Scientists in engineering, chemistry, and public health have begun weighing potentials and dangers on the nanoscale

Small Wonder, BIG Issues

by Lin Larson

THE NEXT BIG THING may be small. Incredibly small.

In scientific and industrial circles, nanotechnology is the buzzword of the day. The U.S. government's National Nanotechnology Initiative funnels more than $1 billion a year into studying matter no larger than one ten-millionth of a meter. Companies like Hewlett-Packard tout their nanotechnology research, while products enhanced by such work—including sunscreen, tennis balls, and khaki trousers—already have hit the market.

But along with the hype came a few red flags. Some scientists are concerned that the environmental and health effects of nanoscale materials remain largely unexplored. Among the scientists are investigators at The University of Iowa who are striving to learn more about how these very small things could have very large effects on people and the world they live in, for good or for ill.

Scientists and other researchers interested in exploring this small, new world on the Iowa campus come from two camps, according to Michelle Scherer, associate professor of civil and environmental engineering in the College of Engineering.

"Most of the work that's been done with nanoparticles has focused on synthetic materials, on making products smaller, better, or faster," says Scherer, who was awarded a Nanoscale Interdisciplinary Research Team grant from the National Science Foundation in fall 2005. "That's nanotechnology. Now we are moving into nanoscience, a very different arena."

Both nanotechnology and nanoscience involve matter that measures 100 nanometers or smaller. A nanometer is one-billionth of a meter. A human hair is about 80,000 nanometers wide.

Nanotechnology refers to the manipulation of matter down to the molecular or atomic scale. The most radical visions for nanotechnology, like the notion of tiny robots that could build anything from the atoms up, are still the province of science fiction. Today's actual nanotechnology is much more prosaic, like fabrics coated with microscopic whiskers that resist stains and wrinkles.

Think Small

A nanometer is one-billionth of a meter, about 10 times the diameter of a hydrogen atom. This is about 80,000 times smaller than the width of a human hair and 100 times smaller than the patterns etched into the silicon wafers of contemporary microelectronics.

Nanoscience is less concerned with technological applications than with how nanoscale matter behaves. Nanoparticles enter the environment in many ways. One way is through mechanical combustion processes in things like cars and incinerators that produce soot and exhaust made up of nanoparticles. Regardless of their origin, they exhibit unique and often surprising properties.

"We've known for decades that there are very small minerals in the environment," says Scherer, who collaborates on a study of iron oxides with Vicki Grassian, professor of chemistry in the College of Liberal Arts and Sciences, and colleagues at Coe College in Cedar Rapids, Iowa, the University of California at Berkeley, and the University of Wisconsin. "What we realize now is that their size can cause dramatically different behavior than what you would expect from larger, comparable particles. Iron minerals play a big part in many environmental processes—carbon cycling, phosphorous cycling, microbial patterns. With the discoveries coming out of nanotechnology, we began wondering whether iron nanoparticles may be more important to these processes than the larger particles we've been studying for decades."

By virtue of their smallness, nanoparticles interact differently with other substances.

"Nanoparticles have a high surface-to-volume ratio," chemistry professor Grassian says. "A lot of the atoms in these small particles are located on their surfaces."

Surfaces—along with edges and defects—are prime sites for chemical reactions. Since a cluster of nanoparticles has more surfaces, edges, and defects than one larger particle

University of Iowa researchers use state-of-the-art technologies in the University's Central Microscopy Research Facility to better understand the environmental impact of nanoparticles. David Cwiertny (above), a postdoctoral research scholar, uses a transmission electron microscope in nano-level investigations with Michelle Scherer, associate professor in the College of Engineering, and Vicki Grassian, professor of chemistry. Courtney Usher, a postdoctoral research fellow, took the images of calcium formate crystallites at left and on page 5 with a scanning electron microscope.

of the same chemical composition, the nanoparticles are more reactive.

Nanomaterials also may circulate or persist in the environment in unexpected ways. Research on carbon nanoparticles called fullerenes—among the first discovered nanomaterials and a potential resource for enhanced computing, communications, and electronics technology—found that they form water-soluble clumps that can kill bacteria and perhaps destabilize ecosystems. Additional reports claim that fullerenes damage brain cells in fish.

