



Update

Nanotechnology: Cause for Concern?

Kristine Chin

Nanotechnology — it's a small science with big stakes. Although it holds a great deal of promise, it also is the reason for a great deal of concern. Some of the same unique properties that make nanoscale materials useful may also pose hazards to humans and the environment. For example, nanoscale materials that are used for targeted drug delivery and other disease treatments, could result in unintended impacts in other uses or applications.

These tiny high-tech materials are already showing up in a multitude of consumer products, such as electronics, cosmetics and paints. The Woodrow Wilson International Center for Scholars' Project on Emerging Nanotechnologies (PEN; www.nanotechproject.org/44) is currently compiling a list of nanotechnology-based consumer products available in the market. The latest figures indicate an 124% jump in products introduced to the market between March 2006 and May 2006 — from 212 to 475.

While the rapid introduction of nanotechnology-based products is unlikely to slow down, not much is known about the potential negative impacts of nanoscale materials. According to the U.S. Environmental Protection Agency (EPA; www.epa.gov), at this early stage of development, there are few detailed studies on the effects of nanoscale materials in the body or the environment.

Voluntary or mandatory?

The EPA is grappling with the monumental task of regulating nanoparticles.* In October 2006, it invited stakeholders to participate in the development of a Nanoscale Materials

*This is the subject of Topical Conference 6: Environmental and Regulatory Policy Issues in Nanotechnology at the AIChE Annual Meeting (Salt Lake City, UT; Nov. 4-9). For more information turn to the preliminary program in this issue or visit www.aiche.org/annual.

Stewardship Program (NMSP) under the Toxic Substances Control Act (TSCA). This resulted in an NMSP concept paper released in July, in which the EPA outlined a two-part NMSP consisting of a basic program and an in-depth program.

The basic program would request the reporting of "all known or reasonably ascertainable information regarding specific nanoscale materials." The in-depth program would require additional data be developed and submitted to EPA over a longer timeframe. It would involve a subset of information reported under the basic program in a greater amount of detail. This would allow the EPA to focus on key data

that would have the greatest environmental and health impact. The EPA concept paper also noted that data claimed as confidential business information (CBI) would be protected "in the same manner as CBI submitted under TSCA in accordance with procedures in 40 CFR parts 2 and 720."

The proposed NMSP received mixed reviews at a public meeting held on August 2 in Arlington, VA. While the American Chemistry Council Nanotechnology Panel (www.americanchemistry.com/nanotechnology) and NanoBusiness Alliance (www.nanobusiness.org) lauded the EPA on the design of the NMSP, the Consumers Union

SIX STEPS TO REDUCING RISK

The Nano Risk Framework was born out of a partnership between DuPont and Environmental Defense that started in 2005. Below is an adaptation of the six-step process from the Nano Risk Framework executive summary (www.nanoriskframework.com)

Step 1. Describe Material and Application. This first step is to develop a general description of the nanomaterial and its intended uses, based on information in the possession of the developer or in the literature. These general descriptions set up the more thorough reviews, in Step 2, of the material's properties, hazards, and exposures. The user also identifies analogous materials and applications that may help fill data gaps in this and other steps.

Step 2. Profile Lifecycle(s). The second step defines a process to develop three sets of profiles of the nanomaterial's properties, inherent hazards, and associated exposures throughout the material's lifecycle. The properties profile identifies and characterizes a nanomaterial's physical and chemical properties. The hazards profile identifies and characterizes the nanomaterial's potential safety, health, and environmental hazards. And the exposure profile identifies and characterizes the opportunities for human or environmental exposure to the nanomaterial — including exposure both through intended use and by accidental release. The user takes into account the nanomaterial's full lifecycle from material sourcing, through production and use, to end-of-life disposal or recycling.

Step 3. Evaluate Risks. In this step, all the information generated in the profiles is reviewed in order to identify and characterize the nature, magnitude, and probability of risks presented by this particular nanomaterial and its anticipated application. In so doing, the user considers gaps in the lifecycle profiles, prioritizes those gaps, and determines how to address them — either by generating data or by using, in place of such data, "reasonable worst case" assumptions or values.

