



# Proceedings

## U.S. EPA 2004 Nanotechnology Science To Achieve Results (STAR) Progress Review Workshop — Nanotechnology and the Environment II

August 18-20, 2004  
Philadelphia, PA



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## **Introduction**

Nanoscale science, engineering, and technology incorporate a variety of disciplines, including chemistry, materials science, biology, engineering, electronics, and physics. The term nanotechnologies refers to technologies in the range of 1-100 nanometers and to the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. There is a potential for truly revolutionary transformative capabilities for an entire host of products and processes, including those that enhance environmental quality and sustainability through pollution prevention, treatment, and remediation. The potential also exists for adverse effects on human health and the environment. Understanding and preventing or mitigating these effects is vital both for the responsible development of the technology and for the U.S. Environmental Protection Agency (EPA) to carry out its mission.

EPA's Office of Research and Development (ORD), National Center for Environmental Research (NCER), as part of its Science To Achieve Results (STAR) program, supports research leading to applications of nanotechnology. EPA is interested in advances in nanotechnology that can improve the protection of human health and the environment, including significant improvements in cost or performance to assess and solve environmental problems. In anticipation of the significant impacts resulting from the development of nanotechnology, EPA is engaging in a variety of activities, including sponsoring research and development on the potential environmental applications and implications of nanotechnology, coordinating and participating in strategic research planning concerning the potential role(s) for emerging technologies with respect to environmental protection, and providing information at a variety of conferences and workshops composed of academic, industry, government, and non-governmental organization (NGO) representatives dealing with possible societal and environmental impacts of novel technologies.

Nanotechnology offers an opportunity to significantly impact environmental sensing research needs. For example, nanotechnology makes it possible to develop parallel arrays of nanoscale sensor elements, which would result in increased sensitivity, accuracy, and spatial resolution in the simultaneous detection of a large number of compounds. Most sensors depend on interactions occurring at the molecular level; hence, nanotechnology-enabled sensors can have a tremendous effect on our capacity to monitor and protect the environment. Nanotechnology is certain to improve existing sensors and benefit the development of new ones. However, there are many challenges such as reducing the cost of materials and devices, while improving accuracy and sensitivity, and delivering the compound to the device when working with very dilute concentrations.

Treatment and remediation techniques also can be greatly improved through nanotechnology. The potential exists to develop inexpensive remediation and treatment technologies that enable the rapid and effective cleanup of recalcitrant compounds, especially those located in inaccessible areas. Currently, many of the methods that the Agency employs to remove toxic contaminants from the environment involve laborious, time-consuming and expensive techniques. Such techniques often require pretreatment processes and removal of portions of the surrounding environment with the consequent disturbance of the ecosystem. The development of technologies that can perform *in situ* and that are able to reach into crevices, below aquifers, and other difficult areas, eliminating the necessity for costly pump-and-treat operations, would greatly facilitate the remediation of many contaminated sites, especially those contained on the Superfund list. Current challenges include the need to increase the stability of nanoparticles utilized in remediation/treatment methodologies, the need to develop manufacturing techniques for the mass production of these materials, and the need to develop improved methods for monitoring the fate and transport of these materials once they enter the natural environment.

Environmentally benign manufacturing and processing methods enabled by nanotechnological advances will result in the elimination of toxic wastes and by-products and facilitate bottom-up chemical and industrial manufacturing that utilizes "green" processes. Such "green" or environmentally benign manufacturing processes will not only eliminate waste streams (via precise manufacturing) as a resultant product, but also will

reduce the risks associated with the use of hazardous reactants and solvents through the use of nonhazardous starting materials. These processes also have the potential to significantly reduce the consumption of energy and to make many of the alternative clean energy sources (e.g., solar, fuel cells) commercially viable. Challenges to the development and adoption of these processes include the need to develop mass manufacturing techniques and the need to educate industry concerning their potential applicability.

NCER also supports research through STAR grants in understanding the implications of nanotechnologies. There is a serious lack of information about the human health and environmental implications of manufactured nanomaterials (e.g., nanoparticles, nanotubes, nanowires, fullerene derivatives, quantum dots, dendrimers, and other nanoscale materials). Potentially harmful effects of nanotechnology might arise as a result of the nature of the nanoparticles themselves, the characteristics of the products made from them, aspects of the manufacturing process involved, and the use of the products or the end-of-life disposal. The large surface area, crystalline structure, type and degree of functionalization, and reactivity of some nanoparticles may facilitate transport in the environment or lead to harm because of their interactions with cellular materials. Because size matters on the nanoscale, harmful effects caused by the composition of the material itself could be increased.

EPA's research concerning environmental implications examines the potential persistence and possible synergistic effects of nanomaterials with other contaminants or naturally occurring compounds in the environment. Reactivity and the types of compounds that result are crucial degradation questions. There also is the issue of the potential bioavailability, bioaccumulation, and biotransformation capacities of nanomaterials. The capacity of these materials to accumulate in certain nanoparts of living systems in various species must be explored along with the metabolic and alteration of these materials and their subsequent effects on living systems. Knowledge about the transport of nanomaterials that reach the environment is important and is currently unknown. How these materials move from one media to another, from one organism or ecosystem to another, and from organisms to the environment and vice versa will be critical for understanding and implementing proper manufacture, use, and end-of-life options. To effectively assess these impacts, a full life-cycle analysis of the materials and products must be undertaken—from starting materials to the manufacture, use, and eventual disposal or reuse.

EPA-sponsored nanotechnology research outlined in this document addresses these challenges and concerns. Researchers in the areas of environmental applications and implications of nanotechnology presented data and results from their work, some of which began in 2002. This Progress Review Workshop brings together EPA's extramural scientists as well as scientists and policymakers from government, academia, and NGOs to consider both the environmental applications and implications of nanotechnology.

The research described in this report has not been subjected to the Agency's required peer review and policy reviews, and does not necessarily reflect the views of the Agency. Therefore, no official endorsement should be inferred. Any opinions, findings, conclusions, or recommendations expressed in this report are those of the investigators who participated in the research or others participating in the Progress Review Workshop, and not necessarily those of EPA or the other federal agencies supporting the research.

For more information on EPA's nanotechnology research, please contact Barbara Karn, Ph.D., at 202-343-9704 (karn.barbara@epa.gov); or Nora Savage, Ph.D., at 202-343-9858 (savage.nora@epa.gov).

## **U.S. EPA 2004 Nanotechnology Science To Achieve Results (STAR) Progress Review Workshop—Nanotechnology and the Environment II**

**Loews Philadelphia Hotel  
1200 Market Street  
Philadelphia, PA 19107**

**August 18–20, 2004**

### **Executive Summary**

#### **OVERVIEW**

The U.S. Environmental Protection Agency's (EPA) 2004 Nanotechnology Science To Achieve Results (STAR) Progress Review Workshop—Nanotechnology and the Environment II was held on August 18–20, 2004, in Philadelphia, PA. The workshop brought together approximately 100 researchers from academia, industry, and government to discuss ongoing research on nanotechnology and the environment. The workshop also served as a stimulus for increased collaborations among the various researchers and resulted in improved knowledge of the environmental aspects of nanotechnology.

#### ***Welcome and Introductory Remarks*** **Steve Lingle, U.S. EPA**

Mr. Lingle welcomed participants to the workshop, noting that EPA provides leadership for federal efforts related to the environmental applications and implications of nanotechnology. The primary role of EPA's National Center for Environmental Research in the Office of Research and Development (ORD) is to support research carried out by the STAR and Small Business Innovation Research (SBIR) Programs. ORD provides the scientific basis for regulatory policy decisions made by EPA and helps set EPA's research agenda. ORD is partnering with the National Institute for Occupational Safety and Health (NIOSH) and the National Science Foundation (NSF) as part of its efforts related to nanotechnology and hopes to include a number of other agencies in these activities. ORD's goal also is attempting to build an environmental nanotechnology research community.

#### ***National Initiative: Overview, Chances, and Risks*** **Mihail Roco, NSF**

Dr. Roco spoke about the National Nanotechnology Initiative's (NNI) efforts to promote a multidomain approach and interagency collaboration in nanotechnology research. One of the main drivers for nanotechnology, apart from scientific interest, is long-term societal effects. In the last 2-3 years, passive nanostructures (e.g., quantum dots, nanotubes) have been created. The next generation of nanodevices that soon will emerge as commercial prototypes are active nanodevices (e.g., actuators). It is anticipated that in approximately 5 years, nanosystems with more complex applications will be in place.

The organizational structure and roles of the NNI were described. At present, there are approximately 40,000 U.S. workers in the field of nanotechnology. In 2000, only five academic institutions had graduate courses related to nanotechnology; today, more than 270 have undergraduate and graduate courses in nanotechnology. At present, the largest use of NNI funds for nanotechnology research is in the field of electronics. About 4 percent of the NNI budget is dedicated to environmental research. Critical long-term issues related to nanotechnology involve sustainable development, product lifecycle, measurement, miti-

gation, cleanup techniques, and interactions with living systems. NNI activities were discussed, including coordination of research and development investments; evaluation and implementation of regulatory standards; educational, health, and environmental implications meetings; and industry and international collaborations. As a field, nanotechnology is growing very rapidly, and a coherent, exploratory plan that includes a focus on societal implications is needed.

***Nanotechnology and the Environment: A Charge to EPA Nanotechnology Grantees***  
**Barbara Karn, U.S. EPA**

The NNI defines nanotechnology as research and development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1-100 nm range; creating and using structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size; and the ability to control or manipulate on the atomic scale. The challenge is to use nanotechnology research to help clean up past environmental damage, correct present environmental problems, prevent future environmental impacts, and help sustain the planet for future generations. A research framework for nanotechnology and the environment includes applications that are reactive to existing problems or proactive in preventing future problems (e.g., sensors, treatment, remediation, green manufacturing, green energy) as well as the implications of interactions of nanomaterials with the environment and the possible risks that may be posed by the use of nanotechnology (e.g., nano-geochemistry, toxicity, fate/transport/transformation, exposure/bioavailability/bioaccumulation, and industrial ecology aspects). The NNI established a set of nine Grand Challenges for Research in Nanotechnology. One of these Grand Challenges is Nanoscale Processes for Environmental Improvement, which includes applications for measurement in the environment, applications for sustainable materials and resources, applications for sustainable processes, implications in natural and global processes, and implications in health and environmental safety.

## **PLENARY TALKS**

***Nanotechnology Applications for Environmental Sensors: Integrated Devices for Real-Time Analyses***  
**Nongjian Tao, Arizona State University**

Monitoring technology is moving in the direction of smaller devices with greater functionality. Nanotechnology will play a significant role in the development of integrated sensors, including sample delivery, sensing elements, and signal processing and transmission. One challenge is signal transduction, which requires converting a chemical binding event into a readable signal. Projects utilizing nanoparticles with a metal ion colorimetric sensor for optical detection and arrays of electrically wired nanosensing elements for electrical detection were highlighted, as was a project that involves developing a palladium nanowire hydrogen sensor. Another emerging technology is carbon nanotube field effect transistor (FET) sensors. In a conventional FET, conduction through the channel is two-dimensional, but detection sensitivity can be enhanced by narrowing the channel to one dimension. Nanotechnology offers several unique features for making future generations of sensors smaller and more functional (e.g., reduced sample solutions, high degree of integration, high sensitivity for single molecule/ion analysis, and faster response time). However, an integrated device needs to solve the interface between nano- and microtechnology, and challenges remain in terms of interconnectivity and sample delivery issues.

***Nanotechnology Applications for Treatment: Cost-Effective and Rapid Technologies,  
Smart Materials or Active Surface Coatings***

**Wilfred Chen, University of California, Riverside**

Nanomaterials provide the ability to manipulate, control, and bind materials at the same atomic and molecular level in addition to novel affinity, capacity, and selectivity because of their unique physical, chemical, and biological properties. Types of nanomaterials that can be used for environmental treatments include smart modified surfaces or membranes, nanostructured materials, molecularly imprinted polymers (MIPs), and nanoscale biopolymers. One example of smart modified surfaces or membranes includes active membranes modified with peptides for heavy metal removal. An array of different polypeptides could be fine tuned for a variety of applications. Smart surfaces are being developed to address bio-fouling. Poly(amidoamine) dendrimers are an example of nanostructured materials that can be used to bind to metals. It may be possible to use combinations of functions in dendrimeric structures for a variety of applications. MIPs are being developed for virus, phosphate, and perchlorate removal. Researchers are developing a tunable biopolymer with metal-binding properties that could be applied to wastewater contamination.

***Nanotechnology Applications for Remediation: Cost-Effective and Rapid Technologies;  
Removal of Contaminants From Soil, Groundwater, and Aqueous Environments***

**Gregory Wilson, U.S. EPA**

A site conceptual model involving a trichloroethylene (TCE) plume at a U.S. Navy site was used to describe the Record of Decision (ROD), part of the process that involves selecting the technology that will be used to clean up a Superfund site. Fewer RODs are being implemented, but they are becoming more complex with a greater mix of remedies. A greater amount of *in situ* treatment is occurring, which addresses technically complex contamination problems. The Superfund Program is developing a nanotechnology component to many of its databases (e.g., the Reach It database) and is partnering with a variety of federal agencies, including the Department of Energy (DOE). DOE's Office of Basic Energy Science is working with NSF to support the construction of five Nanoscale Science Research Centers, which will support nanotechnology research. The role of nanotechnology in environmental remediation was discussed relative to three projects. One project involved nanoscale particle treatment of groundwater at a naval air engineering station in Lakehurst, NJ. Nanoscale iron particles with a palladium catalyst were injected below the surface, reducing TCE concentrations by up to 50 percent after a single injection. Similar results were observed in a project on source area treatment with nanoscale particles at a naval air station in Jacksonville, FL. This project indicated that nano approaches may be feasible from a cost-effective as well as an environmentally effective standpoint. The third project involved micro-scale zero-valent iron (ZVI) treatment of groundwater at Hunter's Point Shipyard in San Francisco, CA. In this project, pneumatic fracturing was used to inject micro-scale ZVI, and 99.1 percent of chlorinated solvents were removed.

***Nanotechnology Applications for Green Manufacturing***

**Lawrence T. Drzal, Michigan State University**

Nanotechnology can enable the transition of traditional manufacturing (the conversion of materials and energy into useful products through a designed process utilizing a combination of chemical, biological, and mechanical processes) to green manufacturing (manufacturing that reduces waste, minimizes pollution, and protects human health and the environment). The morphologies, physical and chemical properties, and self-assembly characteristics of nanoparticles make them attractive to manufacturers, and a large number of manufacturing operations will be impacted by nanotechnology. A number of projects in the field of microelectronics were discussed, including those on nonvolatile computer memory through self-assembly, epitaxial self-assembly of block copolymers on lithographically defined nanopatterned sub-

strates, self-assembled 3-D designer material, and enzyme “ink” for nanomanufacturing. The field of structural polymer composites stands to benefit from nanotechnology. Nanoreinforcements can add multifunctionality to polymers through small additions of these nanoparticles. Some examples include organically modified nanoclays, cellulose nanowhiskers, and graphite nanoplatelets. Other examples of nanotechnology applications for green manufacturing include nanoparticle manufacturing using supercritical CO<sub>2</sub>; incorporation of metal or metal oxide nanoparticles to produce coatings with anticorrosion properties; self-assembled monolayers in mesoporous supports for improved selectivity in separations, reactions, and sensing; reversible self-assembly for end-of-life and recyclability and reuse; and “dematerialization” through increased use of nanoscale materials to replace microscale elements. It is expected that worldwide research and development spending in nanotechnology will rise about 10 percent this year to \$8.6 billion; in 2005, with the private sector likely outspending the public sector in this area.

***Federal Nanotechnology Efforts: Toxicity and the Environment***  
**Nora Savage, U.S. EPA**

Federal agencies participating in the NNI, particularly the regulatory agencies, are aware of the current observations, hypotheses, and deductions concerning nanomaterials. Environmental, societal and educational, and health nanotechnology funding by federal agencies has increased from approximately \$80 million in 2001 to about \$130 million in 2004. The environmental portion has increased from approximately \$18 to 20 million (see Figure at the end of this summary). NNI activities related to health and the environment include EPA and NSF research grants on health and environmental applications and implications of nanotechnology; National Institutes of Health research on the effects of nanoscale materials inside the body; National Toxicology Program work on carbon nanotubes, quantum dots, and titanium dioxide; and the joint NSF and DOE Nanoscale Science Research Centers. EPA is discussing internally how nanomaterials should be approached under existing Toxic Substance Control Act (TSCA) regulations and/or whether new regulations are needed. Potential environmental benefits of nanotechnology as seen by the Agency include improved monitoring and detection capabilities; ultra-green manufacturing and chemical processing; waste minimization through designed pollution prevention at the source; reduced energy usage; commercially viable, alternative clean energy sources; and inexpensive, rapid remediation and treatment technologies. Nanotechnology also carries with it the potential to harm the environment and human health. Human health and ecosystem implications include the potential toxicity of novel materials; potential harm to the environment and/or ecosystem through use, manufacture, and/or disposal; unknown transport, transformation, and fate information of nanomaterials; and potential bioaccumulation and biotransformation issues. At the American Chemical Society’s (ACS) 2005 Annual Meeting, there will be a Nanotechnology and the Environment symposium with 11 sessions, coordinated by Barbara Karn and Nora Savage. This is the third such symposium held at consecutive ACS annual meetings. During this symposium, there will be a panel featuring representatives from several nongovernment organizations who will give their perspectives on nanotechnology and societal impacts.

**SESSION 1: GREEN MANUFACTURING**  
**Chair: Barbara Karn, U.S. EPA**

***Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces***  
**Kristen Fichthorn, Pennsylvania State University**

Nanoparticles are potential building blocks for new and existing materials; however, it is difficult to disperse or assemble “bare” nanoparticles, and nanoparticle forces are poorly understood. In studying nanoparticle forces, these researchers made the following conclusions: (1) current theories do not accurately describe forces for small nanoparticles; (2) solvation forces can be important for colloidal nanoparticles; (3) solvation forces are strongly dependant on particle size, shape, surface, roughness, particle-



solvent interactions, and solvent structure; and (4) solvent-nanoparticle suspensions can be engineered for stability, assembly, and environmental impact.

***Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications***

**Lawrence T. Drzal, Michigan State University**

The objectives of this project are to overcome inherent material limitations of polyhydroxybutyrate (PHB)/polyhydroxyalkanoate (PHA) bioplastics, study the effect of PHB/PHA modification on the thermal and morphological properties, and synthesize functionalized PHB/PHA as a compatibilizer in PHB/PHA-based blends and nanocomposites. Reactive extrusion was used to graft functional groups onto a PHB backbone through a solvent-free process; desired changes in the thermal and morphological properties of PHB can be achieved upon its functionalization. Optimum clay exfoliation and surface chemical modification produced nanocomposites with enhanced properties capable of competing with toughened polyolefin materials. The researchers currently are examining the use of ionic liquids as a new plasticizer for a PHA polymer matrix (replacing phthalates) and as exfoliating agents for layered silicates in “green nanocomposites” prepared from PHAs.