Scherer and her colleagues aren't looking at manufactured "nanowaste," but at naturally occurring particles. Considering how iron minerals help break down environmental pollutants, these nanoparticles might prove beneficial.

"We'd like to know whether there is an additional pathway to remove contaminants from water," Scherer says. "I don't want to make these materials and put them out there, but I want to see how they are made and what they do in the environment. That's the distinction between science and technology."

But others, like Sarah Larsen, associate professor of chemistry, are interested in developing novel nanoscale materials for use in environmental remediation. Larsen works with zeolites, porous crystals that can absorb pollutants or speed chemical reactions. She and her research team have created very small zeolites that combine the crystals' porous structure with the reactive surfaces characteristic of nanoparticles. She thinks these nanoscale zeolites may prove better at cleaning up toxic spills or chemical warfare agents.

"We're particularly interested in the absorption of volatile organic compounds from polluted air or water," Larsen says of her work, much of it funded by the Environmental Protection Agency.

Collaborating with Grassian, Larsen also has found that the smaller zeolites are more effective at converting nitrogen oxides—toxic byproducts of combustion—into harmless nitrogen and oxygen.

"I think we're just scratching the surface in applications for these materials," Larsen says.

Nanomaterials might be useful in mopping up environmental messes, but safety questions have roused concern among environmentalists. The Environmental Defense organization has proposed that the National Nanotechnology Initiative fund at least $100 million annually—about a tenth of its budget—for risk research. Other groups have called for a moratorium on nanomaterial production pending further research.

Grassian has teamed with colleagues in the College of Public Health to survey the health effects of manufactured nanomaterials. Funded by the Environmental Protection Agency, their work explores how nanotechnology affects occupational, environmental, and consumer health.

"We're at a point where the technology for creating nanomaterials and the applications for using them are far outpacing our knowledge about their potential toxicity," says Peter Thorne, professor of occupational and environmental health in the College of Public Health and director of the Environmental Health Sciences Research Center. "We know they are bioactive in a way that is different than different-size materials of the same composition."

Thorne, Grassian, and Patrick O'Shaughnessy, associate professor of occupational and environmental health, have targeted materials currently most common in industry, among them titanium dioxide, silicon oxide and iron oxide nanoparticles, and carbon nanotubes.

"Titanium dioxide is everywhere, in toothpaste, paint, and other products. It's now being produced at five nanometers in size," Grassian says. "The question is, do these relatively nontoxic materials become toxic on the nanoscale? If they do, we should be worried."

The team's current work includes inhalation toxicology studies that compare nanomaterials of different sizes and with different coatings.

"So far, we're finding that some are relatively inert and others more potent, to the point of being mildly toxic," Thorne says.

O'Shaughnessy focuses on strategies that manufacturers might use to protect workers, including instruments that measure air quality and filters that catch extremely small particles. Many nanotechnology firms are small startups unsure what safety measures they should take, and regulatory confusion compounds the problem, O'Shaughnessy says.

"Because these materials are of the same chemical composition as older materials, they might be regulated like their larger counterparts," Thorne says. "That might be inappropriate, since they may prove much more toxic on the nanoscale."

The small size and reactive nature of nanoparticles may mean that they can bind with cellular receptors or access the insides of cells in ways that other materials can't.

"Are they so small that they can pass through the blood-brain barrier and have other systemic effects beyond the lungs? The jury is still out," O'Shaughnessy says.

He and his colleagues point out that medical scientists might harness these properties and turn nontoxic nanoparticles into delivery vehicles for medications.

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To some researchers, the availability of funding for nanotechnology safety research reflects lessons learned from experience with other chemical creations, like chlorofluorocarbons (CFCs). When discovered in the 1920s, CFCs were considered safe and effective refrigerants. Today they are implicated in destruction of the Earth's ozone layer.

"This is the first time as a scientist that I've heard people talking this much about policy," O'Shaughnessy says. "I think government bodies are being proactive—I've never seen an issue where they jumped on it like this."

Industry has joined the safety discussion, he notes, a move that recalls how concerns over genetically modified organisms led to strict regulations in some countries.