Step 4. Assess Risk Management. Here the user evaluates the available options for managing the risks identified in Step 3 and recommends a course of action. Options include engineering controls, protective equipment, risk communication, and product or process modifications.

Step 5. Decide, Document, and Act. In this step, appropriate to the product's stage of development, the user consults with the appropriate review team and decides whether or in what capacity to continue development and production. A worksheet is provided in the appendix for documenting information, assumptions, and decisions.

Step 6. Review and Adapt. Through regularly scheduled reviews as well as triggered reviews, the user updates and re-executes the risk evaluation, ensures that risk-management systems are working as expected, and adapts those systems in the face of new information or new conditions (such as new or altered exposure patterns).

(www.consumersunion.org) and Environmental Defense (www.environmentaldefense.org) were much more critical of its shortcomings. “Two years in the making, EPA’s tepid proposals have actually set back the clock,” said Richard Denison, senior scientist for Environmental Defense at the meeting. “As a government response to addressing the possible downsides of the nanotechnology revolution, it’s simply ‘too little, too late.’”

The EPA is “calling for an open-ended program with no plan B should its voluntary plan A fall short,” criticized Denison. He cited the U.K.’s voluntary plan as an example not to follow. “The U.K. has operated a similar program [to the NMSP] for over nine months and has attracted only seven companies to volunteer. The design and timing of the EPA program is likely to yield similarly disappointing participation, resulting in a very selective and skewed picture of the state of nanotechnology.”

J. Clarence Davies, a senior advisor to the Project on Emerging Nanotechnologies and former assistant administrator for policy, planning and evaluation at the EPA, noted that the NMSP is a useful initiative, but tempered it with the warning — as long as “it does not delay progress in putting in place an adequate oversight system.” Davies strongly suggested that the EPA expeditiously move forward with the NMSP, and identify concrete deadlines for implementing the program, receiving submissions, and ultimately ending the voluntary program.

Taking a proactive stance

While the drama over how to regulate nanoscale materials unfolds, some companies have chosen to be proactive in addressing nanotechnology concerns. In June, DuPont (www.dupont.com) and Environmental Defense released the Nano Risk Framework (box).

“This Framework outlines a disciplined process for the responsible devel-

opment of nanomaterials,” said DuPont vice president and chief sustainability officer Linda Fisher. “At DuPont, we have adopted this approach as a part of our mandatory product stewardship process, and we encourage others to do the same. While we do not see this Framework as a substitute for regulation, we hope that it assists governments in drafting appropriate regulations.”

To evaluate the effectiveness and practicality of the Framework, DuPont conducted demonstration projects on three different classes of nanoscale materials. “Each project represents a different position for DuPont in the value chain and is at a different stage of development,” said DuPont’s global regulatory affairs director Terry Medley. “The projects required different resources, produced varying outcomes, and each demonstrated different aspects of the Framework,” Medley continued. The three projects were:

- A new titanium dioxide-based product, called DuPont Light Stabilizer 210, designed as sun protection for plastics. Although not all of the particles in this product fit the specific definition of nanomaterials, it proved to be a good test of the Framework’s methodology. The Framework helped DuPont develop an exposure and hazard profile for this material prior to commercialization.

- Carbon nanotubes incorporated into polymer nanocomposites to improve mechanical and electrical properties of engineering thermoplastics. The company used the Framework to refine internal management procedures and to identify questions to be answered for such applications before they move from R&D toward commercialization.

- Nano zero-valent iron being evaluated for use in groundwater remediation. The Framework identified questions about the physical safety, fate and transport of the material for this environmental application. DuPont chose not to pursue use of this material until these questions could be addressed.

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Update

R&D UPDATE

Adding Peanuts to the Pump

Move over, soybeans and corn: Peanuts may be elbowing their way into the biodiesel fuel market. Agricultural Research Service (ARS; www.ars.usda.gov) scientists are searching for economically feasible peanut varieties for that very purpose.