***Development of Nanocrystalline Zeolite Materials as Environmental Catalysts***

**Sarah C. Larsen, University of Iowa**

Zeolites are aluminosilicates with well-defined openings of molecular dimensions (0.4-10 nm). Zeolites have a large number of applications in areas such as adsorption, catalysis, and ion exchange. Zeolite particle size can be systematically tuned in the nanometer range by varying reaction conditions, and nanocrystalline zeolites can be used as building blocks for hierarchical zeolite structures (e.g., fibers, films, hollow zeolite structures). Environmental applications for nanocrystalline zeolites and hierarchical structures include adsorption of volatile organic compounds from aqueous solutions or humid environments on functionalized zeolites, selective catalytic reduction of NO<sub>2</sub> with hydrocarbons on nanocrystalline Y zeolites, CR(VI) reduction on iron-loaded hollow zeolite structures, and bifunctional nanocrystalline zeolite catalysts that exhibit different functionality on external and internal surfaces.

***Plasmon-Sensitized TiO<sub>2</sub> Nanoparticles as a Novel Photocatalyst for Solar Applications***

**George Chumanov, Clemson University**

The efficiency of photocatalysis depends on how well charge recombination is prevented; metal nanoparticles can act as an electron sink, promoting interfacial charge transfer and reducing charge recombination. Titania-coated silver nanoparticles were synthesized using a sol-gel technique. In addition, Fe<sup>3+</sup>-doped titania sensitive to visible light was synthesized. Experiments on the degradation of sulforhodamine dye indicate that a true doping effect was observed in an Fe<sup>3+</sup>-doped titania photocatalyst. Efforts are underway to coat silver nanoparticles with Fe<sup>3+</sup>-doped titania, and the photocatalytic activity of Fe<sup>3+</sup>-doped titania and silver coated with Fe<sup>3+</sup>-doped titania will be compared.

***Ecocomposites Reinforced With Cellulose Nanoparticles: An Alternative to Existing Petroleum-Based Polymer Composites***

**William T. Winter, State University of New York**

Cellulose nanoparticles can be made from almost any type of biomass; the properties of these particles vary by source due to species-dependent differences in mean particle size. Sources such as apple pomace, chitin, orange pulp, sugar beet, and wood have been utilized to create nanoparticles and make derivatives such as acetates, maleates, and trimethylsilyl. Additional derivatives are planned. Scale-up of the project's activities will allow for more widespread testing. New techniques are needed to characterize surface

chemistry and interactions. The challenges associated with scale-up include separation of particles from acid, acid recycling, and minimizing reaggregation. Reactive extrusion may provide a route to stronger composites, and an acid-free or reduced process may result from treating the nanoparticles as a coproduct of ethanol production from biomass.

## **SESSION 2: AEROSOLS**

**Chair: Barbara Karn, U.S. EPA**

### *Elemental Composition of Freshly Nucleated Particles*

**Murray V. Johnston, University of Delaware**

Airborne particles are associated with societal implications related to human health and global climate change. Real-time single particle mass spectrometry is used to measure ambient aerosol to determine the chemical composition of individual particles as a function of particle size and to count particles as a function of size and composition. Laser-induced plasma formation can determine the elemental composition of many particle types; the detection efficiency is independent of particle size and composition. Fundamental limitations of nanoparticle transmission contribute to sampling rate limitation because of aerodynamics and Brownian motion. Electrodynamic focusing, which requires particle charging as well as electrodynamic trapping to increase the detection duty factor and overcome inefficient charging, may be used to help address these issues.

### *Ion-Induced Nucleation of Atmospheric Aerosols*

**Peter H. McMurry, University of Minnesota**

The objectives of this project are to determine whether ion-induced nucleation leads to the formation of significant numbers of particles in the atmosphere, and to learn about the physics and chemistry of ion-induced nucleation in the atmosphere. Inclined grid mobility analysis (IGMA) and nano-scanning mobility particle sizing (SMPS) were used to measure size distributions of particles during a nucleation event in Boulder, CO. IGMA enables measurements on nucleated particles as small as 2 nm, and it was determined that nucleation in Boulder is dominated by neutral molecules, not ions. In ongoing work, ion composition during nucleation events is being measured and new nano-SMPS for measuring total size distributions of particles down to 1 nm is under development.

## **SESSION 3: SENSORS**

**Chair: Marti Otto, U.S. EPA**

### *Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for TNT and Carcinogenic Chromium (VI) and Arsenic (V)*

**William C. Troglor, University of California, San Diego**

This project involves the use of fluorescent siloles as luminescent sensors. Siloles are sensitive, selective sensors for nitroaromatic species. Through surface modification of siloles, it may be possible to use them as selective sensors for inorganic oxoanions. The first known hydrosilation of a silole Si-H bond was demonstrated in this work. Silole-amine was found to be less sensitive to some common aqueous oxoanions; however, an increase in luminescence was observed with other analytes. Development of porous Si sensors for pollutants and miniature, low-power devices for integration into systems are underway. A low-power, battery-powered sensor for volatile organic compounds (VOCs) has been built and tested, a prototype for luminescence-based (polysilole) sensors has been constructed, surface chemistry that allows the sensor to detect VOCs in the presence of background humidity was demonstrated, and a method to construct active surface-enhanced Raman spectroscopy substrates on porous Si supports has been discovered.

***Nanosensors for Detection of Aquatic Toxins***

**Robert E. Gawley, University of Miami**

This project involves the development of nanosensors for detection of saxitoxin, which causes paralytic shellfish poisoning, and other marine toxins that are problematic to human health, such as tetrodotoxin, brevetoxin, ciguatoxin, and domoic acid. The objective of this project is to covalently attach fluorescent dendrimers to a surface for sensing. To date, selective and sensitive fluorescent chemosensors have been developed, dendrimers were attached to beads in a spatially resolved manner, and studies of toxic versus nontoxic shellfish extracts have started. Challenges include making a water-soluble dendrimer, creating combinatorial libraries, and developing a new fluorophore with absorption in the visible range to eliminate matrix interference from the shellfish extract.

***Self-Assembly of Nanoparticles in Sensing Platforms***

**Somenath Mitra, New Jersey Institute of Technology**

The objective of this project is to take different steps of a measurement process and integrate them onto one platform. This integration is especially important for environmental monitoring, which involves complex metrics and low concentrations integrated into a single device. Specifically, a single device for monitoring VOCs in air is being developed that exploits the self-assembly properties of carbon nanotubes as they are grown on microstructures. Nanoparticles offer some distinct advantages, such as a very large surface area and unique absorption characteristics. Fabrication requires self-assembly, and the process needs to be fine tuned for each application.

***Advanced Nanosensors for Continuous Monitoring of Heavy Metals***

**Omowunmi Sadik, State University of New York, Binghamton**

The objectives of this project are to synthesize Au nanoparticles in organic medium using a short, simple, and convenient method and to study the potential of the polyamic acid (PAA) metal nanoparticle films for the analysis and removal of heavy metals from aqueous medium. Au nanoparticles were synthesized in organic medium through use of PAA, which acts both as a reducing and capping agent. The potential of the PAA-metal nanoparticle films in the analysis and removal of heavy metals from aqueous medium has been demonstrated. Other metal salts of Co(II), Pd(II), and Ag(I) also can be used to form metal nanoparticles. Future work includes investigating the reduction of other metal salts with PAA and the use of these metal nanoparticles in environmental and other applications.

***Biosensors: Development and Environmental Testing***

**Anne J. Anderson, Utah State University**

The goals of this project are to develop an array of promoter fusions that respond differentially and specifically with light output upon exposure to toxic metals, and to create a gene chip array to detect transcript abundance from cells responding to toxic metals (the pattern of gene activation would specify the metal). *Pseudomonas putida* strains were used to test a luciferase biosensor for the detection of copper and cadmium. *luxAB*::insertional mutants that detect copper and cadmium differentially have been identified, but gene loci await determination. Peptides that increase upon copper exposure have been detected, and one has been correlated with a specific function.

***Compound-Specific Imprinted Microspheres for Optical Sensing***

**Barry K. Lavine, Oklahoma State University**

Chemical sensing based on swellable polymers is a stable, low-cost approach with a fast reaction time. This approach can be operated at near-infrared wavelengths for optical sensing. Using dispersion polymerization, polymeric nanospheres that selectively bind theophylline were prepared. Changes in the swelling of the theophylline-imprinted particles are being measured using surface plasmon resonance (SPR). In preparing a hydrogel membrane, polymer microspheres were directly applied to a gold surface, where they are held in place by electrostatic attractions. Particle swelling can be increased at room temperature by decreasing the amount of recognition monomer and template used in the formulation. A new SPR instrument will be constructed with a sample chamber that will expose the gold to a larger amount of sample, mitigating problems associated with alignment. Also, better stepping motors will be used to control the movement of the rotational stages allowing greater control over the change in the incident light angle.

***Ultrasensitive Pathogen Quantification in Drinking Water Using High***

***Piezoelectric PMN-PT Microcantilevers***

**Wan Y. Shih, Drexel University**

The objective of this project is to develop high piezoelectric microcantilever sensors for real-time, *in situ*, ultrasensitive pathogen detection in water. Three tasks are involved: (1) developing highly piezoelectric lead magnesium niobate-lead titanate (PMN-PT) films for microcantilever miniaturization; (2) fabricating and characterizing highly PMN-PT microcantilever sensors; and (3) using sub-millimeter piezoelectric cantilevers for immediate pathogen detection. High piezoelectric PMN-PT films were successfully constructed with better than improved piezoelectric properties as compared to specially cut single crystals. The *in situ*, real-time detection of *Salmonella* in standing water was demonstrated. The investigators developed 0.4 mm long piezoelectric/glass cantilevers of  $3 \times 10^{-11}$  g/Hz sensitivity that are three to four times more sensitive than 10 MHz quartz crystal microbalance (QCM) in protein/molecular detection and six to seven times more sensitive than 10 MHz QCM planar detection in cell detection. Further sensitivity improvement includes using PMN-PT/Cu microcantilevers with flow cells.

***Nanomaterial-Based Microchip Environmental Assays***

**Joseph Wang, New Mexico State University**

The inherent miniaturization and complete integration of electrochemical detection make it extremely attractive for creating portable (and possibly disposable) stand-alone microsystems. Nanomaterials can be used to facilitate detection, separation, preconcentration, and reaction processes, potentially leading to the integration of multiple functions on a “lab-on-a-chip” device. Carbon nanotubes are useful for promoting electron-transfer reactions and imparting higher resistance to surface fouling. In addition, the electrocatalytic activity and resistance to surface fouling of carbon nanotube materials lead to improved sensitivity, stability, and resolution compared to common carbon-electrode detectors. Nanomaterials offer great promise for enhancing the performance of microchip devices. Such nanomaterials-based microchip devices are expected to have a major impact on environmental monitoring and security surveillance applications.

***Low-Cost Organic Gas Sensors on Plastic for Distributed Environmental Sensing***

**Vivek Subramanian, University of California, Berkeley**

This project involves the development of arrayed organic FETs that are easily arrayed at low cost via printing, flexible for easy dispersal, and trainable via electronic nose architecture. To ensure accuracy, measurements are performed with a calibrated precision semiconductor parameter analyzer. The organic

FET-based sensors show promising responses, including transient behavior and cycle life. Future work will optimize structure and process flow, particularly in terms of stability and reliability. Additional future work includes integration of the latest sensing materials into printed device architecture, deployment in testing of environmentally relevant analytes, and enhancement of specificity through functionalization/doping.

***Chemoreceptive Neuron MOS (CuMOS) Transistors for Environmental Monitoring: Detection in Fluid and Gas Ambients With Field Programmability and High Reliability***

**Edwin C. Kan, Cornell University**

The objective of this project is to develop Chemoreceptive Neuron Metal-Oxide-Silicon (CuMOS) transistors for environmental monitoring that exhibit high sensitivity and selectivity, stability/reliability, simple reset, field reconfigurability, high bandwidth, low power, and low cost. Field Effect Transistor (FET) devices with extended floating gates for chemical sensing have been developed; the floating-gate structure for electron tunneling operations provides more degrees of freedom for sensing. Indicators from *I-V* characteristics include subthreshold slopes and threshold voltages. CuMOS integration enables more flexible and controllable circuits. Future work involves an electrowetting actuator for potential microvalves integrated with the sensors and conventional CuMOS circuitry for fluid delivery and confinement.

***Nanocontact Sensor for Heavy Metal Ion Detection***

**Nongjian Tao, Arizona State University**

Nanocontact sensors are being developed for the detection of heavy metal ions in water. The nanocontact sensors include electrodes separated with atomic-scale gaps, so that a few ions can be detected when the sensors are exposed to a water sample. A ppt-level of detection limit has been demonstrated. The nanocontact sensors also exhibit the ability to selectively detect several different metal ions according to their deposition and striping potentials. Efforts are underway to construct an integrated sensor for simultaneous detection of different species using these nanocontact sensors as sensing elements in an array of electrically wired nanojunctions. Conducting polymer nanojunctions that work for both small and large molecular probes also are being developed.

**SESSION 4: REMEDIATION**

**Chair: Philip Sayre, U.S. EPA**

***Graft Polymerization as a Route To Control Nanofiltration Membrane Surface Properties To Manage Risk of EPA Candidate Contaminants and Reduce Natural Organic Matter Fouling***

**Georges Belfort, Rensselaer Polytechnic Institute**

This project involves using graft polymerization to modify membrane surfaces for commercial use. The objective is to use a patented technique, photooxidation of poly(ether sulfone) (PES), which is light sensitive and inexpensive, to modify membranes to create a series of membranes by grafting monomers for a variety of applications. This approach may improve the selection of candidate contaminants and reduce natural organic matter (NOM) affinity. In studying the fundamental principles of photoinitiated polymerization, it was found that the degree of grafting increases reaction time and that wettability increases with the degree of grafting (although it is not a good predictor with NOM), rejection and flux can be tailored based on the degree of grafting, and a range of monomers can be grafted.

***Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature***

**Dibakar Bhattacharyya, University of Kentucky**

Functionalized materials and membranes can be used for ultra-high capacity metal sorption (Hg, Pb, etc.) reactions and catalysis (nanosized metals, vitamin B12, enzymes) as well as tunable separations (with polypeptides). Nanoparticles offer the advantages of high surface area, significant reduction in materials use, reactivity, capacity for polymer surface coating to alter pollutant partitioning, alteration of reaction pathways, bimetallic properties, and enhanced particle transport in groundwater. The synthesis of metal nano-particles in membranes and polymers can be facilitated by chelation mixed-matrix cellulose acetate membranes, thermolysis and sonication, and di-block copolymers. Nanostructured metal formation and hazardous organic dechlorination with functionalized membranes (and with simultaneous recapture/reuse of dissolved metals) was demonstrated. For example, TCE dechlorination by Fe/Ni and Fe/Pd nanoparticles in a membrane was demonstrated.

***Water Treatment by Dendrimer-Enhanced Filtration: Fundamental Principles and Applications***

**Mamadou S. Diallo, California Institute of Technology**

Dendrimer-enhanced ultrafiltration has a number of advantages over polymer-supported ultrafiltration. The process has a much higher metal binding capacity, and metal binding to dendrimers is much more sensitive to pH due to their globular shape. Dendrimers have a much smaller intrinsic viscosity than linear polymers with similar molar mass. Comparatively smaller operating pressure, energy consumption, and loss of ligands by shear-induced mechanical breakdown could be achieved with dendrimers in tangential/cross-flow ultrafiltration systems typically used to recover metal ions from contaminated water. Work in progress includes metal ion binding measurements for Fe(III), Fe(II), Co(II), Ni(II), and Ag(I); investigations of the effect of dendrimer generation and terminal group on dendrimer retention and membrane fouling; and removal of Cu(II), Ag(I), and Co(II) from membrane concentrates by dendrimer-enhanced ultrafiltration.

***Synthesis, Characterization, and Manipulation of (FeS-PAMAM) Dendrimer Nanocomposites***

**Lajos Balogh, University of Michigan**

Uniform iron sulfide (FeS) nanoparticles have been synthesized using surface-modified polyamidoamine (PAMAM) dendrimers as templates. The nanocomposite particles are polycrystalline, and the nanoparticle morphology can be varied from spherical to rod-like using different anions. The ultraviolet-visible absorbance spectra increase in the 250-1,000 nm range is proportional to the amount of FeS nanoparticles present. FeS nanoparticles displayed different absorbance profiles when PAMAMs of different termini were used as a template. Zeta potential measurements indicated that the formed FeS-PAMAM nanocomposites have the same polarity as the dendrimer templates. To deposit FeS nanoparticulate films onto substrates, PAMAM/poly(sodium styrenesulfonate)(PSS) multilayers were constructed using a layer-by-layer self-assembly method. The formed FeS nanoparticulate films exhibited less absorbance than the corresponding PAMAM/PSS multilayers.

***Hollow and Nanoporous Iron Particles***

**Wei-xian Zhang, Lehigh University**

This project is examining the use of highly porous zero valent iron (ZVI) particles and their applications in degradation and transformation of contaminants. By making porous nanoparticles using an organic polymer as a template, the surface area is greatly increased. Making the particles more porous allows them to absorb more iron, reactive materials, or contaminants. Porous iron was used for testing the reac-

tivity to three standard contaminants, including Cr(VI). It was found that porous iron reduced Cr(VI) concentrations by several orders of magnitude. New applications and efficiencies are being explored.

***Developing Functional Fe<sup>0</sup>-Based Nanoparticles for In Situ Degradation of DNAPL Chlorinated Organic Solvents***

**Gregory V. Lowry, Carnegie Mellon University**

The goal of this project is to synthesize surface-modified Fe<sup>0</sup>-based nanoparticles that can transport in a saturated porous matrix, preferentially localize at the nonaqueous phase liquid (NAPL) water interface, and degrade NAPL to nontoxic products. The approach is to: (1) understand the factors controlling reactivity/lifetime of Fe<sup>0</sup> nanoparticles by comparing the effectiveness of two particle types; (2) identify block copolymers that provide the desired transport and targeting behavior through polymer selection and synthesizing polymer-coated particles; and (3) characterize polymer/particles in terms of size, NAPL-water partitioning, and transport. Fe<sup>0</sup> nanoparticles are highly reactive, fully utilized, and very efficient in TCE-water systems. Polymer-particle hybrid particles have been synthesized that are in the nano size range (approximately 100 nm), have good NAPL-water partitioning, and exhibit good transportability. Polymer-coated Fe<sup>0</sup> particles have been synthesized but not yet optimized.

***A Bioengineering Approach to Environmental Remediation***

**Daniel R. Strongin, Temple University**

The goals of this project are to examine the use of ferritin as a (photo)catalyst, study ferritin as a template for the growth of oxide and metallic nanoparticles, and examine the functionalization of the ferritin shell. Horse spleen ferritin and *Listeria innocua*, a ferritin-like protein, were studied. Researchers found that ferritin facilitates the reduction of Cr(VI) to Cr(III). Ferritin can function as a template for the growth of oxide and metallic nanoparticles. Functionalization of a ferritin-like protein shell to form a photosensitizer also was demonstrated.