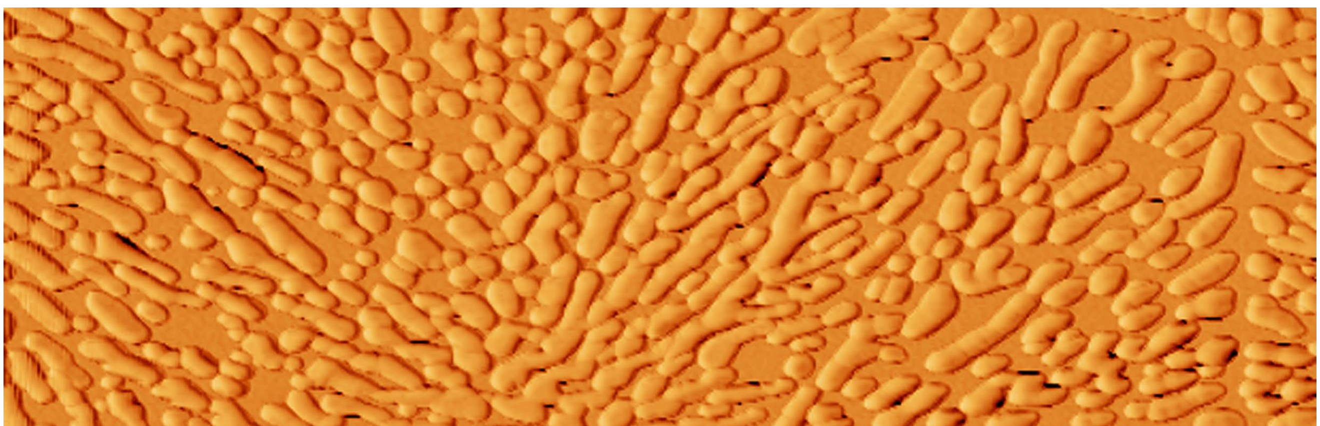
Scherer is uncertain whether environmental and health research can keep pace with the growth of nanotechnology—and whether research findings will be heeded.

"Unfortunately, the United States does not operate on the precautionary principle," Scherer says. "But there is a lot of work going on in this area, and the debate about the safety of these particles is pretty intense, so we can only hope that any red flags will be given serious consideration."

Next year's proposed federal budget includes $1.2 billion targeted for the National Nanotechnology Initiative. Grassian says she and other UI researchers are discussing ways to develop a possible initiative at The University of Iowa devoted to the study of nanoscience and nanomaterials, with special attention to implications for the environment and human health. The UI initiative would support research in disciplines across campus, according to Grassian, who also holds appointments in chemical and biochemical engineering in the College of Engineering and in environmental and occupational health in the College of Public Health.

Grassian hopes that the nanotechnology safety debates culminate in a new paradigm, one that considers products from creation through disposal.

"What harm could I be doing when making it? Where is it going to be used? What happens at the end of its life cycle?" Grassian says. "I think we're mapping out a new way of thinking for the chemical and manufacturing industries."



Origins of Nanotechnology

The term "nanotechnology" was popularized by the 1986 book *Engines of Creation* by Eric Drexler. In the book, Drexler picked up on ideas dating back to a talk given in 1959 by physicist Richard P. Feynman at the annual meeting of the American Physical Society at the California Institute of Technology. Feynman's talk, "There's Plenty of Room at the Bottom," discussed the possibilities of manipulating matter down to the level of individual atoms and what this might mean for improvements in technology.

"The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big," Feynman said.

Drexler expanded on this concept to envision molecular machines able to manufacture just about anything that could be designed. In recent years, the term has found application in a wide array of endeavors that involve matter on the nanometer scale, whether manufactured, manipulated, or otherwise altered by human intervention.

On the University of Iowa campus, nanoscience research is taking place in dozens of departments and programs, including biology, chemistry, dentistry, engineering, mathematics, pharmacy, physics, and even English. The research ranges from the practical to the sublime, covering environmental science, computational chemistry and molecular modeling, semiconductor devices, pharmaceutics—and science fiction, whose writers may help scientists imagine possibilities, both the potentials and the risks, according to Brooks Landon, professor of English.

"It's hard picturing one-billionth of anything," says Landon, who has spent most of his career in the scholarly study of science fiction literature and movies. "If you read the scientific reports, they read like science fiction, because so much of it is speculative and everyone is having to imagine what is going on at the nanoscale level."