary and may present further challenges for environmental scientists and engineers. Few students are being trained in environmental nanotechnology, and few laboratories are currently equipped to conduct research in this area, detect nanopollution, and develop effective treatment and remediation technologies.

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