**SESSION 5: IMPLICATIONS**

**Chair: Philip Sayre, U.S. EPA**

***Implications of Nanomaterials Manufacture and Use***

**Earl R. Beaver, Practical Sustainability, LLC**

The approach of this project involves identifying sustainability aspects/impacts along the life cycle of nanomaterials; constructing an inventory of resource use, waste, and emissions in manufacturing; and expanding the analysis in upstream and downstream directions. Quantitative and qualitative aspects of sustainability assessment are being integrated for emerging nanotechnologies, and the most important sustainability cost and benefit drivers for near-term nanomaterials are being identified. Next steps include continuing to develop the inventory, collecting safety and life cycle analysis (LCA) data on materials used in manufacturing, expanding analysis of cost/benefit drivers to extraction and end of life, and soliciting comments on the resulting product.

***A Life Cycle Assessment Approach for Evaluating Future Nanotechnology Applications***

**Shannon Lloyd, Carnegie Mellon University**

The motivation for applying an LCA approach includes reducing material and energy consumption, reducing environmental discharge, using life cycle design early in product life cycles, optimizing economic and social value, identifying regulatory needs, and addressing public concerns. Two applications are being examined: (1) life cycle implications of using nanocomposites for automotive body panel weight reduction; and (2) life cycle implications of using nanofabrication to position and stabilize nanoscale

particles in automotive catalysts. This work incorporated multiple LCA models, technology forecasting to extend beyond environmental inventories, and expert elicitation to characterize expected impacts. A framework was developed for making more informed decisions throughout research and development, comparing current products to those expected from emerging technologies, and helping address public concerns about emerging technologies. Specific nanotechnology LCA challenges include establishing an inventory for nanomaterials and nanoprocesses, and determining whether risks are qualitatively/quantitatively different.

## **SESSION 6: TREATMENT**

**Chair: Anita Street, U.S. EPA**

### ***Transition Metal Nanocarbides as De-NO<sub>x</sub> Catalysts***

**S. Ismat Shah, University of Delaware**

An alternative catalyst is required to achieve mandated reductions of NO<sub>x</sub> emissions, considering the limited availability of Pt-group metals. Transition metal carbides have catalytic properties similar to those of Pt-group metals, and tungsten carbide (WC) has been used in isomerization reactions as a replacement for Pt. WC nanoparticles effectively reduce NO<sub>x</sub>, with the WC composition and structure determining conversion efficiency. CO emission can add to the conversion efficiency. Future steps include reactor studies and quantification of catalysis data, systematic studies of the particle size effect on the de-NO<sub>x</sub> activity and stability, intentional addition of oxygen to synthesize W-O-C to stabilize the catalyst, and catalytic studies under a true exhaust mixture to measure the effect of CO/CO<sub>2</sub> and S.

### ***Simultaneous Environmental Monitoring and Purification Through Smart Particles***

**Wolfgang M. Sigmund, University of Florida**

A multifunctional particle design was optimized to specific reactors. A TiO<sub>2</sub>/silica gel nanocomposite is an effective alternative to carbon technology for removing elemental Hg. A high-efficiency anatase-carbon nanotube photocatalyst more than a factor of 200 times more efficient based on TiO<sub>2</sub> weight was developed, but this work was stopped because of potential toxicity. A reduced-cost hard magnetic composite photocatalyst comprised of barium ferrite, silica, and titania was developed. The specific surface area was increased by two orders of magnitude from  $\leq 0.25$  m<sup>2</sup>/g to 31.7 m<sup>2</sup>/g for magnetic functional particles. A magnetically agitated photocatalytic reactor was optimized with respect to agitation frequency based on modeling efforts.

### ***Nanoscale Biopolymers With Customizable Properties for Heavy Metal Remediation***

**Ann Loi, University of California, Riverside**

Metal chelating polymers require toxic solvents for synthesis, require ultrafiltration, and can clog membranes. One solution is to develop metal-binding materials that can be recovered by environmental stimuli. Metal chelating biopolymers are based on biological building blocks. They are nanoscale biopolymers that are specially preprogrammed within a DNA template, economically produced by bacteria, environmentally friendly, and have tunable properties based on changes in environmental conditions (e.g., pH, temperature). Nanoscale elastin-like protein biopolymers can be designed with customized properties, such as specificity and tunable transition. These biopolymers may provide a novel, environmentally friendly, and green engineering method for the removal of heavy metals from water and soil.



***Combined Ozonation-Nanofiltration for Drinking Water Treatment***  
**Simon Davies, Michigan State University**

This project is studying a combined ozonation/nanofiltration process to reduce the problems associated with use of these processes individually. Fouling studies indicate that ozonation at low dosages reduces fouling; if ozone dosage is high enough, no fouling occurs. The reaction of ozone with foulants appears to be enhanced at the membrane surface, presumably due to the catalytic degradation of ozone by TiO<sub>2</sub>. Chlorination disinfection by-product (DBP) studies indicate that a combined ozonation/nanofiltration process yields better results than with ozone alone. Lower DBP concentrations are obtained with tighter membranes. In the range studied, ozone dosage has little effect on trihalomethane or haloacetic acid precursor removal. A 1 kD molecular weight cutoff membrane results in good removal for all of the DBPs studied; 5 kD yields good removal of chlorinated DBPs.

**SESSION 7: FATE, TRANSPORT, AND TRANSFORMATION**

**Chair: Kevin Dreher**

***Adsorption and Release of Contaminants Onto Engineered Nanoparticles***  
**Mason Tomson, Rice University**

The objective of this project is to create the information needed to ensure that avoidable, deleterious outcomes of nanomaterial production and use never materialize. The researchers aim to develop the information needed to predict: the risk of nanomaterials related to adsorption and desorption of contaminants; impact of naturally occurring sorbents, NOM, heavy metals, and surfactants; and fate of nanoparticles in soil and water. This work is expected to provide information needed to assess whether there is a substantial risk posed by nanoparticles disposed of in groundwaters. It also should yield the necessary parameters for understanding the fate of engineered nanoparticles in the environment and for future development of risk assessment of the engineered nanoparticles.

***Impacts of Manufactured Nanomaterials on Human Health and the Environment: A Focus on Nanoparticle Aerosol and Atmospherically Processed Nanoparticle Aerosol***  
**Vicki Grassian, University of Iowa**

The objectives of this project are to fully characterize a variety of manufactured nanomaterials in terms of their size, shape, bulk, and surface properties; determine if engineered nanomaterials are particularly deleterious to health compared to particles from combustion processes that have been more extensively studied; and evaluate the relative health effects caused by different surface coatings on the nanoparticles. It is expected that these studies will help answer questions as to the potential impact of manufactured nanomaterials on human health. Two important factors are the comparison of the potential health effects of manufactured nanomaterials to other anthropogenic sources of ultrafine particles from combustion processes and the effect of surface coatings, from manufacturing and atmospheric processing, on the toxicity of these particles.

***Chemical and Biological Behavior of Carbon Nanotubes in Estuarine Sedimentary Systems***  
**P. Lee Ferguson, University of South Carolina**

The four objectives of this project are to: (1) determine factors controlling the fate of single-wall nanotubes (SWNTs) in estuarine seawater, sediment, and sediment-ingesting organisms; (2) examine the impact of SWNTs on the disposition of model organic contaminants in estuarine sediments; (3) determine whether the presence of SWNTs in estuarine sediments affects the bioavailability of model organic contaminants to suspension- and deposit-feeding estuarine invertebrates; and (4) assess the toxicity of SWNTs to a model deposit-feeding estuarine invertebrate in seawater and/or in combination with estua-

rine sediments. Fate tracking in estuarine sediments is expected to provide information about potential disposition of SWNTs discharged to the aquatic environment. Sorption and bioavailability studies will reveal the possible impact of SWNTs on the fate and effect of hydrophobic organic contaminants in estuarine sediments. In addition, toxicity studies are expected to lead to an increased understanding of the potential effects of SWNTs on trophically important estuarine invertebrates in sediments.

***Transformations of Biologically Conjugated CdSe Quantum Dots Released Into Water and Biofilms***  
**Patricia Holden, University of California, Santa Barbara**

The goals of this project are to determine the fate of CdSe quantum dots (QDs) under abiotic and biotic conditions, toxicity of QDs to bacteria, damage of QDs to DNA, and the method by which QD coating or conjugation alters effects. This project also will compare the effects of dissolved Cd and Se. QD breakdown in aqueous solutions will be quantified and pH, reducing conditions, light, and oxygen will be examined using bare, core-shell, conjugated QDs. *Staphylococcus aureus* and *Pseudomonas aeruginosa* will be used to study growth effects, QD fates, and breakdown products. To investigate DNA damage, oxidation of isolated guanine and adenine by time correlated single photon counting spectroscopy will be examined, as will the effects of bacterial biofilms.

***Repercussion of Carbon-Based Manufactured Nanoparticles on Microbial Processes in Environmental Systems***  
**Ronald Turco, Purdue University**

This project aims to answer the following questions: (1) How are environmental microorganisms impacted by manufactured nanomaterials? (2) What is the ultimate fate of manufactured nanomaterial in the environment? Investigators will examine how aerobic microorganisms in soil react to and alter themselves (or not) in the presence of carbon-based manufactured nanoparticles. They also will examine how aerobic microorganisms in soil react to and alter carbon-based manufactured nanoparticles and how the change in their chemical structure during this process affects toxicity and impacts soil processes. In addition, baseline information on the toxic effects of carbon-based manufactured nanoparticles on aquatic bacteria will be determined.

***Fate, Transport, Transformation, and Toxicity of Nanomaterials in Conventional Drinking Water Treatment Processes***  
**Yongsheng Chen, Arizona State University**

The goals of this project are to characterize the fundamental properties of nanomaterials in aquatic environments, examine the interactions between nanomaterials and toxic pollutants and viruses, evaluate the removal efficiency of nanomaterials by a sand filtration process, and test the toxicity of nanomaterials in drinking water using the cell culture model of the epithelium. Results are expected to provide fundamental information about the fate, transport, and transformation of nanomaterials in drinking water resources. This work may represent the first evidence that such nanomaterials can or cannot be removed by conventional drinking water treatment processes. An improved toxicity assessment will be developed for the potential exposure risks of nanomaterials in drinking water. This research will provide essential information to support policy and decisionmaking regarding handling, disposal, and management of nanomaterials in commerce, manufacturing, and the environment.

## **SESSION 8: TOXICOLOGY**

**Chair: Kevin Dreher, U.S. EPA**

### ***Short-Term Chronic Toxicity of Photocatalytic Nanoparticles to Bacteria, Algae, and Zooplankton*** **Chin-Pao Huang, University of Delaware**

The objectives of this project are to determine: (1) the acute toxicity of photocatalytic nanoparticles to a mixed bacterial culture; (2) the short-term chronic toxicity of photocatalytic nanoparticles to pure bacterial culture, daphnia, and green algae; (3) the short-term chronic toxicity of copper (II) to green algae in the presence of photocatalytic nanoparticles; and (4) the short-term chronic toxicity of chlorinated phenols to pure bacteria culture and daphnia in the presence of photocatalytic nanoparticles. This work should provide insight into the mechanism of the ecotoxicity of nanoparticles with regard to particle size, chemical composition, surface charges, and photocatalysis. The research also will help to understand the ecotoxicity of chemical hazards as affected by photocatalytic nanoparticles.

### ***Evaluation of Nanoparticle Interactions With Skin*** **Nancy Monteiro-Reviere, North Carolina State University**

This project is focused on assessing the nature of the interactions between manufactured nanoparticles and the skin (currently, there are few data on these interactions), particularly in terms of dermal absorption, cutaneous toxicity, and distribution to skin following systemic exposure. Nanoparticles to be studied include carbon bucky balls and nanotubes, iron oxide nanocrystals, and cadmium selenide nanocrystals. Model systems to be tested include human epidermal keratinocyte cell culture, porcine skin flow through diffusion cells, and isolated perfused porcine skin flap. This work should provide data on the ability of a range of manufactured nanoparticles to interact with skin, an initial assessment of potential vehicle effects, and boundaries for a dermal risk assessment on manufactured nanoparticle exposure.

### ***Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity*** **Robert Hurt, Brown University**

Carbon nanotubes/fibers share important properties with asbestos, such as high aspect ratio, small diameter, durability, and transition metal content. It is hypothesized that fibrous geometry and surface-reactive transition metal impurities are major determinants of toxicity. The approach includes fabricating nanomaterials, characterizing them postprocessing, mobilizing transition metals *in vitro*, and creating acute cellular toxicity assays. Synthesis and characterization are underway for a panel of carbon nanomaterials.

## **CLOSING REMARKS**

**Barbara Karn, U.S. EPA**

Dr. Karn thanked presenters and participants for their participation in the meeting, noting that a proceedings document will be published. A third nanotechnology grantees meeting is planned for October 2005, and investigators from the European Union and Canada may be asked to participate. Participants were reminded that the ACS Annual Meeting will be held in March 2005. Other upcoming meetings that will have at least one session on nanomaterials include the Society of Environmental Toxicology and American Society of Mechanical Engineers. Grantees were informed that if they need assistance in promoting environmental messages regarding nanotechnology at professional society meetings, EPA is available to help with these efforts. Participants were invited to remain at the workshop for a presentation by Dr. Raymond Oliver that was rescheduled and given immediately following Dr. Karn's closing remarks.

***Nanomanufacturing Futures: The Perceived Technological and Commercial Opportunities and the Concerns Over Societal and Environmental Impact***

**Raymond Oliver, Leeds University**

The Royal Academy Working Group Study, which began in the summer of 2003, was discussed. The goals of the study were to define nanoscience and technology; summarize the current state of scientific knowledge on nanotechnology; identify specific applications; identify what environmental, health and safety, ethical, and social implications may arise; and identify areas where regulation should be considered. The study used corroborated evidence and input from academics, industry experts, representatives of health and environmental groups, nongovernment organizations representatives, regulators, and the public in Europe. Study findings indicate that nanotechnology offers great opportunities with many benefits now and in the future. Public discussion has to be started and continued throughout the development of nanotechnologies. Most nanotechnologies pose no new risks to health, safety, or the environment, although there are concerns about the potential impacts of manufactured nanoparticles and nanotubes that are free rather than embedded in other materials. Workplace exposure limits should be reviewed, and manufactured nanoparticles should undergo a full and independent safety assessment by a scientific advisory body before use. It is critical to take ethical considerations seriously with regard to nanotechnology. There is a large area of instrument development needed for inline and online tools that work at the 20 nm to less than 1 nm scale. One of the ways through which nanoscience and technology will become successful is the synthesis and assembly of highly organized structures. Significantly improved material properties for performance and self-assembly and directed-assembly will become the cornerstone of using synthetic materials to develop nano- and meso-scale structured materials.

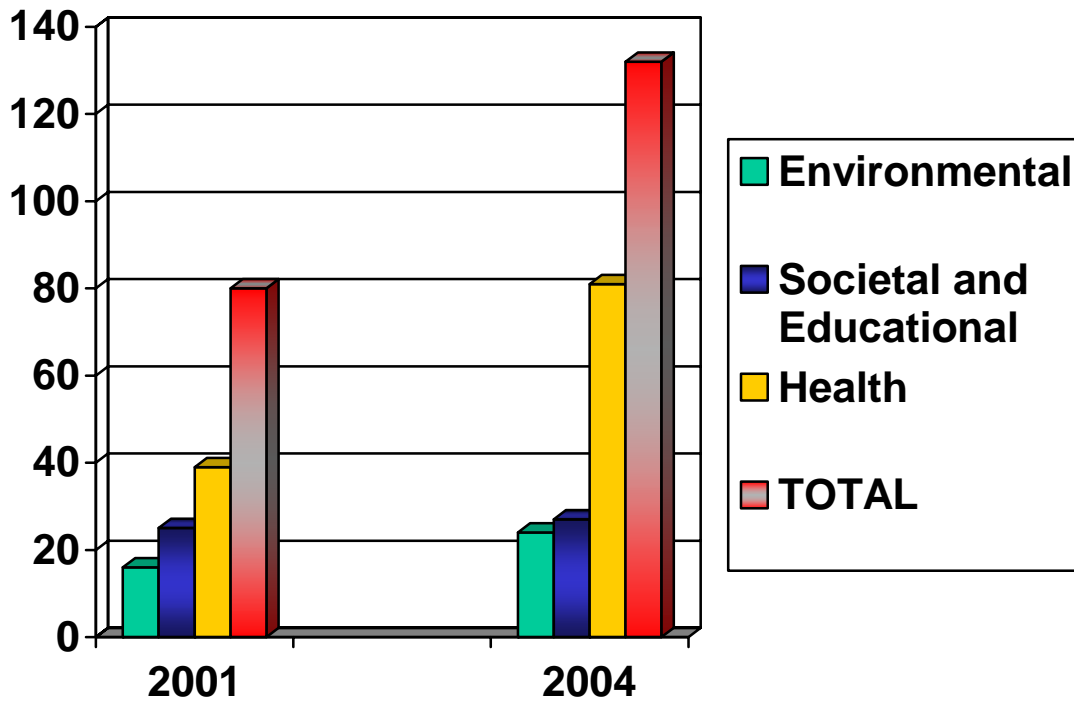


Figure 1. NNI nanotechnology funding.



## **Section 1. Green Manufacturing**

Nanotechnology offers the possibility of changing the manufacturing process in two ways: (1) incorporating nanotechnology for efficient, controlled manufacturing would drastically reduce waste products; and (2) the use of nanomaterials as catalysts for greater efficiency in current manufacturing processes would minimize or eliminate the use of toxic materials and the generation of undesirable by-products and effluents. Research may involve nanotechnology related to improved industrial processes and starting material requirements, development of new chemical and industrial procedures, and materials to replace current hazardous constituents and processes, resulting in reductions in energy, materials, and waste. Potential examples of types of nanotechnology research that may lead to reduction or elimination of pollutants of concern include: atomic-level synthesis of new and improved catalysts for industrial processes; adding information into molecules (analogous to DNA) that build new molecules; self-assembling molecules as the foundation for new chemicals and materials; and building molecules “just in time” in microscale reactors.





## **Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces**

*Kristen Fichthorn*

*Department of Chemical Engineering, Pennsylvania State University, University Park, PA*

### **Abstract**

Nanoparticles hold great promise for a diverse array of materials applications, ranging from electronic circuits to bulk materials with novel mechanical properties to biological materials. Many applications involve colloidal nanoparticles, whose effective use in nanotechnology hinges on their selective assembly or their stabilization against aggregation. Various methods have been used to stabilize colloidal nanoparticles; however, all involve dispersant molecules such as surfactants or polyelectrolytes. These dispersants not only alter the chemistry and physics of nanoparticle systems, but also because they occupy a significant mass fraction of a suspension, they produce a tremendous waste stream during processing. An improved understanding of the forces between “bare” colloidal nanoparticles could lead to new and environmentally beneficial strategies for engineering colloidal nanoparticle suspensions. Historically, Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been used to describe electrostatic and van der Waals interactions in colloidal systems. However, the assumptions of DLVO theory do not apply to nanoparticles. Further, recent studies suggest that forces that are not taken into account by DLVO theory, such as solvation and depletion, could be important in colloidal nanoparticle systems. From a theoretical point of view, it is now possible to simulate colloidal nanoparticles using large-scale, parallel molecular dynamics (MD). These studies can yield atomic-scale detail that is not currently accessible with experimental methods, and they can be used to resolve the origins and magnitudes of forces between colloidal nanoparticles.

