

## Nano particles Without Macroproblems

### Quick and dirty advice for keeping nanotech clean



PHOTO: David Clugston

BY BARBARA KARN, H. SCOTT MATTHEWS // SEPTEMBER 2007

Little by little, nanotechnology has crept up on us. From a mostly academic exercise 20 years ago, it has swiftly progressed to the point where the technology is just about everywhere: in fact, there may very well be engineered nanomaterials in the clothes you're wearing at this very moment. If they were sold to you as wrinkle-free or stainproof, the fibers were almost certainly treated with nanotech processes that stave off stains and creases.

More than 500 products on the market today incorporate some kind of nanotechnology. With nanotech, sunscreens protect better against ultraviolet rays, paint can block cellphone signals, glass windows remain streak-free, washing machines can kill harmful bacteria, food storage bags can keep their contents fresher, tennis and badminton rackets are stiffer and lighter, and dietary supplements can claim to help ward off colds, flu, and anthrax. Toothpaste, hockey sticks, engine oil, and even a breast cream have all gotten

the nano treatment lately [see photo, "[Fair Warning?](#)"]. By 2015, according to the U.S. National Science Foundation, such goods and services could add more than US \$1 trillion per year to the global economy.

The news, however, is not all good. There is a growing body of evidence that nanotechnological chemicals and related substances could pollute the air, soil, and water and damage human health. Preliminary studies from Arizona State University suggest that nanoparticles accumulate in the food chain and could cause problems later on. But if we act quickly, nanotechnology presents a distinct opportunity: we have a chance to deploy it properly—from both environmental and health perspectives.

This is an opportunity the semiconductor industry missed. Research into possible environmental and health implications of solvents and other chemicals, including arsine and trichloroethylene, wasn't done at the birth of the industry, before such toxic substances were widespread in the environment. If it had been, we might not be stuck with polluted sites left by manufacturing plants.

For nanotechnology, the chance to act responsibly won't be there forever. New nanomanufacturing processes are being brought online every day, and if we're not careful, we could be jolted years from now by unintended consequences and messes to clean up. What's at stake is potentially greater than the billions of dollars in health and environmental costs particular to nanotech: for the first time, industrial society has the opportunity to usher in a new paradigm for dealing with the blights that until now have been seen as inevitable in big new industries. Instead of cleaning up the waste stream at the end of a product's or process's life, regulators and manufacturers—usually aware of the health and environmental issues they are facing—can solve many problems by preventing pollution before it occurs. For example, simply not using a material that's a known environmental hazard or designing processes that run at lower temperatures can prevent pollution problems.

And so it is with nanotechnology: our experience with small particles suggests that some of the nanoparticles we are already manufacturing could cause problems. We need to look at nanotechnology broadly, anticipate its adverse effects, and prevent problems. Prudently avoiding a crisis is always better than trying to repair damage later on.

**When we talk** about nanotechnology, we mean that the materials involved exist as microscopic particles with at least one dimension that is between 1 and 100 nanometers. To put this in perspective, consider that the typical nanosize particle of titanium dioxide in sunscreen is 20 nm in diameter. The particle is a clump of about a million molecules. A grain of pollen is about 1000 times the size of this titanium dioxide nanoparticle; bacterial cells are around 100 times as large, and the width of a human hair is about 4000 times as great.

*Nanoparticles can be smaller by a factor of 1000 than the airpollutants we are just now beginning to understand and regulate*

A molecule of water, at 0.2 nm, is smaller than the nanoscale. But the deoxyribonucleic acid (DNA) molecule is 2 nm in diameter, and a particle of soot can be less than 100 nm. So, are DNA and soot examples of nanotechnology? No. By definition, nanotechnology does not include incidental by-products of human activities, such as soot, natural nanoparticles, such as those emitted by volcanoes, or unaltered nanoparticles from biological processes, such as proteins, cell fragments, viruses, or DNA. Nanotechnology refers to manufactured materials in the nanosize range, or to manufactured products containing these materials.