Agronomist Wilson Faircloth at the ARS National Peanut Research Laboratory in Dawson, GA, and Daniel Geller, a collaborative engineer at the Univ. of Georgia (Athens; www.uga.edu), are testing a peanut called Georganic. It's not up to commercial edible standards for peanuts, but is high in oil and has low production costs.

Georganic — or similar varieties — will likely be the future of peanut biodiesel because it can be planted and grown with just one herbicide applica-

tion for weed control, compared to the three to four applications typically sprayed during a growing season for edible peanuts. Also, these fuel peanuts are grown without fungicides, which are the greatest input cost in traditional peanut production. The research team is also studying conservation tillage and selection of varieties with high tolerance to multiple diseases.

Currently, there are 24 peanut varieties being scrutinized in this biodiesel screening project. Promising varieties also include DP-1 and Georgia-04S, a new high-oleic-acid, Spanish-type peanut. It has been found that high-oleic-acid peanuts, a quality desired for extended shelf life of food products, also make the best biodiesel fuel.

Today, soybean oil is the primary oil used in the U.S. for biodiesel fuel production. Soybeans produce approxi-

mately 50 gal of fuel per acre, while traditionally grown peanuts can produce approximately 120–130 gal of biodiesel fuel per acre.

Researchers Think Pink to Produce Green Solar Energy

When it comes to producing earth-friendly solar energy, pink may be the new green, according to Ohio State University (Columbus; www.osu.edu) researchers. Scientists here have developed new dye-sensitized solar cells (DSSCs) that get their pink color from a mixture of red dye and white metal oxide powder present in materials that capture light. Currently, the best of these new pink materials convert light to electricity with only half the efficiency of commercially-available silicon-based solar cells — “but they do so at only one quarter of the cost,” said

Industry and Academia Continue to Collaborate

Collaboration efforts between academia and industry continue on a healthy pace. Recently, BASF Catalysis Research (Iselin, NJ; www.basf.com) made a three-year research commitment of \$600,000 to the Earth and Environmental Engineering Dept. of Columbia Univ.'s Fu Foundation School of Engineering and Applied Science (New York; www.eee.columbia.edu) for graduate and post-doctoral studies into environmentally benign technologies utilizing heterogeneous catalysts.

Designed to support the research of four Columbia students, “the program is directed toward ‘green/sustainable’ technology and pollution abatement — issues that are of great importance to the world, to Columbia and to BASF,” explains Robert Farrauto, a research fellow in Hydrogen and Fuel Cells at BASF and an adjunct professor in the Earth and Environmental Engineering Dept. at Columbia. Potential research topics include catalytic reforming of biofuels to hydrogen, conversion of greenhouse gases to useful chemicals and fuels, and catalytic issues related to pollution abatement from diesel combustion engines.

Participants in the program will have the opportunity to take basic research concepts into a production environment, and publish their findings in professional journals. Student researchers will interact with scientists at BASF Catalysis research centers in both



Union Carbide Corp. (UCC) and WVU signed an agreement on August 20 that will establish a research campus on 58 acres of donated property located at UCC's Technology Park in South Charleston. Photo courtesy of The Dow Chemical Co.

Iselin, NJ and Ludwigshafen, Germany. Farrauto, along with Columbia Professor Marco Castaldi of the Earth and Engineering Dept., will jointly supervise the research efforts. The program will begin during this fall semester.

While BASF has made a monetary donation, Union Carbide (UCC), a subsidiary of The Dow Chemical Co. (Midland, MI; www.dow.com), has donated property and facilities to West Virginia Univ. (Morgantown; WVU;

www.wvu.edu) for the establishment of a research campus. The donation consists of 58 acres located at UCC's Technology Park in South Charleston, along with several research and development laboratories, including a 125,000 ft² building currently in use as a multi-tenant research and development incubator. “This donation on the part of Dow demonstrates our commitment to the importance of academic research and the ability for collaboration,” said Allan Fowler, vice president of West Virginia Operations of Dow.