Parallel MD is used to simulate two solid nanoparticles immersed in a liquid solvent. In these studies, we are interested in the interplay between solvation and van der Waals forces. The bulk solvent is simulated as more than 100,000 Lennard-Jones (LJ) or n-decane molecules. Four different types of nanoparticles are being studied: small (1.6 nm diameter) and large (6.0 nm diameter) rough, spherical nanoparticles, as well as cubic and icosahedral crystals. To investigate the influence of surface roughness, the nanoparticles are rotated so that they make contact from different angles and have different contacting surfaces. The nanoparticles can be either solvophilic (solvent loving) or solvophobic (solvent fearing). Solvation forces for solvophilic and solvophobic nanoparticles have been calculated for the different nanoparticle systems. In all of the solvophilic nanoparticle systems, the solvation forces oscillate between attraction and repulsion. The oscillatory behavior is caused by the solvent’s ordering near the surface. This effect is particularly evident for the cubic nanoparticles, which exhibit the strongest solvation forces. A comparison of solvation forces and van der Waals forces indicates that solvation forces can be comparable to van der Waals forces. This indicates that solvation forces may be beneficial in preventing nanoparticles from aggregating and that stable nanoparticle dispersions may be achieved in suitable nanoparticle-solvent systems. Solvophilic solvation forces can be highly sensitive to the relative orientation of the nanoparticles and that these forces can cause the nanoparticles to rotate in solution to minimize their free energy. This effect is especially pronounced for the icosahedral nanoparticles, which alternate their relative orientation as they approach each other. In this case, solvation forces may be utilized to align nanoparticles for applications in self assembly. Solvation forces for solvophobic nanoparticles are always attractive. In this case, solvent molecules are repelled from the interparticle region and the density there is lower than the bulk density. The solvophobic solvation forces for nanoparticles in n-decane are particularly interesting, as they exhibit a region of uniform attraction followed by a sudden jump of the forces to zero. These attractive forces can be greater than the van der Waals forces. They arise from an interesting ordering of n-decane around the nanoparticles, in which the molecules orient themselves normal to the particle surfaces, to increase van der Waals attraction between the decane molecules and minimize contact with the nanoparticles. In this orientation, solvent is repelled from the interparticle gap until the gap exceeds twice the end-to-end distance of a decane molecule, at which point solvent enters the interparticle region and assumes a bulk-like structure.

## Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces

*Darrell Velegol and Kristen Fichthorn\**

*Department of Chemical Engineering (\*also in Department of Physics),  
Pennsylvania State University, University Park, PA*

### Environmental Implication/Application

Due to their remarkable electronic, optical, magnetic, and mechanical properties, nanoparticle systems will play a central role in electronic and material systems (Kruis et al., 1998), biomedical materials and devices (Gref et al., 1994; Gref et al., 1995; Hrkach, 1997), and environmental remediation systems (Ponder et al., 2000). A central challenge in using nanoparticles is manufacturing bulk quantities of dispersed nanoparticles. Manufacturers like MER Corporation and Carboxyl produce carbon nanotubes but sell it by the gram. Nissan Chemical Industries sells SNOWTEX silica nanoparticles in bulk; however, these are not dispersions of discrete particles, but rather “a string of pearls made of 10 to 50 nm” particles. Nanotechnology is limited by the ability to produce dispersed particles. The engineering challenge is how to stabilize bulk quantities of nanoparticles without using a huge amount of adsorbed dispersant, which then later effects a large environmental cost. For small batches, nanoparticle stability has been at least partially achieved in a manner similar to that for micron size particles. Surfactants, polymers, or another material coating (Andres et al., 1998; Yang et al., 2000) are added to the particles to stabilize them. However, for nanoparticle dispersions, these coatings can negate some of the benefits of the nanoparticles. For example, by adding a surfactant layer onto the particles, one adds two surfactant diameters to the particle size (often greater than 10 nm). Perhaps more importantly, because the nanoparticles have a huge amount of surface area per volume (e.g., 10 nm silica particles have  $\sim 300,000 \text{ m}^2/\text{g}$ ), huge amounts of the coating must be used, which will eventually end up as a large waste stream. Nanotechnology will eventually require extensive production of particles, and so even commercially scalable techniques like sol-gel processing will require knowing how to maintain stable dispersions of bare nanoparticles. Our engineering goal is: Can suspensions of “bare” nanoparticles be dispersed, preventing a huge waste stream of additives? Nanoparticles are synthesized by many methods, most of which can be categorized into liquid-phase methods, aerosol methods, plasma methods, or mechanical methods. To achieve a stable dispersion of nanoparticles, one must either liberate particles that are held in aggregates, or ensure that the initial primary particles resist aggregation. Currently, nanoparticle stability cannot be controlled because we do not understand nanoparticle forces. What little intuition does exist comes from extrapolating the classical DLVO model (Hunter, 1986) for interparticle forces down to the nanometer regime. Not only does DLVO theory often fail qualitatively, even for particles greater than 100 nm in diameter (Velegol et al., 1996; Behrens et al., 1998; Behrens et al., 2000), but also it neglects phenomena such as fluid ordering (Israelachvili, 1992), which could be critical to nanoparticle systems.

This research project has three primary objectives: (1) model nanoparticle forces, especially van der Waals, depletion, and solvation forces; (2) develop the experimental technique of “particle force light scattering” (PFLS) to measure nanoparticle forces; and (3) synergize the MD calculations and PFLS measurements to study real systems (e.g., silica in water), including measurements of bulk stability or rheology. This research project plans to synergize modeling and experiments, leading to predictive models for van der Waals, solvation, and depletion forces. The essential feature of the project is to use molecular dynamics to model forces (especially van der Waals, solvation, and depletion forces), and to verify the modeling using experiments. For nanoparticle systems, these forces are poorly understood, and this limits the ability to control dispersion. The modeling is important, as forces can be analyzed individually by turning them “on and off.” The qualitative (and perhaps quantitative) accuracy of the MD calculations will be verified by direct force measurements using the technique of PFLS. This technique will be developed to measure sub-piconewton forces that are pertinent to nanoparticle systems. These measurements will be compared with bulk stability and rheology measurements, where possible, to see whether other factors (e.g., hydrodynamic shear) play a larger role in dispersion than expected.

## Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications

Lawrence T. Drzal, Manjusri Misra, and Amar K. Mohanty  
Michigan State University, East Lansing, MI

### Abstract

Renewable resource-based “green” nanocomposites are the next generation of materials that provide a combination of performance and environmental compatibility. This research project seeks to replace/substitute existing petroleum-derived polypropylene (PP)/TPO (thermoplastic olefin) based nanocomposites with environmentally friendly nanocomposites produced from bacterial-based bioplastic (polyhydroxyalkanoate, PHA) reinforced with compatibilized nanoclay for automotive applications. These nanocomposites are “sustainable” materials because they are recyclable, stable in use but can be “triggered” to biodegrade under composting conditions, environmentally benign, and commercially viable. To achieve “sustainability,” this research project will address all of the critical components such as environment, economics, life-cycle analysis, energy, and education.

The objectives of this research project are to synergistically combine biobased “green” plastic materials technology and nanotechnology in a new manner that will have a positive impact on the environment through its increased use in industrial applications. The objectives of this research project include: (1) nanoclay/bioplastics mechanical property optimization; (2) research into bioplastic toughening methods and into new alternative, ecofriendly compatibilizers; and (3) verification of sustainability through life-cycle analysis. A concurrent objective is to educate both graduate and undergraduate students on the importance of nanotechnology with special importance on the environmental benefits of “green” nanocomposites from an environmental prospective.

The PHA bioplastic is the only water-resistant biopolymer from renewable resources with the potential for automotive applications as a result of its highly crystalline morphology. The project is based on an interactive approach that includes the interrelated topics of: (1) toughening of the bioplastic matrix with natural rubber to mimic the properties of TPO; (2) plasticization with vegetable oil—to replace existing undesirable phthalates; (3) synthesis of compatibilizer to bind clay and bioplastic; and (4) investigation and development of cost-effective, reduced-step extrusion processing. A unique university-industry team composed of Michigan State University, General Motors, Metabolix (bioplastic manufacturer), and Nanocor (producer of nanoclay) has been assembled to ensure industrial and commercial viability.

*Environmentally Benign Materials:* Because the bioplastic is a renewable resource-based material, the resulting green nanocomposites are eco-friendly because of their recyclability and compostability/biodegradability. This could result in a substantial reduction in greenhouse gases and reduction in the Nation’s reliance on oil and enhancement of national security.

*Fuel Savings and Emissions Reduction Due to Lighter Auto Parts:* The proposed lightweight green nanocomposites would reduce vehicle weight and would contribute significantly to fuel savings. About 7 L of fuel per kg of vehicle weight could be saved over the life of a typical vehicle, or about 15 billion L annually. In addition, approximately 3 kg of CO<sub>2</sub> are produced by combustion of 1 kg of fuel, thereby reducing CO<sub>2</sub> emissions.

*Replacement of Phthalate Plasticizers:* In the plastics industry, to improve processability, phthalate plasticizers (a suspected endocrine disrupter) are used extensively in petroleum-based plastics. This research project will use natural rubber as a toughening agent and derivitized soybean oil as a plasticizer, which would create a significant positive impact on the environment as well as on the agricultural and manufacturing industries.

*Industrial Impact:* Petroleum-based plastics are nonbiodegradable and add to global warming. Although performance limitations and high initial costs have restricted the adoption of bioplastics to niche markets, the availability of higher performance “green” plastics will prove to be beneficial for the “greening” of U.S. automobiles and for recycling.

## **Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications**

*Lawrence T. Drzal, Manjusri Misra, and Amar K. Mohanty  
Michigan State University, East Lansing, MI*

### **Environmental Implication/Application**

This research project is expected to create a basis for a new generation of green nanocomposites made from bioplastic and commercial organically modified clay in the presence of a compatibilizer. The development of a compatibilizer, formulation of the bioplastic and novel processing performed in this project have the potential to produce high-impact and high-strength green nanocomposites that can substitute/replace petroleum-based nanocomposites.

New environmental regulations, societal concerns, and growing environmental awareness have triggered the search for new products and processes that are compatible with the environment. This research will help to develop the science and technology base necessary for sustainable green nanocomposite materials from renewable resources for automotive applications. These materials will replace petroleum plastic clay-based nanocomposites.

## **Development of Nanocrystalline Zeolite Materials as Environmental Catalysts: From Environmentally Benign Synthesis to Emission Abatement**

*Sarah Larsen*

*Department of Chemistry, University of Iowa, Iowa City, IA*

### **Abstract**

This research project involves the development of nanometer-sized zeolites and hierarchical zeolite structures as environmental catalysts. Zeolites, which are widely used in applications in separations and catalysis, are aluminosilicate molecular sieves with pores of molecular dimensions. The crystal size of zeolites formed during conventional synthesis range in size from 1,000 to 10,000 nm. However, for some applications it would be advantageous to employ much smaller nanometer-sized zeolite crystals in the range of 10 to 100 nm. Specific advantages to be gained by using zeolite nanostructures include facile adsorption and desorption, which will form dense films to facilitate separation applications and optical transparency.

A two-pronged approach based on: (1) the synthesis and characterization, and (2) subsequent application of nanocrystalline zeolites as environmental catalysts has been undertaken. The first aspect involved the synthesis and characterization of nanocrystalline silicalite (particle sizes ranging from 20 nm to 1,000 nm), nanocrystalline ZSM-5 (particle sizes ranging from 15-200 nm), and nanocrystalline NaY (particle sizes of 25, 50, and 75 nm). The size-dependent properties of the nanocrystalline zeolites were investigated by powder x-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption isotherms, and solid state nuclear magnetic resonance. Hierarchical structures such as rectangular fibers and hollow spheres and tubes were formed from these nanocrystalline zeolites. The second aspect of this approach is the application of these nanocrystalline zeolites and hierarchical structures for applications related to environmental catalysis. The use of these nanocrystalline zeolites and hierarchical structures has been evaluated for the following potential applications: (1) adsorption of volatile organic compounds (VOCs), such as toluene from air and water; (2) selective catalytic reduction (SCR) of NO<sub>2</sub> with propylene (or urea) investigated by Fourier Transform Infrared Spectroscopy and solid-state Nuclear Magnetic Resonance; and (3) reduction of Cr(VI) to Cr(III) using iron-loaded hollow zeolite structures.

In the current phase of this project, reactivity studies are being undertaken to evaluate the activity of the nanocrystalline zeolites as environmental catalysts. One unique characteristic of nanocrystalline zeolites relative to conventional zeolites is that the external surface area is the same order of magnitude as the internal surface area. Applications are being examined in which the external surface of the nanocrystalline zeolite is utilized for the decomposition of reactant molecules, and the internal surface is used for further reaction or for storage. Functionalization of the external surface as a method of varying the hydrophobic/hydrophilic properties of the zeolites also is being examined. In addition, the adsorption of VOCs on the nanocrystalline zeolites will be investigated further, particularly in humid environments and for a variety of different VOCs.

## Development of Nanocrystalline Zeolite Materials as Environmental Catalysts: From Environmentally Benign Synthesis to Emission Abatement

Sarah Larsen

Department of Chemistry, University of Iowa, Iowa City, IA

### Environmental Implication/Application

Environmental catalysis involves the use of catalysts to solve environmental problems, in areas such as emission abatement and environmentally benign synthesis. Many new catalysts and catalytic processes have been developed to meet the challenges posed by environmental concerns. Recently, zeolites have emerged as important materials for applications in environmental catalysis. Zeolites are aluminosilicate molecular sieves with pores of molecular dimensions. Zeolites can be synthesized with a wide range of pore sizes and topologies and are used in applications such as catalysis and chemical separations. The crystal size of zeolites formed during conventional synthesis range in size from 1,000 to 10,000 nm. However, for some applications it would be advantageous to employ much smaller nanometer-sized zeolite crystals in the range of 10-100 nm. Specific advantages to be gained by using zeolite nanostructures include facile adsorption and desorption, which will form dense films to facilitate separations applications and optical transparency. Several applications of nanometer-sized zeolites to environmental catalysis are described below.

*Environmental Remediation: NO<sub>x</sub> Emissions Abatement.* The emission of NO<sub>x</sub> and N<sub>2</sub>O from stationary and automotive sources, such as power plants and lean-burn engines, is a major environmental pollution issue. NO<sub>x</sub> leads to the production of ground level ozone and acid rain, and N<sub>2</sub>O is a greenhouse gas. The catalytic reduction of nitrogen oxides to N<sub>2</sub> is an important environmental challenge for scientists and engineers. Recently, the selective catalytic reduction of NO<sub>x</sub> and N<sub>2</sub>O by hydrocarbons (SCR-HC) over transition-metal exchanged zeolites, particularly in the presence of oxygen, has attracted much interest for emission abatement applications in stationary sources, such as natural gas fueled power plants. SCR-HC of NO<sub>x</sub> and N<sub>2</sub>O shows promise for applications to lean-burn gasoline and diesel engines where noble-metal three-way catalysts are not effective at reducing NO<sub>x</sub> in the presence of excess oxygen. The SCR activity of nanocrystalline zeolites, such as NaY, has been investigated.

*Environmental Remediation: Photocatalytic Decomposition of Organic Contaminants.* The next system that will be investigated involves the photocatalytic oxidation (PCO) of volatile organic compounds (VOCs) and heavy metals such as chromium(IV). Photocatalysts, such as TiO<sub>2</sub>, can be used to degrade a wide range of organic compounds found in polluted water and air. TiO<sub>2</sub> photocatalysts are active at ambient temperatures and pressures in the presence of UV irradiation and oxygen. Potential applications include purifying enclosed atmospheres, such as those found in spacecrafts, offices, industrial plants, and homes. The major pollutants in these applications are oxygenates and aromatics. TiO<sub>2</sub> photocatalysts have been shown to oxidize toluene, trichloroethylene (TCE), methanol/ethanol, and a number of other organic compounds. Additionally, iron nanoparticles have been shown to reduce Cr(VI) to Cr(III) in solution using light. The use of nanometer-sized zeolite TiO<sub>2</sub> composites and iron-exchanged zeolites will be evaluated for applications in environmental remediation of VOCs and chromium, respectively.

*Adsorption of VOCs.* Zeolites are extremely good adsorbents for many applications involving the adsorption of VOCs from polluted water or air. In this last application, the advantages of nanocrystalline zeolites for the adsorption of VOCs from water and air will be exploited. The nanocrystalline zeolites synthesized in our laboratory will be evaluated for the adsorption of a representative VOC, such as toluene. The adsorption properties of commercial and synthesized zeolites for toluene will be compared. In addition, the nanocrystalline zeolites will be chemically modified to tailor the hydrophobic/hydrophilic properties for appli-

cations in particular chemical environments. For example, nanocrystalline ZSM5 has been functionalized with octamethylsilane such that the hydrophobicity was dramatically increased. The functionalized zeolites will be evaluated for the adsorption of toluene in aqueous solution.



## **Plasmon Sensitized TiO<sub>2</sub> Nanoparticles as a Novel Photocatalyst for Solar Applications**

*George Chumanov*

*Department of Chemistry, Biotechnology Research Center,  
Clemson University, Clemson, SC*

### **Abstract**

Efficient conversion of sunlight into electrical and/or chemical energy is of great technological importance for modern society and future generations. One attractive possibility for utilization of solar energy is based on the ability of small semiconductor particles to function as photocatalysts promoting various oxidation and reduction reactions under sunlight. Titanium dioxide (TiO<sub>2</sub>) is the most promising material for such applications because it is an efficient, environmentally friendly, and relatively inexpensive photocatalyst. However, wide technological usage of this photocatalyst is largely hindered by the fact that ultraviolet (UV) light does not constitute a significant fraction of the solar spectrum that is required for its activation. Any improvement of photocatalytic efficiency of TiO<sub>2</sub> by shifting its optical response from UV to the visible spectral range will have a profoundly positive effect. The main objective of the proposed research is to synthesize and test a novel photocatalyst that consists of small silver or gold nanoparticles covered with a thin TiO<sub>2</sub> shell. Silver and gold nanoparticles are very efficient systems for the interaction with visible light due to the excitation of plasmon resonances. It is expected that, due to the coupling of plasmon resonances in the core with the electron-hole pair generation in the shell, these hybrid Ag/Au TiO<sub>2</sub> nanoparticles will exhibit photocatalytic activity in the visible spectral range, thereby more efficiently utilizing solar energy.

A coating of silver and gold nanoparticles of different sizes with TiO<sub>2</sub> layers of various thicknesses will be accomplished by sol-gel chemical reactions. High temperature calcination and hydrothermal treatment will be used to convert amorphous TiO<sub>2</sub> layers into the anatase form. Other hybrid nanoparticles include an open TiO<sub>2</sub> shell around metal cores, hollow TiO<sub>2</sub> nanoparticles, and Ag/Au@TiO<sub>2</sub> particles with small RuO<sub>2</sub> and Pt clusters attached to their surface. All particles will be characterized by UV-Vis absorption, luminescence and Raman scattering spectroscopy, electron and scanning tunneling microscopy, and x-ray diffraction. The photocatalytic activity of hybrid nanoparticles will be assessed in model experiments using photoreduction of methylviologen and photocatalytic degradation of 4-chlorophenol.