Some bulk substances behave differently from nanosize particles. For example, a coin made of gold is the color of gold, but nanoscale gold is red; bulk gold is inert, but nanogold can be a catalyst for chemical reactions. The fact that nanoparticles have intrinsic and unique properties is the driving force for nanoscale research and commerce.

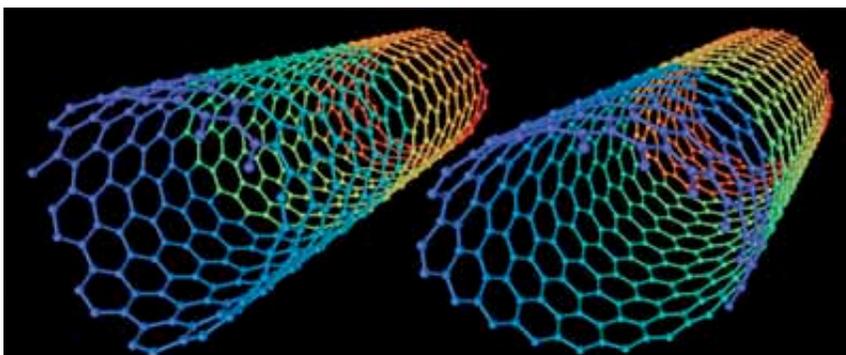


Photo: Michael Ströck

#### Tube Tangle

The electronics industry is at the forefront of this revolution. For example, all hard-disk storage today is based on a magnetic effect that occurs at the nanoscale level, where ones and zeros are changes in the magnetic poles of the nanoparticles. In fact, you'll find the vast majority of nanomaterials in electronics—

Nanotubes could enable batteries to be recharged thousands of times instead of just hundreds, but they may damage the environment or threaten human health.

in computer memories, batteries, displays, solar cells, capacitors, fuel cells, filters,

antistatic coatings, and flame retardants. In the future, nanowires may power medical implants or cellphones by generating tiny currents when subtle movements make them vibrate and displace ions. Carbon nanotubes, which conduct electricity much more efficiently than traditional wires, could form the basis of batteries that could be recharged thousands of times. Carbon nanotubes can also be used in flat screens that are more efficient than today's displays [see photo, "Tube Tangle"].

as nanotechnology spreads across industries, concerns about its environmental and health effects are spreading as well. The concerns stem from the small size of nanoparticles as well as from the atoms that compose them. Consider the class of airborne pollutants known as particulates. The U.S. Environmental Protection Agency (EPA) and many U.S. states currently regulate "coarse" particulate matter, less than 10 000 nm in diameter. In air pollution terms, nanoparticles are considered ultrafine particles, less than 0.1 micrometer or 100 nm. Airborne particles are released, for example, from fuel combustion or brake linings. Coarse particles and smaller ones can trigger asthma, bronchitis, and other respiratory diseases, make cold symptoms worse, and decrease lung function. Children and the elderly are especially at risk.

As a general rule, the health effects of smaller particles are more worrisome than effects from larger ones. Nanoparticles can be smaller by factors of 100 to 10 000 than the air pollutants we are just now beginning to regulate, and they could be even more harmful. Günter Oberdörster, a professor of environmental medicine in the school of medicine and dentistry at the University of Rochester, New York, studying ultrafine particles in 1992, found a nonlinear relationship between toxicity and particle size: as nanoparticles get smaller, their toxicity increases disproportionately.

Coarse particulate air pollution can damage lungs, but such particles are simply too big to get past the lungs and enter other parts of the body. Nanoparticles, on the other hand, can be more invasive. Nancy Monteiro-Riviere, a professor of investigative dermatology and toxicology at North Carolina State University, in Raleigh, discovered last year that some nanoparticles can penetrate the skin and could enter the bloodstream. Similarly, when swallowed, nanoparticles may be able to pass through the wall of the stomach or lining of the intestines.