The WVU Charleston Research Campus, as it will be known, will serve as a center of research and economic development focusing on energy and chemical technology. Initially, WVU will relocate its Charleston extension and extended learning offices to the property. In the future, it expects to develop research and academic initiatives benefiting residents of the Charleston area. The donation transaction is expected to be completed by early fall.



Yiying Wu, assistant professor of chemistry at Ohio State. And Wu is hoping for even better, adding, "We believe that DSSC efficiency can reach levels comparable to any solar cell."

Pink is a typical color for DSSCs. Most use dyes containing ruthenium, which has a red color; the metal oxide powder that turns the mix pink is most often titanium oxide or zinc oxide, which are both whitish in color. But Wu's materials are novel in that he's using more complex metals and exploring different particle shapes to boost the amount of electricity produced. In a recent issue of the *Journal of the American Chemical Society (JACS)*, he and his team report that they have made a new DSSC material using zinc stannate. Wu and his colleagues chose zinc stannate because it belongs to a class of more complex oxides with tunable properties. "This opens up new possibilities for how scientists may tailor the properties of DSSCs in the future," he said.

Scientists have been researching DSSCs since the 1990s. In DSSCs, dye molecules coat tiny metal oxide particles that are packed together into a thin film. The dye molecules capture light energy and release electrons, and the particles act like electrical wires to carry the electrons away to an electrical circuit. But since electrons can get lost when traveling between particles, Wu is working on designs that incorporate tiny nano-wires that carry electrons directly to a circuit.

They are also exploring the use of nano-trees — nano-wires shaped like the branches of a tree. "We asked ourselves, what structure is best for gathering light and also transporting materials — a tree! The leaves provide a high surface area for capturing light, and the branches transport the nutrients to the roots," Wu said. "In our DSSC design, the dye-coated particles would provide the surface area, and the nano-trees would branch out in between them, to transport the electrons."

PROCESS TECHNOLOGY

Paraffin Wax Removal Enhances Oil Recovery

Declining oil discoveries compounded with increasing oil demand will require the petroleum industry to focus on improving the efficiency of oil production. One problem area is the build up of wax compounds that precipitate out of the crude oil and cause blockages in well-bores, production tubing and surface flow equipment.

The wax deposits occur when the temperature and pressure in the tubing move below the cloud point of the oil, causing paraffin wax crystals to form in the oil and collect within the tubing. They also cause the viscosity to increase, further choking off flow lines. The end result — a significant drop in production rates of oil from the affected wells. Experts estimate that the total annual cost of paraffin wax build up in well-bores can be around \$18 billion.

Typical solutions to this problem involve applying an array of chemical solvents to attack deposits and prevent build-up. However, these solutions alone can create environmental liabilities and issues with disposal. To this end, Avalon Oil &

Gas, Inc. (Minneapolis, MN; www.avalonoilinc.com), has launched an environmentally safe paraffin-wax mitigation technology, dubbed Ultrasonic Mitigation Solutions, which was patented last month. The technology involves the use of ultrasonic waves to break up current deposits in the production tubing and prevent future formations of the wax molecules.

Ultrasonic frequency generating devices are positioned adjacent to the production tubing walls, producing at least three optimal ultrasonic frequencies to prevent precipitation. Typically, one frequency is tuned to disintegrate any of the wax that forms, while the second frequency is designed to break down the wax by transforming molecules into smaller molecules. The third frequency inhibits the wax from attaching to the production tubing walls. These frequencies can be varied to better prevent the wax buildup in specific installations.

With Ultrasonic Mitigation Solutions, oil producers will not incur the cost and operational impact of repeated mechanical pigging operations and costly workovers. "The estimated return on investment to producers can be tremendous, especially when compared to the workover costs of a problem well, which could exceed \$1 million/well," noted Kent Rodriguez, president and CEO of Avalon.

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