Ag/Au@TiO<sub>2</sub> particles represent a new system with unknown chemical and physical properties. These nanoparticles will exhibit enhanced photocatalytic activity as compared to TiO<sub>2</sub> conventional catalyst. This new material will have a positive impact on the development of new solar-based technologies, including photoremediation of environmental pollutants, photovoltaic cells, photochemical splitting of water, and artificial photosynthesis. The synthetic approaches developed for the preparation of Ag/Au@TiO<sub>2</sub> hybrid nanoparticles can be extended to include other metals and semiconductors. The proposed research will answer the fundamental question about the possibility of utilization of energy stored in the form of plasmon resonances in metal nanoparticles to carry different chemical reactions.

## Plasmon Sensitized TiO<sub>2</sub> Nanoparticles as a Novel Photocatalyst for Solar Applications

*George Chumanov*

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### Environmental Implication/Application

Efficient conversion of sunlight into electrical and/or chemical energy is of great technological importance for modern society and future generations. Intensive research in this field in recent decades resulted in the fundamental understanding of principles that govern photochemical reactions. This knowledge provides a strong foundation for the development of an artificial photosynthetic system of practical significance. One attractive possibility is to use the photoinduced heterogeneous electron transfer from small semiconductor particles to drive different oxidation and reduction reactions. Titanium dioxide (TiO<sub>2</sub>) is considered the most technologically promising material for these applications because it is an environmentally friendly, relatively inexpensive, and potentially efficient photocatalyst. However, the photocatalytic activity of TiO<sub>2</sub> requires the sensitization with ultraviolet radiation that comprises only a small portion of the solar spectrum, thereby limiting the solar efficiency of this material.

The main objective of this proposed research is to develop a novel hybrid photocatalyst that consists of silver or gold nanoparticles encapsulated into a TiO<sub>2</sub> shell (Ag/Au@TiO<sub>2</sub>). Silver and gold nanoparticles are very efficient systems for capturing energy from the visible portion of the spectrum due to the excitation of plasmon resonances. Thus, the hybrid Ag/Au@TiO<sub>2</sub> nanoparticles will utilize solar energy for photochemical reactions more efficiently than bare TiO<sub>2</sub>.

It is expected that the development of this novel photocatalyst will have a positive impact on the advancement of new, solar-based, environmentally friendly technologies. For example: (1) The hybrid photocatalysts will be used for photochemical destruction of the environmental pollutants, polychlorinated phenols. Photooxidation of these pollutants using bare TiO<sub>2</sub> particles was successfully accomplished in the field under solar illumination. However, low solar efficiency of these photocatalysts limits its wide practical application. (2) Based on Ag/Au@TiO<sub>2</sub> nanoparticles, more procedures will be developed for photoremediation of a wide range of organic and inorganic pollutants such as in the removal of heavy metals in purification of water by sun-induced photoreduction processes. (3) This hybrid photocatalyst can be used for producing oxygen and hydrogen from water using solar energy. It is difficult to overemphasize the importance of hydrogen-powered technologies for the future. A vivid example is hydrogen-powered cars, an area of research and development in which governments and the private sector around the world put a great deal of effort and resources. (4) Ag/Au@TiO<sub>2</sub> hybrid nanoparticles have a potential for the photovoltaic devices capable of direct conversion of solar energy into electricity. Devices using TiO<sub>2</sub> nanoparticles sensitized with organic chromophores already have proved to be very efficient for photovoltaics. However, their lifetime and durability is limited by photo-bleaching of organic molecules under prolonged solar irradiation. This problem is expected to be eradicated for Ag/Au@TiO<sub>2</sub> nanoparticles in which the inorganic metal core functions as a light-capturing chromophoric species. (5) Ag/Au@TiO<sub>2</sub> nanoparticles represent new systems with unknown chemical and physical properties. Further exploration of these materials may result in novel application in other areas such as photonics and microelectronics. (6) The synthetic approaches developed for the preparation of Ag/Au@TiO<sub>2</sub> hybrid nanoparticles can be extended to include other metals and semiconductors. Other hybrid/semiconductor nanoparticles also may find applications in various environmentally friendly, photochemical, solar technologies. The development of Ag/Au@TiO<sub>2</sub> nanoparticles signifies a new field in material science with wide possibilities for practical developments. (7) Finally, this proposed study addresses the fundamental question about utilization of optical energy stored in the form of plasmon resonance for carrying out various chemical reactions.

In summary, the potential impact of this research relates to the advancement of currently existing technologies and the development of new solar technologies, including photoremediation of environmental pollutants, direct conversion of solar energy into electricity in photovoltaic devices, and splitting water to oxygen and hydrogen.

## **Graft Polymerization as a Route To Control Nanofiltration Membrane Surface Properties To Manage Risk of EPA Candidate Contaminants and Reduce NOM Fouling**

*Georges Belfort*

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### **Abstract**

A UV-assisted photochemical graft polymerization technique was used to produce modified poly(ether sulfone) ultrafiltration (UF) membranes that exhibit reduced interaction with natural organic matter (NOM), as a route to reduce the fouling caused by NOM. Six different hydrophilic monomers were evaluated for their ability to reduce fouling by NOM: two are neutral monomers, N-vinyl-2-pyrrolidinone (NVP) and 2-hydroxyethyl methacrylate (HEMA); two are weakly acidic (carboxylic) monomers, acrylic acid (AA) and 2-acrylamidoglycolic acid (AAG); and two are strongly acidic (sulfonic) monomers, 3-sulfopropyl methacrylate (SPMA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS).

Grafting increased membrane surface wettability and shifted the membrane pore size distribution to smaller sizes, which increased NOM rejection (except in the case of NVP). Total fouling appeared to depend primarily on solute rejection, and varied in a complex way that could be interpreted in the context of the NOM molecular weight distribution. Reversible fouling resulting from cake formation was only weakly dependent on membrane surface chemistry; in contrast, irreversible fouling exhibited a marked dependence on surface chemistry. Membranes modified with the weak acid AA monomer were able to reduce irreversible fouling to zero, in contrast to other strongly hydrophilic monomers such as HEMA and AAG, which increased irreversible fouling relative to the unmodified membrane. The wettability (or hydrophilicity) is not an appropriate parameter for estimating reduced fouling potential for NOM feeds, as it is for feeds containing protein. We hypothesize that this is a consequence of the structural and chemical heterogeneity of NOM.

The AA-modified membranes exhibited excellent filtration performance over multiple runs, and outperformed a regenerated cellulose membrane having similar initial NOM rejection.

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### **Environmental Implication/Application**

Results from this project will provide important treatability data for several contaminants from the Candidate Contaminant List, and one contaminant (arsenic) that is currently regulated. The EPA has identified this as a research priority. Treatability data will be provided using as-received nanofiltration membranes, and membranes modified at the molecular scale. Such data will be collected in complex mixtures containing natural organic matter (NOM) that will be representative of water treatment conditions. Effects of organic matter having a wide range of composition and properties on treatment will be quantified. Results from this project also will provide new approaches to develop membrane materials that have superior performance characteristics in terms of both enhanced rejection of contaminants and resistance to fouling by NOM. This project will identify innovative and cost-effective ways to reduce the risk of organic and inorganic anions in potable water sources, which will be of interest to practicing engineers who design water treatment facilities, researchers in the membrane and water treatment fields, and membrane manufacturers.

The proposed research also will expand our understanding of the role of membrane charge and NOM fouling layers on solute rejection by nanofiltration processes. This will identify new ways to assess treatment technologies, and will assist practicing engineers and researchers in designing and implementing these technologies. The materials and processes developed in this research will provide new options for controlling risks from contaminants in water supplies. In this way, we seek to protect human health, and improve the performance of membrane treatment technologies while reducing their cost.

## **Ecocomposites Reinforced With Cellulose Nanoparticles: An Alternative to Existing Petroleum-Based Polymer Composites**

*William T. Winter*

*College of Environmental Science and Forestry, State University of New York, Syracuse, NY*

### **Abstract**

The broad objective of this research project is to produce wholly biobased and biodegradable nanocomposites using cellulose nanocrystals and nanofibers dispersed in biodegradable matrices. These nanocomposites will be compared in terms of thermal, mechanical, and biodegradation properties with existing glass-filled composites made from petrochemicals. During the past 4 months, a 22 L reactor has been acquired, and the problems of scaleup in nanocrystal batch size are being explored. In addition, our own composite objects will be extruded for testing, and biodegradation tests will be developed that are based on ASTM and ISO protocols.

## **Ecocomposites Reinforced with Cellulose Nanoparticles: An Alternative to Existing Petroleum-Based Polymer Composites**

*William T. Winter*

*College of Environmental Science and Forestry, State University of New York, Syracuse, NY*

### **Environmental Implication/Application**

The development of ecocomposites reinforced with cellulose nanoparticles as an alternative to existing petroleum based polymer composites offers three principal environmental impacts. First, the particles being used are made of cellulose, the most abundant and sustainable carbon compound on earth with some  $10^{13}$  tons biosynthesized each year and that replaces inorganic fillers such as chopped glass fiber. Second, because the cellulose nanoparticles have lower densities and are used in smaller quantities to achieve a given level of reinforcement, products made with such composites will be lighter than corresponding glass-filled materials. In transportation applications, lighter materials map into improved fuel economies as it takes more energy to move a heavy object than it does to move a light one. Reduced fuel consumption, in turn, leads to lower emissions of toxic gases. Finally, because the ecocomposites are made from both biodegradable matrices such as polylactic acids, or seed oil-based polyesters and reinforced with biodegradable cellulose particles, it will be demonstrated that the resulting composites are biodegradable under landfill or composting conditions. This makes such materials particularly appropriate for single use applications such as the production of certain packaging materials, Ag films, and many objects used in biomedical applications.





## **Section 2. Aerosols**

EPA is interested in furthering the scientific understanding of the microphysical phenomena of aerosol particles. Aerosols can be nanoscale, in the size range of 1-100 nm. Aerosol research will provide better data for models used in atmospheric and stratospheric particle concentration predictions. Such understanding will lead to protection of human health in terms of providing mechanisms for minimizing respiratory health effects, as well as providing protection from stratospheric ozone depletion that results from particle deposition on cloud condensation nuclei.



## **Elemental Composition of Freshly Nucleated Particles**

*Murray Johnston  
University of Delaware, Newark, DE*

### **Abstract**

The objective of this research project is to develop a method for real-time sampling and analysis of individual airborne nanoparticles between 5 and 100 nm in diameter. The size range covered by this method is much smaller than existing single particle methods for chemical analysis. Because particles in this size range have had relatively little time to grow or transform in the atmosphere, their chemical compositions should more closely reflect particle formation mechanisms than larger particles that have undergone significant transformation. Chemical composition measurements are performed with the use of a high-energy laser pulse to create a laser induced plasma (LIP) that quantitatively converts the particle into positively charged atomic ions.

Relative to conventional laser ablation, which is used in most single particle experiments, the LIP is produced with a 100x higher laser fluence. The higher laser fluence is thought to completely disintegrate the particle into atoms and then quantitatively convert the atoms to positively charged atomic ions. This concept has been confirmed through the study of single particle mass spectra of particle compositions typically found in urban air. In most cases, the measured relative peak areas of different atomic ions match, within experimental error, the expected peak areas based on the elemental composition of the particle. Some important exceptions are noted; for instance, transition and heavy metals tended to quench the LIP, inhibiting quantitative analysis. An important advantage of LIP over conventional laser ablation is that the detection efficiency (defined as the number of particles detected divided by the number of particles irradiated with the laser) remains independent of particle size and composition. In particular, ammonium sulfate particles are detected by LIP with the same efficiency as other particle composition types. In contrast, ammonium sulfate is very difficult to detect with conventional laser ablation and has represented an important limitation of the technique in previous field studies.

## **Elemental Composition of Freshly Nucleated Particles**

*Murray Johnston  
University of Delaware, Newark, DE*

### **Environmental Implication/Application**

Ultrafine particles (defined as 100 nm in diameter and below) and nanoparticles (defined as 50 nm in diameter and below) are important components of ambient aerosol that significantly influence global climate and human health.

Nanoparticles are precursors for larger particles in the accumulation mode. Accumulation mode particles affect the earth's temperature by directly and indirectly (through cloud formation) scattering incoming solar radiation. Understanding the chemical composition of these particles and their precursors allows the impact of human activities on climate change to be more accurately assessed.

There is growing evidence that ultrafine particles and nanoparticles are toxic and that particle number concentration can be an important indicator of human health. Predicting the concentration of these particles in the atmosphere requires an understanding of the processes that lead to new particle formation and to the growth of existing particles. Insight into these processes can be gained through chemical composition measurements. The chemical composition of an individual particle is determined by its origin (formation) and transformation (growth) in the atmosphere. By performing chemical composition measurements on successively smaller particles, we should be able to distinguish chemical components involved in formation from those involved in growth and perhaps to quantify the relative contributions of the various sources to ambient particle loadings.

## Ion-Induced Nucleation of Atmospheric Aerosols

*Peter McMurry<sup>1</sup>, Kenjiro Iida<sup>1</sup>, and Fred Eisele<sup>2</sup>*

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<sup>2</sup>Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO*

### Abstract

The goals of this research project are to determine whether or not regional nucleation events that have been observed in the lower troposphere are due to ion-induced nucleation, and if so, to identify the chemical species that participate in the formation and growth of ionic embryos. This project involves both atmospheric observations and modeling to interpret those observations. An inclined grid mobility analyzer (IGMA) is being used to measure the distributions of positive and negative ions in the 0.5-5 nm size range as well as a nano-scanning mobility particle sizer (nano-SMPS) to measure mobility distributions of nanoparticles in the 3-40 nm diameter range, and a conventional SMPS and optical particle counter to measure particle size distributions from 30 nm-2  $\mu$ m. In addition, measurements of ion composition are being made using a quadrupole mass spectrometer. Measurements have been conducted in Atlanta, GA (August 2002), and Boulder, CO (2004-2005).

Data from several nucleation events in Boulder have been analyzed, and it has been concluded that in most cases nucleation is not ion-induced, but rather involves the clustering and subsequent growth of neutral species. However, during several nucleation events, there is evidence that negative ion-induced nucleation occurs. These conclusions are made by examining the transformation of size-dependent aerosol charge distributions during nucleation events. As nucleated particles grow by condensation of species such as sulfuric acid, they also collide with small ions. Due to such charge transfer processes, nucleated particles will eventually “forget” their original charge states as they grow. However, if growth is sufficiently fast, then particles will “remember” their initial charge state long enough to enable one to determine it by measuring the charge distributions of the freshly nucleated particles. A model has been developed that accounts for charge transformation and growth, and enables us to calculate size-dependent charge distributions that would be expected if nucleation were ion-induced or neutral. The conclusions are obtained by comparing predictions of this model with our measurements.

Currently, measured ion composition during nucleation events is being reconciled with theoretically predicted ion composition, based on known kinetics of ion-molecule reactions. This work will enable us to determine the chemical processes that are responsible for the ion-induced nucleation events.

## **Ion-Induced Nucleation of Atmospheric Aerosols**

*Peter McMurry*

*Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN*

### **Environmental Implication/Application**

It is necessary to understand nucleation to establish the relationship between anthropogenic and biogenic emissions and atmospheric aerosol effects, including their effects on human health and global climate. Nucleation, for example, can produce high concentrations of very small particles, and recent toxicology research has shown that at a given mass concentration, particles in the 20 nm diameter range have a much greater impact on the lung function of laboratory test animals than approximately 200 nm particles. Nucleated particles also can grow into cloud condensation nuclei (CCN), and can thereby affect precipitation patterns and albedo. Understanding such microphysical phenomena is essential to develop valid models for predicting atmospheric aerosol size distributions and the effects of aerosols on the environment. This research project is providing the tools to investigate the relative roles of homogeneous and ion-induced nucleation. In addition, this research is continuing our pattern of developing new measurement methods, applying them in atmospheric field studies, and comparing our measurements with model predictions.

### **Section 3. Sensors**

Protection of human health and ecosystems requires rapid, precise sensors capable of detecting pollutants at the molecular level. Major improvements in process control, compliance monitoring, and environmental decision-making could be achieved if more accurate, less costly, more sensitive techniques were available. Nanotechnology offers the possibility of sensors enabled to be selective or specific, detect multiple analytes, and monitor their presence in real time. Examples of research in sensors include: the development of nano-sensors for efficient and rapid *in situ* biochemical detection of pollutants, ultrafines, heavy metals and pathogens in the environment; sensors capable of continuous measurement over large areas; integration of nano-enabled sensors for real-time continuous monitoring; and sensors that utilize lab-on-a-chip technology. Research also may involve sensors that can be used in monitoring or process control to detect or minimize pollutants or their impact on the environment.





## **Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for Carcinogenic Chromium(VI) and Arsenic(V)**

*William C. Trogler*

*Department of Chemistry and Biochemistry, University of California at San Diego, San Diego, CA*

### **Abstract**

The chief goal of this research project is to develop new selective solid state sensors for carcinogenic and toxic chromium(VI) and arsenic(V) based on redox quenching of the luminescence from nano-structured porous silicon and polysiloles. Nano-structured porous silicon as well as polysilole nanowire coatings will be chemically modified to enhance the binding of the chromate and arsenate anions. Chemical modification to vary the redox potential of the polysilole excited state also will be used as a way to impart chemical selectivity. Both approaches will be combined by encapsulating the polysilole in a nanotextured microcavity between two Bragg stacks constructed from porous silicon. Such optical devices have been shown to provide significant detection sensitivity enhancements. The nanoporous material will readily admit small inorganic analytes, such as chromate and arsenate, and exclude biomolecules that might confound the measurements. Sensors based on silicon wafer and polymer technologies also are readily adaptable to fabrication. The fluorescence quenching detection modality also is manufacturable. The essential electronics require a blue or ultraviolet LED as the excitation source and an inexpensive photodiode detector. Potential applications of such real-time detection devices include remote sensing and industrial process control. The focus on chromium(VI) and arsenic(V) detection is dictated by the redox quenching mechanism that is being used, as well as by the importance of chromium(VI) and arsenic(V) as regulated chemicals under the Safe Drinking Water Act.

Chromium(VI) detectors will be developed that can sense the analyte at concentrations at least as low as the 0.1 ppm action level mandated by the Safe Drinking Water Act with at least a 10 percent accuracy. For arsenic(V), the target range is 10-50 ppb at the same level of analytical accuracy. The deployment of remote sensors for natural waters and for industrial wastewater that could be used to signal alerts in real time would become possible. An electronic sensor method would prove more beneficial than the grab-sampling procedure currently used for detecting these problematic water contaminants. A second goal of this project is the development of polymer-coated "litmus paper" for qualitative detection of chromium(VI) and arsenic(V). Given the low expense of polymer-coated paper, this could prove to be a useful adjunct to current qualitative methods.