In 2003, Chiu-wing Lam of NASA's Johnson Space Center, in Houston, instilled carbon nanotubes into the lungs of mice and reported that they triggered granulomas, or areas of inflammation. In a similar experiment, David Warheit at Dupont's Haskell Laboratory for Toxicity and Industrial Medicine, in Newark, Del., found such inflammation in rats' lungs in the same year. Perhaps most troubling of all, nanoparticles can make their way into the brain by passing from the nose through the blood-brain barrier, a membrane that protects the brain from chemicals in the blood while allowing oxygen, carbon dioxide, sugars, and certain amino acids to pass through unaltered.

In 2004, experiments by Eva Oberdörster, a lecturer in biological sciences at Southern Methodist University, in Dallas, found that the buckyball, a nanostructure made of carbon atoms, can penetrate the brains of bass via the gills. There, the nanoparticles trigger a reaction in brain enzymes called oxidative stress, a change in brain chemistry that indicates harm. Eva Oberdörster (a daughter of Günter) also discovered that buckyballs are toxic to daphnia, tiny freshwater fleas used to test toxicity in aquatic systems [see photo, "Aquatic Mine Canaries"]. The buckyballs did not clump together and sink harmlessly to the bottom of the test sites as researchers had expected.

In 2005 Daniel Watts, of the New Jersey Institute of Technology, in Newark, reported that nanoparticles of aluminum oxide slowed plant growth; the same nanomaterials are used in some scratch-resistant coatings.



Researchers are also concerned about persistence. Because of their small size and light weight, nanoparticles can stay aloft in the



Photo: U.S. Environmental Protection Agency

#### **Aquatic Mine Canaries**

In laboratory tests, nanomaterials are toxic to daphnia, tiny freshwater fleas. formulate intelligent regulations to protect the public's health and the environment.

upper atmosphere much longer than coarse particulate air pollutants, and current filter technologies for controlling particles have holes that are a thousand times too big to trap nanoparticles. Nanoparticles may also bioaccumulate. For example, bacteria can ingest them, so the particles could become part of our food chain. And we know that chemical pollutants, like some pesticides, can also accumulate in the chain. At the moment, though, we don't know what effect nanomaterials will have on the food supply.

These are just a few of the studies that are raising a yellow flag in the race to develop - nanotechnology. And they suggest the need for much more study, so that agencies can

**It won't be easy.** Because there is an infinite variety of nanomaterials, determining the specific risks of each one can be challenging. Researchers are studying them by grouping them not only by size—an obvious choice—but also by chemical composition, shape, structure, and their state of aggregation. Chemically, materials can consist of a single element like carbon or metals like silver and gold or be found as compounds like cadmium selenide or indium phosphide. Examples of structures and shapes include crystals, spheres, tubes, and wires. The aggregation state refers to how the material clumps—or doesn't clump.

Some of these classification groups may prove to be more relevant than others to researchers looking for environmental or health effects. For example, the intrinsic toxicity of cadmium, the reactivity of nanogold, or the shape of nanowires could each make materials riskier to deal with.

Scientists have just begun trying to connect specific nanomaterials with the harm they might cause. Policy-makers are using the information to determine how best to protect the public from risks. Because nanoparticles generally do not exist outside of the laboratory or factory as free particles, regulators should be most concerned about the beginning and the end of a product's life. During manufacturing, emissions of nanoparticles can cause environmental or health problems, and at the end of the product's life, the disposal or deterioration of the item can also release particles.

**The electronics industry,** a key user of nanotechnology, can be a leader in investigating and preventing damage to the environment and health. It already has tools—used in designing products to be environmentally friendly—that look at all phases of a product's life cycle from manufacture to use and disposal. As it has in the past, the industry can encourage designers to make choices based on careful consideration of health and the environment rather than on cost or performance alone. For example, many consumer electronics companies eliminated lead-based solder from their products; the European Union banned it in products in 2006. And semiconductor companies have replaced toxic solvents in many processes with plain water.

One bright sign is that industry groups and government agencies are beginning to include concerns about nanotechnology in their long-term research planning. An encouraging new initiative is Green Nanotechnology, pioneered by the EPA and the Woodrow Wilson International Center for Scholars, in Washington, D.C. The two organizations are developing a framework and recommended practices that would help prevent manufacturers from releasing substances currently recognized as pollutants into the atmosphere, as well as prevent the manufacture of

products containing nanomaterials that would knowingly harm the environment. The development of guidelines for Green Nanotechnology would let consumers or governments reward companies that are performing well, on the model of Energy Star, a joint program of the EPA and the Department of Energy. It sets guidelines for energy efficiency of consumer products and allows products that meet those guidelines to display Energy Star labels.