Those that benefit from remote sensing applications would include research scientists trying to understand the variations in chromium and arsenic pollutants in natural waters, municipal source water monitoring, as well as federal regulatory monitoring. Because electronic sensors can be engineered either wired or wireless, the range of possible applications is truly immense. Industries involved in metal working and electroplating also would benefit from the ability to monitor waste streams for continuous compliance (in real time) with pollution regulations. Electronic sensors also could be employed to monitor mine runoff for the presence of toxic soluble chromium and arsenic that could enter ground or natural water systems. Chromium is widely used as a corrosion inhibitor in closed water boilers and chillers. Electronic sensors could be used to monitor leaks into nearby groundwater as well as into heat exchange systems.

The simple "litmus paper" application of the thin film polymer indicators could prove useful for field studies and monitoring. Such test strips also would find application in science education (both K-12 and university level) for informing the public about metals in water supplies. Qualitative test strips would be most economically feasible for monitoring water supplies for compliance at the tap, which is the ultimate measure of safety.

## **Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for Carcinogenic Chromium(VI) and Arsenic(V)**

*William C. Trogler*

*Department of Chemistry and Biochemistry, University of California at San Diego, San Diego, CA*

### **Environmental Implication/Application**

There has been interest in the device properties of polymers since the first discovery of an electroluminescent organic polymer. The combination of good structural properties, fabrication, and high efficiency of electroluminescence are important for the development of large-area, light-emitting displays. These same properties also make such materials excellent candidates for luminescent chemical sensors. This research project has shown how luminescent polysiloles developed for LED applications also can be used as sensitive TNT and picric acid (explosive) detectors. Chromium(VI) is an especially problematic contaminant of drinking water because it has been identified as a human carcinogen due to its ease of uptake. In the case of chromium, it could be argued that carcinogenic chromium(VI) should be regulated more stringently than the less toxic chromium(III). Sensors with redox selectivity could be particularly useful in this regard. This project will summarize how functionalization of polymer end groups, as well as those along the chain, can be used to modify their sensor properties for organic vs. inorganic oxidants. Nanoparticles of the luminescent polymers and monomers also can be prepared by rapid precipitation. Their high surface area and adsorptive properties offer sensor detection levels far greater than for bulk phases. Laser scattering measurements support atomic force microscopy (AFM) imaging studies, which show nanoparticle sizes in the 80-100 nm range.

## **Nanosensors for Detection of Aquatic Toxins**

*Robert E. Gawley  
University of Miami, Coral Gables, FL*

### **Abstract**

The objectives of this research project are to design and prepare nanoscale sensors for the detection of marine toxins domoic acid, brevetoxin, ciguatoxin, cylindrospermopsin, and tetrodotoxin. Most of these marine toxins bind specifically to protein receptor sites with a high affinity ( $K_d$  typically in the nm range). The protein receptor sites for several of these toxins have been characterized, and include two characteristic features. One is an array of amino acid side chains that complement structural features of the toxin, which facilitates and strengthens binding of the toxin into the receptor site. A second feature is a solvent-excluded pocket in which the amino acid side chains are arrayed. This preorganized feature of toxin receptor sites will be mimicked by design of synthetic receptors at the nanoscale (nanosensors). To optimize the sensitivity and the selectivity of the nanosensor, combinatorial synthesis techniques will be employed to optimize binding in libraries of peptidic host molecules immobilized on solid support (polystyrene beads). Unlike side chain arrays in the native (protein) receptors, this study will not be limited to L-amino acids, or even to natural amino acids. In this way, short peptide sequences will be produced that wrap around toxins and bind them by providing an array of side chains similar to the native receptor. To mimic the solvent-excluded pocket of protein receptor sites, the combinatorially designed peptide will be incorporated at the core of a dendritic polymer, still on a solid support.

The marriage of combinatorial design and dendrimer synthesis on solid support will provide large libraries (up to 100,000 members) of polypeptide hosts inside dendritic polymers, with each individual host molecule attached uniquely to a polystyrene bead. This is a novel approach in nanosensor design. To our knowledge, this is the first time combinatorially designed peptidic hosts have been incorporated into a dendrimer. Qualitative evaluation of toxin binding can be done simply with a fluorescence microscope. Quantitative analysis will be done with a specific host after it has been synthesized in bulk.

At present, environmental monitoring for aquatic toxins is most commonly done by mouse bioassay. Alternative methods, such as liquid chromatography coupled with mass spectroscopy (LC-MS), are extraordinarily expensive and not suitable for high-throughput analysis. To move away from mouse bioassay, an inexpensive, fast method is needed. This project will identify nanoscale sensors attached to polystyrene beads that can detect toxins using only a hand-held UV lamp and a magnifying glass. The science behind the design of toxin sensors will lead to further developments as well. These synthetic receptors also could be used to immobilize the toxins. Although beyond the scope of the present work, the same design features to be used for mimicking toxin receptor sites also can be used to mimic enzyme receptor sites. Thus, by using models of enzyme active sites, we anticipate being able to use this methodology to mimic enzyme reactions to produce solid-phase catalysts.

## **Nanosensors for Detection of Aquatic Toxins**

*Robert E. Gawley  
University of Miami, Coral Gables, FL*

### **Environmental Implication/Application**

This research is aimed at the development of efficient and rapid detection of the marine toxins such as saxitoxin in environmental samples. Using our ability to work at the molecular level to create large structures with fundamentally new molecular organization, preliminary data have been obtained showing that the toxin can be detected at concentrations below that of the standard method of detection, mouse bioassay. At present, most of the developmental work with toxin standards has been completed, but we recently obtained several environmental samples for the Washington State Department of Health, and have begun to evaluate our sensors on those samples.

Future work will be aimed at environmentally robust chemosensors that are small and portable, and which will be able to detect saxitoxin quickly and inexpensively.

## **Micro-Integrated Sensing Systems by Controlled Self-Assembly of Nanoparticles**

*Somenath Mitra*

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### **Abstract**

The increasing need for inexpensive, portable monitoring devices have added new impetus to miniaturization of chemical analysis systems. It is well known that miniaturization yields many functional and economical benefits because of the reduction of the sample size, decrease in reagent consumption, and inexpensive mass production. Figures of merit necessary for different measurements are high sensitivity, selectivity, reproducibility, short response time, and long-term stability. To solve real-world environmental problems, the sensors need to meet these requirements. The limited success of the sensors in trace environmental monitoring is due to the relatively low sensitivity and high detection limit of the sensors.

A method to enhance sensitivity in any analytical measurement is to preconcentrate the species of interest. Sorbent trapping during air sampling and solid-phase extraction are common preconcentration techniques that allow larger volumes of analyte to be concentrated and then released into the detector, thus resulting in a high signal-to-noise ratio.

Methods of self-assembly of nanoparticles in micro-channels for analyte preconcentration will be presented. The first approach involves gas-phase preconcentration at the nanoscale via quantum interactions on carbon nanotubes (CNTs) directly self-assembled on the devices. This is achieved by chemical vapor deposition (CVD) techniques. The other approach involves solid-phase extraction in microfluidic channels on silica nanoparticles. The nanoparticles are self-assembled via sol-gel synthesis.

## **Micro-Integrated Sensing Systems by Controlled Self-Assembly of Nanoparticles**

*Somenath Mitra*

*Department of Chemistry, New Jersey Institute of Technology, Newark, NJ*

### **Environmental Implication/Application**

At present, there is a need for the development of low cost micro-sensing and measurement devices that can be used for real-time measurements with high sensitivity. Although microsensors have been around for many years, their application in environmental sensing has been limited due to low sensitivity and high detection limits. High sensitivity in the sensors proposed will be achieved by nanoscale quantum adsorption and separation processes on self-assembled carbon nanotubes (CNTs). The sensing devices developed in this project will be: (1) functionally simple and rugged; (2) completely automated for continuous monitoring; (3) cost-effective; and (4) sensitive down to the ppb level. The sensing systems will be developed with air monitoring in mind. It can be used for regulatory purposes, in process control, or for monitoring fugitive emissions from industry. It also will have applications in homeland defense applications, such as in monitoring chemical warfare agents and explosive vapors. This research project also will develop new areas in next-generation sensing and analysis and in nanotechnology. The major new developments will be: (1) fundamental understanding of a microconcentration on carbon nanotubes; (2) self-assembly of CNTs in microfluidic devices by CVD; and (3) functionalization of CNTs.

## Advanced Nanosensors for Continuous Monitoring of Heavy Metals

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### Abstract

The overall objective of this research project is to utilize novel colloidal-metal nanoparticles that are incorporated into a bed of electrically conducting polymers (ECPs) for the development of nanosensors. The feasibility of designing advanced conducting materials for sensor and remediation applications has been explored. Specifically, the synthesis of: (1) polyamic acid (PAA)-silver nanoparticle composites membranes; (2) polyoxy-dianiline films; and (3) electrochemical deposition of gold nanoparticle films on functionalized conducting polymer substrates has been examined. A short description of our fast and simple synthetic approach to gold nanoparticles will be presented. This one-step, synthesis of stable gold nanoparticles uses PAA as both the reducing and stabilizing agents. The nanostructured materials were characterized using electrochemical and morphological techniques such as Fourier-transform infrared spectroscopy, cyclic voltammetry, galvanostatic methods, energy-dispersive spectroscopy, and transmission electron microscopy. Novel gold nanoparticles were prepared through the reduction of AuCl<sub>3</sub> by PAA in organic medium in less than 1 hour. The PAA acts as a reducing agent of the metal salt and a stabilizing agent of the resulting gold (Au) nanoparticles. The procedure resulted in gold nanoparticles capped with the  $\pi$ -conjugated PAA. Depending on the reactant concentrations and ratios, the PAA-metal hybrid was synthesized either as well-dispersed or aggregated particles. The size of the particles, which can be controlled by varying the PAA:AuCl<sub>3</sub> ratios, ranged from  $4.0 \pm 0.7$  nm to  $7.8 \pm 1.0$  nm. Potential applications and environmental implications of the proposed materials also will be discussed.

Current widespread interest in metal nanomaterials is driven by a large number of potential applications, including environmental catalysts, ultrafast optical switches, sensors and surface-enhanced spectroscopies. Many of these applications require the nanoparticles to be stable and evenly distributed with precise control of size, geometry, and morphology. The stable dispersion of nanoparticles in water is important to many applications. However, the water-based synthesis of nanoparticles is fraught with inherent problems such as ionic interaction, low reactant concentration, and difficulty in removing the residue of stabilizers after synthesis. Particles synthesized in organic solvents can be made at a relatively high concentration with a predefined size and shape and with improved monodispersibility when compared with those prepared in aqueous media. Most reports on the synthesis of gold nanoparticles in nonpolar organic solvents have followed the Brust protocol<sup>1</sup>, wherein aqueous chloroaurate ions are transferred into the organic solvent using phase-transfer molecules (tetraalkylammonium salts).

KBH<sub>4</sub> or alcohol has been used for the reduction of the gold salt to form the nanoparticles before being stabilized and protected by the linear polymer. Other researchers have since reported the stabilization of Au nanoparticles using linear polymers. Polymer molecules that possess functional groups such as SH, CN, and NH<sub>2</sub>, can provide sites to bind with Au nanoparticles and prevent them from aggregating because those functional groups are known to have a high affinity for Au. Poly(dithiafulvene) represents the first example where a polymer was used both as a reducing agent and a stabilizing agent in the preparation of gold nanoparticles in organic medium. However, the reaction with poly(dithiafulvene) took 24 hours.

This study provides the first report on the synthesis and stabilization of gold nanoparticles using PAA both as a reducing and stabilizing agent in the solution phase. This approach is based on the reduction of gold III chloride by the PAA and its subsequent capping and stabilization of the resulting gold nanoparticles. Reduction of AuCl<sub>3</sub> by this  $\pi$ -conjugated polymer at room temperature led to gold nanoparticles with narrow size distribution and high dispersity, with the resulting oxidized conjugated polymers protecting the gold nanoparticles as stable colloidal solution. The size of the nanoparticles was controlled by simple variation in the PAA:AuCl<sub>3</sub> molar ratio. Unlike poly(amidoamine) dendrimer-encapsulated gold nanoparticles that are only

stable for 1 day before sedimentation, the current synthesis and stabilization with PAA allows stability for several months with no change in dispersion, nanoparticle density, size distribution, or absorption spectra when stored at  $-20\text{ }^{\circ}\text{C}$ . Furthermore, the PAA-capped gold nanoparticles are formed in less than 1 hour in a rapid, one-step, single-phase synthesis compared to those produced in 12 hours to 1 day.<sup>2</sup> Also, some current approaches are performed in two phases and thus require extraction into the organic medium. The PAA reaction enables the direct formation and stabilization of the nanoparticles in the organic medium.

In a typical reaction,  $\text{AuCl}_3$  crystals (1.5 mg,  $5 \times 10^{-6}$  moles) were dissolved in 6 mL of dimethylformamide (DMF) solutions containing various amounts of PAA (0.5 mg, 1.0 mg and 3.0 mg) and were left to stand at room temperature. The resulting solutions contained PAA: $\text{AuCl}_3$  in 1:100, 2:100, and 6:100 mole ratios, respectively. PAA was synthesized by an adaptation of the method previously reported by Echigo. Its average molecular weight was estimated to be about 10,000 using gel permeation chromatography (GPC).

Briefly, 0.010 mol of 4,4 oxydianiline (ODA) was dissolved in 125 mL of acetonitrile. 50 mL of acetonitrile containing 0.01 mol of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride – PMDA) was then added dropwise for 1 hour to the stirred ODA solution. Yellow PAA precipitates were formed, and the stirring was continued overnight. The PAA was filtered and dried at room temperature for 24 hours. The  $M_w$  of PAA was estimated to be 10,000 using GPC. All solvation processes were achieved by sonication.

The reaction medium gradually changed color from yellow, through orange, and finally to purple (see Figure 1). A control reaction with no PAA was run concurrently. There was no color change with this solution, as the solution retained its original yellow color. The color change in the reaction with the PAA was attributed to the reduction of the  $\text{AuCl}_3$  by PAA to produce the gold nanoparticles. PAA is simultaneously oxidized in the process. Figure 1a also shows the ultraviolet-visible absorption spectrum of the reaction progress during the formation of the PAA-capped gold nanoparticles in dimethylformamide. It is evident that there is a gradual increase in intensity at 540 nm, indicating the formation of the gold nanoparticles. The shape and position of the final band is characteristic of gold nanoparticles with a diameter below 10 nm. This has been attributed to localized surface plasmon oscillation. The isosbestic point at 510 nm is indicative of the involvement of two major species in the reaction medium. The reaction occurred in a similar manner in dimethylsulfoxide and dimethylacetamide, although the rate of reaction was relatively much slower in the former solvent.

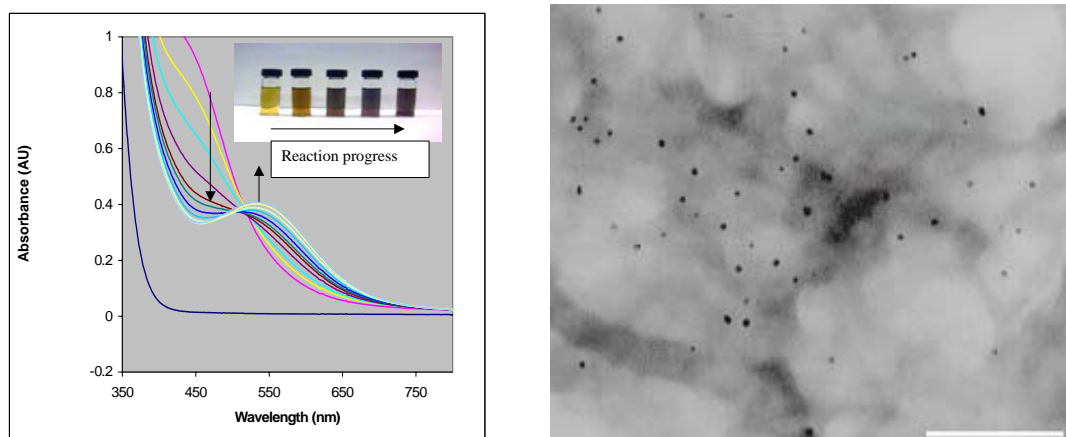
Figure 1b shows the transmission electron microscopy (TEM) of the PAA-capped gold nanoparticles when a 2:100 mole ratio of PAA: $\text{AuCl}_3$  was used for synthesis. The image clearly shows that the nanoparticles are uniformly distributed and well dispersed throughout the polymer. No particle aggregation was seen. This indicated that the  $\pi$ -conjugated PAA stabilized the gold nanoparticle and prevented the aggregation by both steric and electrostatic stabilization mechanisms. The use of conjugation in the stabilizing nanoparticles is a well-known concept. Additional stabilization also is believed to arise from the interaction of the gold with the basic nitrogen centers in the polymer backbone. The average particle size in this case was  $5.1 \pm 0.9$  nm. The nanoparticles were very consistent in size and dispersion pattern. It is evident that the particles became smaller in size to approximately  $4.0 \pm 0.7$  nm when the PAA: $\text{AuCl}_3$  mole ratio was increased to 6:100. This is due to the presence of more PAA molecules that are available for the capping and stabilization of the gold nanoparticles. On the other hand, the reduction of the PAA: $\text{AuCl}_3$  mole ratio to 1:100 resulted in slightly larger particles with more aggregation due to less PAA molecules in the reaction medium that are available to stabilize the nanoparticles. The size of the nanoparticles in this case was in the range of  $7.8 \pm 1.0$  nm. This phenomenon of a higher polymer concentration giving rise to smaller particles has already been observed for polymeric thiols.

This reaction was confirmed using HNMR spectroscopy.<sup>1</sup> The chemical shifts of the hydrogens  $H_a$  and  $H_b$  in the reactant PAA and the oxidized PAA were unchanged at  $\delta$  10.5. The same applied to  $H_c$  ( $\delta$  8.3). This meant that part of the PAA molecule remained unchanged after the reaction. On the other hand, the chemical shifts of  $H_d$  ( $\delta$  7.7) and  $H_e$  ( $\delta$  6.8) in the reactant PAA are typical of a *para*-substituted benzene aromatic system. However, the nature of the peaks and their chemical shifts after the reaction changed significantly ( $\delta$  7- $\delta$  8), and these could be attributed to the  $\pi$ -conjugated PAA stabilizing the nanoparticles.



The polymer nanoparticle hybrid was initially tested for the determination of copper using cysteine having a strong affinity for the metal of interests. The effect of polymer-modified gold nanoparticles oxidation time on the recovery of copper was investigated by keeping all factors constant and varying the times taken for the polymer oxidation. The recovery of copper at 10, 100, 200, and 500 sec was 34.7, 75.0, 83.9, and 99.7 percent, respectively. These results can be explained by the fact that more polymer oxidation time increases the number of carbon atoms oxidized to  $\text{COOH}$  moieties, thus enabling more cysteine molecules to be covalently bonded. Based on additional spectroscopic characterization, there is significant specificity of the materials towards the metal even when it is sequestered within the polymers. Further work is required to prove the feasibility of this technique for other metals.

In conclusion, this study shows the first example in which gold nanoparticles were prepared using the reduction of  $\text{AuCl}_3$  by PAA in organic medium. The PAA was oxidized in the process, thus resulting in the capping of the gold nanoparticles with the  $\pi$ -conjugated PAA. Depending on the reactant concentrations, the PAA-capped gold nanoparticles were synthesized either as well-dispersed or aggregated particles. Particle size ranged from  $4.0 \pm 0.7$  to  $7.8 \pm 1.0$  nm. The size of the particles formed and whether aggregation of the particles occurs or not depends on the PAA: $\text{AuCl}_3$  mole ratio. This method can be applied to the preparation of other PAA-capped metal nanoparticles and bimetallic particles in organic solvents.



**Figure 1.** (a) The UV/Vis absorption spectrum for the formation of PAA capped gold nanoparticles; (b) TEM image of reaction resulting from 2:100 mole ratio of PAA: $\text{AuCl}_3$  in DMF.

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## Advanced Nanosensors for Continuous Monitoring of Heavy Metals

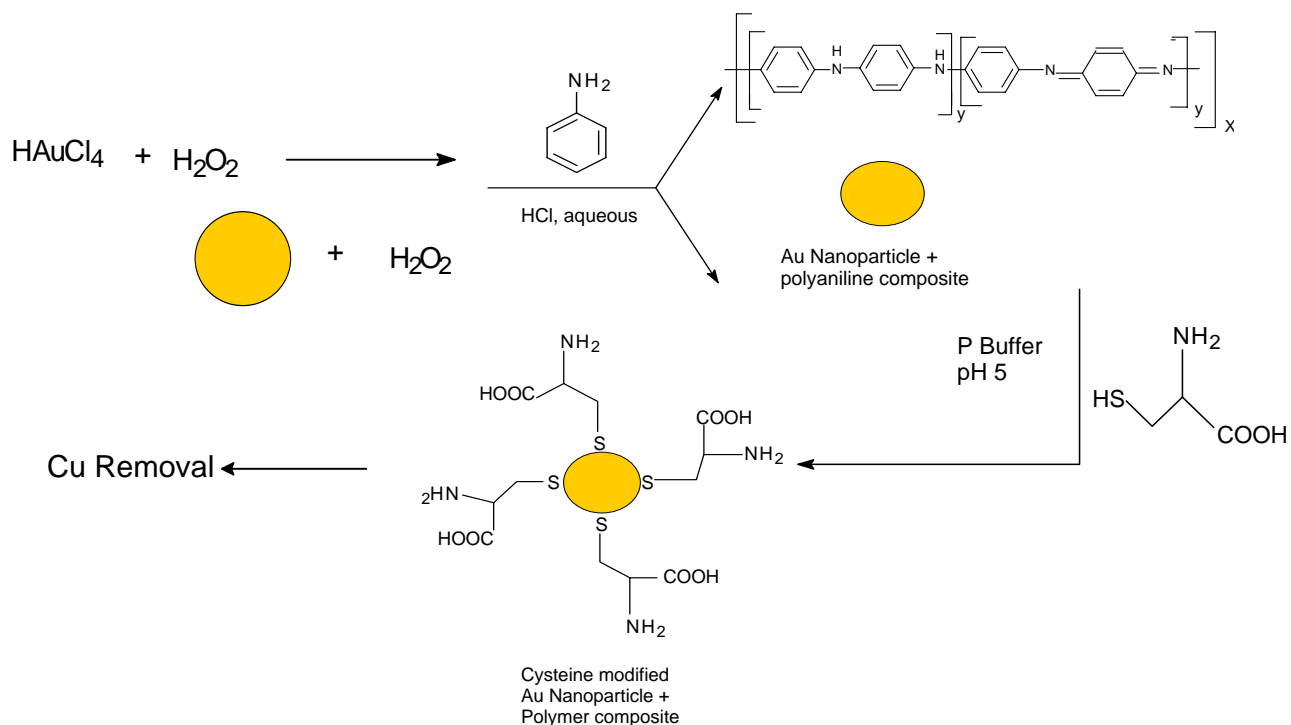
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### Environmental Implication/Application

The early impact of nanotechnology research could be 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.<sup>1</sup> Nanoparticles could provide enormous flexibility for *in situ* remediation. For example, nanoparticles have been anchored onto a solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, or gaseous process streams.<sup>2</sup> 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.<sup>3</sup> The technology also holds great promise for immobilizing heavy metals and radionuclides.<sup>4,5</sup> The oxidation of polyaniline modified gold nanoparticles (PGN) has been investigated on the recovery of copper by keeping all parameters constant (see Figure 1) and varying the times taken for the PGN oxidation. The results of this investigation showed that the recovery at 10 sec, 100 sec, 200 sec, and 500 sec was 34.7 percent, 75.0 percent, 83.9 percent, and 99.7percent, respectively.



**Figure 1.** Investigation of the removal of  $\text{Cu}^{2+}$  from aqueous and organic media using nanostructured materials.

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## Metal Biosensors: Development and Environmental Testing

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### Abstract

Environmental and health risks of toxic metals are based on total metal concentration assayed chemically. However, chelation and sorption may influence metal bioavailability. The goal of this project is to use metabolic changes induced in microbes on contact with the toxic metals to detect bioavailable copper (Cu) and cadmium (Cd). The deliverables will be two types of arrays, one based on live cell response and the second based on gene sequences, to be employed in the specific detection of low doses of bioavailable metals in solution. Metal detection using the cell array is based on increased production of light because the cells contain fusions of a luxAB cassette, encoding light production, with promoters that increase in activity when they detect the metal. Thus, one cell line in the array will emit light only when Cu is present and another only when Cd is present. The gene array will be used by preparing RNA from the biosensor after metal exposure and assessing which genes show changes in transcript level. The pattern of transcript abundance will be metal specific.

The microbe used in the construction of these molecular-based sensors is *Pseudomonas putida* strains KT2440, selected because its genome is completely sequenced. Previous work with mutants of *P. putida* strain Corvallis detected less than 1 mg/L free Cu. These mutants possessed fusions of the promoters of genes involved in protecting the cells against oxidative stress with a luxAB cassette. Light emission from these constructs decreased in the presence of toxic metals, but the responses had little metal specificity, presumably because of induced cell death in the compromised mutants. However, the literature suggests that other promoters, for example for genes encoding proteins involved in efflux, may respond with greater specificity and with increased expression to low doses of the metals. To understand the issue of toxicity and its impact on the biosensors, the threshold was determined for toxicity upon Cu exposure for wild-type KT2440. Loss in culturability occurred at about 10 mg/L Cu for both KT2440 and Corvallis, a value more than tenfold higher than the free Cu concentrations that we aim to detect.

To initiate the production of the cell and gene arrays, random promoter fusions were generated in KT2440 with inserts of the luxAB cassette and we measured how light emission changed after exposure to metal. In trials examining 18 members of an insertion library with exposure to the lesser toxic Fe<sup>3+</sup>, six of these mutants responded with increased rather than decreased light emission. By examining the site of the luxAB insertion, one of the genes that increased in gene expression was found in GTP pyrophosphokinase. Its product, guanosine 3',5'-bispyrophosphate (ppGpp), accumulates in bacteria in response to either amino acid or energy source starvation. Consequently, to our knowledge this is a novel response of the bacterial cell to metal exposure. Studies of responses to Cu and Cd are underway to determine whether this gene is another general response gene or one with specificity. We propose that the cell arrays will consist of promoter fusions that respond with increased light emission after Cu or Cd exposure. The genes identified through determining the site on the KT2440 genome bearing the luxAB insertion will be used in the gene array.

The second approach to identify genes that would be likely candidates for promoter fusions and in the construction of a gene array is based on reverse genetics. This method relies on the identification of the KT2440 proteins that change in accumulation in response to metals. Two-dimensional gel electrophoresis demonstrates changes in levels of several distinct peptides after exposure of KT2440 to Cu and iron (Fe), showing degrees of specificity in response to these different metals. By MALDITOF analysis, two of the peptides that changed in response to 10 mg/L Cu were shown to correspond to a flagellin, which decreased threefold, and the lipoamide dehydrogenase component of 2-oxoglutarate dehydrogenase (OGDH), which increased threefold. These proteins are not among a published list of genes in KT2440 that are predicted to be involved in metal responses. This finding illustrates the value in this reverse genomics approach. However, decreased flagellin production has been correlated by other workers with water stress in the cell for *P. putida*. The increase in the OGDH

suggests that carbon flow through the tricarboxylic acid (TCA) cycle may be enhanced by Cu exposure as anticipated from activated metabolism to overcome stress. The availability of the complete genomic sequence of KT2440 permits synthesis of the promoters for these genes to directly construct the luxAB fusions. These findings confirm that specific sequences in the genome of KT2440 can be harnessed for the detection of toxic metals. Such detection is a prelude to the use of the constructs to probe the bioavailability of different metal complexes occurring in the biological and geological world.

## Metal Biosensors: Development and Environmental Testing

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### Environmental Implication/Application

Pseudomonads are common in soil and water, either free in the planktonic state or attached to soil and biotic matter, including living plant roots. This research project demonstrates that two *Pseudomonas putida* isolates, Corvallis and KT2440, respond by changes in gene expression to free ions of the toxic metals, Cu and Cd. The cells are more susceptible to necrosis to Cu than to Cd. These findings indicate that bacteria when exposed to these metals, such as from a mine site or from industrial waste, may show a dose-dependent decrease in population. Such changes may have ecological effects, for example, in plant performance if the pseudomonads are beneficial root colonizers or in biodegradation of pollutants if the pseudomonads have bioremediation potential.

Changes in metabolism in response to Cu and Cd have been detected by observing altered production of peptides and changes in promoter activities. Some of these changes are common to both metals, as expected in responses that are triggered by oxidative stress, whereas others differ between these metals. Fusions made between the promoters of the responding genes and luxAB genes, such that an active luciferase can be produced, have generated microbial cells that act as biosensors for the free metal ions at the 0.01 to 0.1 mg/L metal ion concentration. These biosensors demonstrate that free ions of Cu and Cd are bioavailable and have the potential to affect life forms. Thus, the biosensors offer the potential to determine bioavailability of metals, such as Cu and Cd, in water samples and in pore waters from soils, in potentially contaminated locations.

## **Compound Specific Imprinted Microspheres for Optical Sensing**

*Barry K. Lavine*

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### **Abstract**

The use of molecularly imprinted polymers is being investigated as the basis of a sensitive and selective sensing method for the detection of pharmaceutical and other emerging organic contaminants, which are at parts per billion levels, in aquatic environments. Moderately crosslinked molecularly imprinted polymeric microspheres (ca. 1 micron in diameter), which are designed to swell and shrink as a function of analyte concentration in aqueous media, have been prepared. These microspheres are incorporated into hydrogel membranes. Chemical sensing is based on changes in the refractive index of the membrane that accompanies swelling of the molecularly imprinted microspheres. These changes are measured by surface plasmon resonance (SPR) spectroscopy. For SPR, the polymer microspheres are directly applied to a gold surface where they are held in place by electrostatic attraction. Encapsulation of the polymeric microspheres is achieved by micropipetting the membrane formulation onto the surface of the SPR substrate, where it is distributed across the gold surface by spatula prior to polymerization.

The prototype SPR sensor is both sensitive and specific. The addition of as little as  $1.0 \times 10^{-7}$  M theophylline is sufficient to cause a change in the refractive index of the membrane, which was detected by SPR. Higher concentrations of theophylline produced a larger change in refractive index. In contrast, the same membrane showed no response to  $1.0 \times 10^{-4}$  M caffeine. (Caffeine and theophylline differ by only a single methyl group.) This result, we believe, is significant for two reasons. First, selectivity has been introduced into SPR analyses using these membranes. Studies where biological receptors have been used to functionalize gold (Au) or silver (Ag) surfaces with analyte specific receptors for pollutant monitoring have often been unsuccessful due to problems associated with antigen stability and crossreactivity. Second, the likelihood is high that parts per billion detection limits for theophylline and other so-called emerging organic contaminants can be achieved with this approach to chemical sensing once the polymeric formulation used to develop the imprinted polymer and hydrogel membrane are optimized. Currently, a polymer formulation is being used, which was developed from N-isopropylacrylamide or N-N-propylacrylamide (transduction monomer), methacrylic acid (recognition monomer), and moderate concentrations of methylenebisacrylamide (crosslinker), and a template to prepare molecularly imprinted polymers that swell in the presence of the targeted analyte. However, the concentration of the recognition monomer is probably too high. Furthermore, the thickness of the membrane is approximately 75 nm, and the size of the microspheres is approximately 800 nm. The membrane needs to be thinner to minimize diffusion distances, ensuring facile mass transfer. Smaller microspheres (approximately 200 nm) will mean that a larger number of polymer particles can be immobilized on the Au surface, and the entire particle will lie within the region of the evanescent wave.

The proposed technology has several important advantages for chemical sensing. The hydrogel membrane can serve as a "filter" to block out larger molecules (e.g., humic acid that might otherwise foul the microspheres). Another advantage of this approach to sensing is that it can be implemented at any wavelength. The microspheres are stable. They are not subject to photodegradation and can undergo multiple swelling and shrinking cycles without degrading. Furthermore, swelling and shrinking of the microspheres has a minimal effect on the size of the hydrogel, and does not generate enough force to affect adhesion of the hydrogel to a substrate. By comparison, previously reported approaches to chemical sensing that involve polymer swelling share the common feature that swelling introduces stress, causing the polymer to crack and tear as well as delaminate.

## **Compound Specific Imprinted Microspheres for Optical Sensing**

*Barry K. Lavine*

*Department of Chemistry, Oklahoma State University, Stillwater, OK*

### **Environmental Implication/Application**

Steroids, hormones, antibiotics, and numerous other prescription and nonprescription drugs (e.g., caffeine and ibuprofen) are present in streams throughout the United States at parts per billion (ppb) levels. These compounds enter the environment through wastewater. Some of these compounds may be indicators of human and animal fecal waste, whereas others have human or environmental health implications. As a first step towards investigating the transport of these contaminants in the Nation's waterways, it will be necessary to develop inexpensive field-based methods that can monitor the concentration of these organic contaminants in a variety of aquatic environments. This research project includes the development of field deployable sensors specifically tuned towards these so-called emerging organic contaminants.



## Ultrasensitive Pathogen Quantification in Drinking Water Using High Piezoelectric PMN-PT Microcantilevers

Wan Y. Shih and Wei-Heng Shih

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA

### Abstract

Highly piezoelectric cantilevers offer the advantages of simple electrical detection and better capabilities to withstand damping in water. It is especially suitable for *in situ* aqueous detection of bioagents or microbes. Binding of antigens to the antibody immobilized on the cantilever surface increases the cantilever's mass and reduces its resonance frequency, which is detected by monitoring the resonance frequency shift. Detection of cells, proteins, and specific antigen-antibody binding has been demonstrated with a lead zirconate titanate (PZT)/stainless steel cantilever. In addition, we have shown that detection sensitivity increased with a decreasing cantilever size,  $L$ , as  $L^{-4}$ . In this project, we have pursued both: (1) developing highly piezoelectric lead magnesium niobate-lead titanate (PMN-PT) microcantilevers for better detection sensitivity; and (2) investigating *in situ* detection of water-born pathogens such as *Salmonella typhimurium*.

With PZT/glass cantilevers of less than 0.5 millimeter in length, we have: (1) achieved better than  $3 \times 10^{-11}$  g/Hz mass detection sensitivity; (2) obtained resonance frequency shifts 3-7 times higher than those of a 10 MHz quartz crystal microbalance (QCM) in the same test conditions; and (3) demonstrated better than  $10^4$  cells/mL concentration detection sensitivity exceeding the infectious dosage of *S. typhimurium* ( $10^5$  cells/mL) and the concentration detection limit of commercial ELISA assays ( $10^5$  cells/mL). Detection selectivity was illustrated between *Salmonella* and yeast.

For PMN-PT microcantilever fabrication, an innovative low-temperature approach was developed to synthesize freestanding lead magnesium niobate-lead titanate (PMN-PT) films as thin as 20  $\mu\text{m}$  thick with piezoelectric properties better than those of specially-cut single crystals. After electroplating 4- $\mu\text{m}$  thick Cu, PMN-PT/Cu microcantilevers were made by wire-saw cutting. With a 600  $\mu\text{m}$  length, PMN-PT/Cu microcantilevers were shown to exhibit better than  $10^{-12}$  g/Hz (less than the mass of a single cell) mass detection sensitivity. It is expected that further reducing the cantilever length to less than 100  $\mu\text{m}$  will achieve better femtogram sensitivity.

## **.Ultrasensitive Pathogen Quantification in Drinking Water Using High Piezoelectric PMN-PT Microcantilevers**

*Wan Y. Shih*

*Department of Materials Science and Engineering, Drexel University, Philadelphia, PA*

### **Environmental Implication/Application**

Current pathogen detection procedures rely on passing sample water collected from the environment through a filter and examining the filter for colony formation a day later, which is slow and not quantitative. The piezoelectric microcantilever sensors developed in our laboratory will detect and quantify pathogens directly from the environment with unprecedented femtogram sensitivity. The sensors also are easily portable.

## Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring

Joseph Wang  
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### Abstract

This research project will address the needs for innovative nanotechnological tools for continuous environmental monitoring of priority pollutants. The objective of this project is to create a novel nanomaterial-based submersible microfluidic device for rapidly, continuously, and economically monitoring different classes of priority pollutants. The unique properties of metal nanoparticles and carbon nanotubes will be exploited for enhancing the separation and detection processes, respectively, in microchip environmental assays, and to understand the relationship between the physical and chemical properties of these nanomaterials and the observed behavior. The miniaturized “Laboratory-on-a-Cable” will incorporate all of the steps of the analytical protocol into the submersible remotely deployed device.

This project will address the challenge of transforming the “Lab-on-a-Chip” concept to an effective environmental monitoring system and will exploit the unique properties of nanomaterials for enhancing such chip-based environmental assays. “Lab-on-a-Chip” technologies can dramatically change the speed and scale at which environmental analyses are performed. The ultimate goal of this project is to develop a submersible microfluidic device, based on the integration of all the necessary sample handling/preparatory steps and nanomaterial-based assays on a cable platform. The new “Laboratory-on-a-Cable” concept relies on the integration of continuous sampling, sample pretreatment, particle-based separations, and a nanotube-based detection step into a single-sealed miniaturized submersible package. Nanoparticle and nanotube materials will be examined toward the enhancement of the separation and detection processes, respectively. Factors governing the improvements imparted by these nanomaterials will be identified, and structural-performance correlations will be established. New “world-to-chip” interfaces will be examined toward the goal of effective online sample introduction, and will assess the challenges of transforming the new microchip to a continuous monitoring system. The parameters governing the microchip behavior will be optimized, and the analytical performance will be characterized and validated.

This research project will enhance the understanding of the use of nanoparticles and carbon-nanotubes as separation carriers and detectors, respectively, in chip-based environmental assays. The resulting submersible microfluidic device will enable transporting the entire laboratory to the sample source, and will offer significant advantages in terms of speed, cost, efficiency, sample/reagent consumption, and automation. Performing *in situ* all of the necessary steps of the analytical protocol should have an enormous impact on the way contaminated sites are monitored. Such development of a miniaturized system, with negligible waste production, holds great promise for meeting the requirements of field “Green Analytical Chemistry.”

Understanding the correlation between the properties of nanomaterials and the measurement processes will have broader implications on the use of nanomaterials in analytical chemistry, on the fields of microfluidic devices, and on nanotechnology, in general.