Recently, there was a small but significant victory: manufacturers of gold nanoparticles used for paint and, potentially, environmental cleanup and cancer treatment, developed a manufacturing method that eliminated the use of a toxic organic chemical and replaced it with water, reducing energy use at the same time.

**Green Nano also means** using nanotechnology itself to clean up production processes. The semiconductor industry can replace dangerous chemicals such as the perfluorooctane sulfonate polymers used in photo resists, antireflective coatings, and reagents with less toxic nano alternatives. Nanomembranes can filter out waste and pollutants in chemical processes. Nano-enabled sensors can improve process control and monitor emissions. Nanoproducts that improve energy efficiency, such as solar cells or better conducting materials, indirectly improve the environment through lower power-plant emissions.

The United States and other governments can help. In 1996, four U.S. agencies formed the Nanoscale Science, Engineering, and Technology (NSET) subcommittee of the National Science and Technology Council's Committee on Technology to coordinate federal funding of nanotechnology research and development. Today, 26 agencies work together on the NSET. Although there is no dedicated funding for nanotechnology in the federal budget, the subcommittee compiles a budget by annually aggregating the research in nanotechnology scattered across the R&D budgets of all its member agencies.

In 2005, nanotechnology research's budget totaled approximately \$1.2 billion. But only about 3 percent of that went to research in environment, health, and safety issues, in spite of the fact that the group has declared that one of its main goals is to support responsible development of nanotechnology.

The EPA leads a partnership between the National Science Foundation, the Centers for Disease Control and Prevention, and the National Institute of Environmental Health Sciences to fund environmental health and safety research. It is the largest such research program, totaling some \$21 million in more than 50 projects from 2003 through 2006. Research programs funded by this partnership are looking at the movement of different types of nanomaterials through the environment, the physical and chemical characteristics of nanomaterials that determine toxicity, and how nanomaterials enter the body.

The National Institute for Occupational Safety and Health laboratories are studying nanotech health issues related to the workplace, and the National Toxicology Program is testing individual nanomaterials for their effects.

Current programs to assess the risks of nanotechnologies are not enough, however, given the rapid advance of the technologies themselves.

**Nanotechnology is already part of our lives.** It will continue to roll out across industries and converge with advances in other rapidly developing fields including biotechnology, information technology, and cognitive science. It will enable amazing innovations.

And we don't have to sacrifice our lakes, rivers, air, and health to enjoy them. At today's still-early stage, we can develop nanotechnology correctly in the first place. It's an opportunity we should not miss.

#### **About the Author**

BARBARA KARN is an environmental scientist in the U.S. Environmental Protection Agency's Office of Research and Development. She recently returned from a stint at the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars at the Smithsonian Institution, in Washington, D.C. The opinions expressed here are hers and should in no way be construed as EPA policy.

H. SCOTT MATTHEWS is an associate professor in the Departments of Civil and Environmental Engineering and Engineering and Public Policy and is research director of the Green Design Institute at Carnegie Mellon University, in Pittsburgh. He recently served as program and conference chair of the IEEE International Symposium on Electronics and the Environment (<http://www.iseesummit.org>).

**To Probe Further**

More extensive information about what the U.S. government is doing in the field of nanotechnology is available at <http://www.nano.gov>.

The Wilson Center's project on emerging nanotech provides webcasts, reports, and databases at <http://www.nanotechproject.org>.

EPA publications on nanotechnology, including the EPA's white paper on nanotechnology, are available at <http://www.epa.gov/ncer/nano>.

For the EPA Toxic Substances Control Act regulatory information, see <http://www.epa.gov/oppt/nano>. For the joint semiconductor/chemical industry road map for nanotechnology environmental and health issues see <http://www.chemicalvision2020.org/techroadmaps.html>.