## **Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring**

*Joseph Wang  
Arizona State University, Tempe AZ*

### **Environmental Implication/Application**

“Lab-on-a-Chip” technologies can dramatically change the speed and scale at which environmental analyses are performed. New and innovative nanomaterial-based strategies were introduced for enhancing the performance of microchip devices for environmental assays. These developments indicate that nanomaterials and microchip devices hold a great promise for environmental monitoring of priority pollutants. The resulting microfluidic device will enable transporting the entire laboratory to the sample source, and will offer significant advantages in terms of speed, cost, efficiency, sample/reagent consumption, and automation.

## **Low-Cost Organic Gas Sensors on Plastic for Distributed Environmental Monitoring**

*Vivek Subramanian*

*Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, CA*

### **Abstract**

The ability to monitor various chemical species in large expanses of currently unmonitored land resources will enable proactive response to environmental problems and also will assist in the development of more accurate models of environmental phenomena. Unfortunately, the widespread deployment of chemical sensors is generally economically unfeasible using currently available sensor technology, primarily because individual sensors are too expensive to be deployed on such large scales.

In recent years, there has been tremendous interest in organic transistors as a means of realizing ultra-low-cost electronics, particularly because they may potentially be printed at extremely low cost on cheap substrates such as plastic and paper. More recently, several groups have demonstrated that organic transistor channels show tremendous environmental sensitivity, though they usually lack specificity. Specificity may be achieved using arrays of organic transistors with different channel materials, thus generating unique, highly specific signatures on chemical exposure. Because such devices may be formed entirely by solution-based processing techniques, including inkjet printing, these are an attractive means of realizing low-cost gas sensors for environmental monitoring.

Our success in realizing such a sensor technology will be reported, and our development of arrayed sensors based on organic transistors will be described. The repeatability and robustness of the same are being studied as well as their usability in the detection of environmental contaminants, with the initial focus aimed at organic solvents often used in industrial applications. Initial results indicate that robust, albeit slow, cycling of organic sensors for reliable detection of several solvents is highly possible. This is promising, as most environmental monitoring applications will not require high-speed responses. Also, simultaneous differential sensing of various chemicals will be demonstrated, thus establishing the potential of these sensors in electronic noses.

## **Low-Cost Organic Gas Sensors on Plastic for Distributed Environmental Monitoring**

*Vivek Subramanian*

*Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, CA*

### **Environmental Implication/Application**

In this research project, the development of low-cost arrayed sensors for distributed environmental monitoring has the following environmental benefits: (1) It will result in the development of a ubiquitous sensor technology for proactive environmental monitoring, thus enabling rapid response to environmental contaminants. (2) The sensor technology itself has potentially low environmental impact relative to alternative sensor technologies, because it is a low-cost, low-waste fabrication technology. As the technology matures, it may enable replacement of these other, less environmentally benign, sensor technologies.

## **The Silicon Olfactory Bulb: A Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS Transistors (CvMOS)**

*Edwin C. Kan and Bradley A. Minch*

*School of Electrical and Computer Engineering, Cornell University, Ithaca, NY*

### **Abstract**

An ideal microsensor for autonomously monitoring chemical and molecular environmental hazards in both water and air should simultaneously have a high sensitivity, a high selectivity, a large dynamic range, a low manufacturing cost, simple calibration/reset protocols, a long lifetime, field reconfigurability, and low power consumption. These requirements arise from considering the rapid deployment and autonomous operation of a microsensor network monitoring a large area. We have developed a Si-based neuron MOS transistor with a novel extended floating-gate structure that permits molecular/chemical sensing. Our sensor, called a chemoreceptive neuron MOS (CvMOS) transistor, is expected to simultaneously meet all of these requirements, and can be fabricated by minor modification or simple postprocessing of conventional CMOS integrated circuits. The modular structure and fabrication of this new device permits us to use CMOS devices optimized for high sensitivity and large dynamic range and affords us complete flexibility in the design and composition of the molecular/chemoreceptive sites. The performance of this new sensor has proved to be vastly superior to that of existing chemical microsensors, such as the ion-sensitive FET (ISFET) and the CHEMFET, in nearly every important respect resulting from the internal transistor gain, no need for a liquid reference potential, and much better isolation between the electronics and microfluidics. During the first half of the project period, selectivity between species like Na<sup>+</sup> and K<sup>+</sup> has been demonstrated with various nonfunctionalized polymer finger coatings. Modification of contact angles in the microfluidic channel interface, sensitive to the ionic strength and species, also has been demonstrated.

The preliminary process flow and testing of CvMOS transistors with generic molecular receptive areas for vapor and liquid sensing (e.g., water, acetone, etc.) already have been established. The preliminary measurements have validated most of our assumptions on the performance of these devices. In the 3-year proposed effort, prototype arrays will be fabricated of these novel microsensors with various molecular/chemoreceptive surface coatings, and their sensitivities will be characterized. Surface adsorption kinetics will be studied to facilitate fast and reliable coating selection. This study will start with polymer coatings that have been used in vapor and liquid sensors through volume expansion monitoring. A new table of target agents and coatings will be gathered from CvMOS reading to achieve selectivity. Also, a micropower neuromorphic electronic interface will be developed for such sensor arrays whose structure and function is based on what is known about the olfactory and gustatory sensory systems of animals. This interface, called the silicon olfactory bulb, will provide a distilled set of informative features that can be used by a recognition system to perform analysis and risk assessment. During the first half of the project period, integrated sensing analog circuits have been demonstrated to distinguish species and concentration without the use of the fluid potential. The required analog circuit can be implemented on the same foundry chip with CvMOS.

A complete system, including both a sensor array and the silicon olfactory bulb, will be developed that can be fully integrated, perhaps on a single chip, and that will dissipate only a few hundred microwatts of power in total. Such devices could be manufactured in large numbers very inexpensively and deployed rapidly as environmental sensors, running autonomously for long periods of time on either solar power or miniature chemical batteries. During the first half of the project period, the characteristics of CvMOS have been demonstrated in the proof-of-concept manner for sensitivity, selectivity, power consumption, and system integrability with CMOS technology and circuits. The developed CvMOS sensor with its all-around sensor specification for an autonomous microsystem deployment can bring great benefit to the environmental sensing in a wide deployment mode. The new sensor is inexpensive to be integrated with other necessary electronics for data processing and communication (on the same chip), and can achieve a wide range of selectivity and sensitivity. It is ready for product development to target at specific chemicals or molecules in ocean or in air.

## **The Silicon Olfactory Bulb: A Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS Transistors (CvMOS)**

*Edwin C. Kan and Bradley A. Minch  
School of Electrical and Computer Engineering, Cornell University, Ithaca, NY*

### **Environmental Implication/Application**

This research project seeks to develop a complete system, including both a sensor array and the silicon olfactory bulb, which can be a fully integrated monitoring device. This device, perhaps placed on a chip, will dissipate only a few hundred microwatts of power in operation. Such devices could be manufactured in large numbers very inexpensively and deployed rapidly as environmental sensors. Powering of these devices for autonomous, lengthy operation can be accomplished using either solar or miniature chemical batteries.



## A Nanocontact Sensor for Heavy Metal Ion Detection

Nongjian Tao

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### Abstract

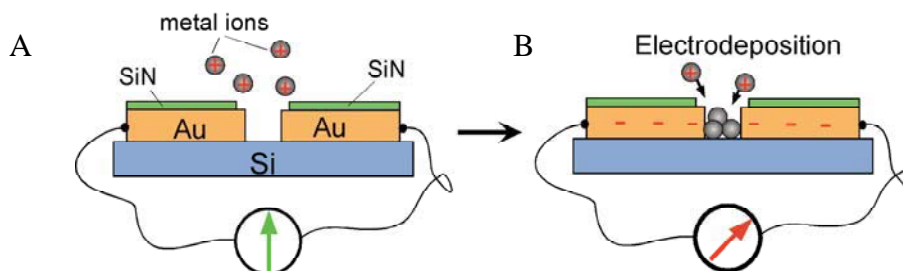
Because of the toxicity of heavy metal ions to a broad range of living organisms, including humans, and the fact that these pollutants are nonbiodegradable, there is an urgent demand for an *in situ* sensor that is sensitive enough to monitor heavy metal ions before the concentration reaches a dangerous level. We have been developing an integrated sensor chip to meet such demand. The sensor chip consists of an array of nano-scale sensing elements. Three different sensing elements (nanocontacts, molecular junctions, and polymer nanojunctions) were fabricated. Metal ion detections using these sensing elements were demonstrated. In addition to metal ions, these sensing elements also are capable of detecting a variety of other chemical and biological species. This research project's goal is to develop a highly integrated sensor for simultaneous detection of a range of different chemical species.

*Nanocontacts.* This sensor starts with an array of electrode pairs fabricated on a silicon chip. The separation between the two electrodes in each pair is as small as a few nm (see Figure 1). When the electrodes are exposed to a solution containing heavy metal ions, the ions can be deposited into the gap by controlling the electrode potentials. Once the deposited metal bridges the gap, a sudden jump in the conductance between the electrodes occurs, which can be easily detected. Because the gap can be made as narrow as a few nm or less, the deposition of even a few ions into the gap is enough to trigger a large change in the conductance, thus providing a sensitive detection of metal ions. Previous experiments have shown that the conductance of such a small bridge is quantized and given by  $NG_0$ , where  $N$  is an integer and  $G_0$  is conductance quantum ( $=2e^2/h$ ,  $e$  is the electron charge and  $h$  is the Planck constant). For this reason, the bridge is often called quantum point contact. The metal bridge also can be stripped off (or dissolved) by sweeping the potential anodically. The potentials at which deposition and dissolution take place provide identity of the metal ions, a principle similar to that of anodic stripping analysis. This nanocontact sensor is simple and can sensitively and selectively detect heavy metal ions, but it is limited to metal ions. To detect other environmentally important species with the same sensor chip, two other sensing elements, molecular junctions and conducting polymer junctions on the sensor chip (described below), have been added.

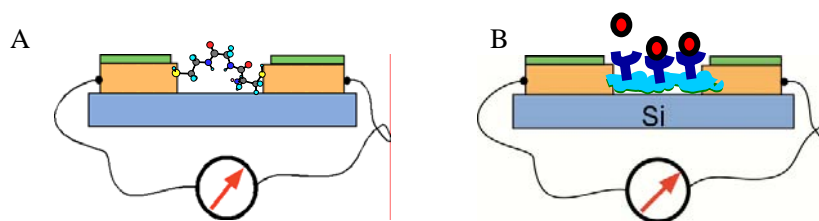
*Molecular Junction.* Molecular junctions have been fabricated by bridging the narrow gaps of the electrodes described above with molecules, which allows us to directly measure the conductance of the molecules (see Figure 2). To demonstrate metal ion detections, peptides with different sequences were chosen to bridge the gap. When a metal ion binds onto the peptides, a change in the conductance is detected. The metal ion-induced conductance change is sensitive to the sequence of the peptides. By selecting appropriate sequences, different metal ions on the peptides can be detected. Metal ion binding was studied on short peptides, and a conductance increase was observed in each case. The conductance increase is highly sensitive to the sequence of the peptide. For example, the binding of a  $\text{Cu}^{2+}$  onto cysteamine-Cys causes only a 10 percent conductance increase, but the binding onto cysteamine-Gly-Gly-Cys increases the conductance approximately 300 times. Therefore, the peptide sequence can be tuned to maximize the metal-ion binding-induced conductance change for sensor applications. The conductance change also is dependent on the type of metal ions. For example, the binding of  $\text{Ni}^{2+}$  onto cysteamine-Gly-Gly-Cys increases the conductance approximately 100 times, which is several times smaller than the case of  $\text{Cu}^{2+}$  binding. This metal ion dependence shows that different metal ions can be identified from the conductance measurement, even if they all bind to the peptide.

*Conducting Polymer Junctions.* Because most molecules are not good conductors, the molecular junction approach is limited to relative small molecules (see Figure 2). To detect large biologically relevant molecules, the gap between the nanoelectrodes was bridged with conducting polymers to form a metal-polymer-metal junction. For selective detection of a particular target species, appropriate probe molecules were attached onto the polymers such that a specific binding of the target species onto the probe molecules is detected as a change

in the conductance of the polymer junction. For metal ion sensor applications, oligopeptides were attached to the polymer junctions via peptide bonds. One example is to attach Gly-Gly-His to a polyaniline junction. The tripeptide was chosen because of its large binding constant for copper ions. When exposing the sensor to other metal ions, little response was detected, which shows the high degree of selectivity. The experiment demonstrates the feasibility of detecting metal ions using the polymer junctions.



**Figure 1.** (A) A drop of sample solution is placed onto a pair of nanoelectrodes separated with an atomic scale gap on a silicon chip. (B) Holding the nanoelectrodes at a negative potential, electrochemical deposition of a single or a few metal atoms into the gap can form a nanocontact between the two nanoelectrodes and result in a quantum jump in the conductance.



**Figure 2.** (A) A molecular junction is formed by bridging a pair of nanoelectrodes with molecules terminated with linker groups that can bond to the nanoelectrodes covalently. (B) Bridging the nanoelectrodes with conducting polymers results in polymer junctions. By attaching different molecular probes onto the polymers, specific interactions between a target species and the molecule probes are detected as a change in the conductance of the polymer junction.

## A Nanocontact Sensor for Heavy Metal Ion Detection

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### Environmental Implication/Application

The threat of heavy metal pollution is a serious environmental concern because of the toxicity of such metals on a broad range of living organisms, including humans, and the consequence of heavy metals not being biodegradable. Due to the difficulty in the remediation of sites contaminated with heavy metals, there is an urgent demand for an *in situ* sensor that is sensitive enough to monitor heavy metal ions before the concentration reaches a dangerous level. To date, heavy metals in the environment are usually measured with spectroscopic techniques, including atomic absorption and inductively coupled plasma-mass spectroscopy (ICP-MS). These techniques are well established but require samples to be collected and transported to the laboratory for analysis because the instrumentation is bulky, expensive, and requires significant maintenance and operator expertise. Moreover, sample preservations and pretreatments, generally required by these techniques, may cause sample contamination. *In situ* measurements, performed in the natural environment, are highly desirable because they provide an early detection of trace metal contaminants while minimizing errors, labor, and cost associated with collection, transport, and storage of samples for subsequent laboratory analysis. A nanocontact sensor has been developed for *in situ* detection of heavy metal ion pollution in water. The sensor can be extremely sensitive with the potential capability of detecting a few metal ions. The selectivity is based on different redox potentials of metal ions, a principle that has been successfully used in anodic stripping technique. The initial success has encouraged us to extend the nanocontacts sensor to an integrated nanosensor that can detect not only metal ions but also other environmentally important species. The integrated nanosensor includes both the nanocontact sensors and two other sensing elements, molecular junctions and conducting polymer nanojunctions. The three types of sensing elements can be fabricated on a silicon chip using a common approach. Also, various chemical species, including metal ions, can be detected using these sensing elements. The sensor will be particularly suitable for an initial onsite screening test of polluted samples, thus leading to early warning and prevention of various chemical pollutions.



## **Section 4. Remediation**

Cost-effective remediation techniques pose a major challenge for EPA in the development of adequate hazard removal techniques that protect the public and safeguard the environment. EPA supports research that addresses new remediation approaches that are more effective in removing contamination in a more cost-effective manner than currently available techniques. Substances of significant concern in remediation of soils, sediment, and groundwater include heavy metals (e.g., mercury, lead, cadmium) and organic compounds (e.g., benzene, chlorinated solvents, creosote, toluene). Nanotechnology offers the possibility of more effective remediation due to the higher surface to volume ratios of nanomaterials, and it offers the possibility of novel collection and separation protocols due to the unique physical properties of nanomaterials. Specific control and design of materials at the molecular level may impart increased affinity, capacity, and selectivity for pollutants. Reducing releases of such hazardous materials to the air and water, providing safe drinking water, and minimizing quantities and exposure to hazardous wastes are among EPA's goals.



## Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature

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### Abstract

The use of nanosized metals is emerging as an important technology for the detoxification of organics and for green synthesis. Studies involving these particles have shown increased reaction rates by several orders of magnitude. To obtain isolated nanoparticles with narrow size distributions, it is necessary to reduce the metal ions in the presence of polymers or surfactants. Our present work addresses the reduction of chlorinated organics by bimetallic nanosystems comprised of nanoscale Fe/Ni particles confined within various polymeric membrane matrices. The following synthesis techniques have been developed in support of this work: (1) direct membrane-phase metal particle formation based on the classic phase-inversion method for membrane preparation, (2) use of metal chelating polymers on membrane supports, and (3) external particle synthesis in solution followed by membrane incorporation. Using these methods, we have obtained very exciting results both in terms of synthesis of nanoparticles in membrane domain and resulting organic dechlorination. For the second method, controlled separation of background toxic metals along with organic reduction also is possible.

Following U.S. EPA quality assurance guidelines, trichloroethylene (TCE) degradation behavior has been quantified, resulting in ethane and Cl<sup>-</sup> formation using these nanocomposite membranes. Regardless of the method employed, test membranes contained only milligram levels (rather than grams) of reactive metal particles. A comparison of both surface-area normalized rate constants and metal loadings with literature values indicates significant enhancement to the traditional application of zero-valent metal nanoparticle technology. Using *in situ* techniques to immobilize nanoparticles, one can reduce particle loss, prevent particle agglomeration, and provide a means to recapture (and feasibly recycle) metal ions, which can form nonreactive hydroxide coatings on the surfaces of particles. When *ex situ* particle synthesis is employed, the Fe/Ni particles agglomerate during incorporation into the membrane phase. The agglomerates possess less available reactive surface area (Fe/Ni/H<sub>2</sub>O interface), based on electron-microscopic characterization and comparison of dechlorination rates. In addition, the use of membrane immobilization (as opposed to beads and direct ground injection) allows for the potential application of this technology to novel hybridized separation/recycle processes in the areas of industrial and municipal water treatment. Considering the performance of the bimetallic systems, the incorporation of a second metal with a high affinity for hydrogenolysis has the greatest impact on reaction rates for the given set of variables investigated.

To date, this project successfully demonstrated: (1) formation of nanoscale particles directly in cellulose acetate membranes in the 20-30 nm range; (2) crosslinking of polyacids (poly-acrylic acid) on conventional microfiltration membrane supports to entrap metals and to form (after reduction) approximately 30 nm metal particles; (3) the ability to synthesize immobilized Fe/Ni nanoparticles with a more uniform elemental distribution for superior dechlorination performance using a two-step deposition process (reduction of Fe followed by electroless plating and reduction of Ni) as opposed to the simultaneous reduction of Fe and Ni; (4) large conversions for TCE using a very small quantity of bimetallic (Fe/Ni ratio 4:1) nanoparticles in 60 min, (5) production of ethane (identified in the headspace) with only trace levels (if any) of other chlorinated intermediate by-products found in both the aqueous and headspace phases; (6) development of a novel method for preparation of Fe nanoparticles and recovery as stable slurry using anaerobic synthesis conditions; and (7) immobilization of Fe nanoparticles prepared in solution within a cellulose acetate matrix (as one example) while avoiding metal oxidation. Preliminary results with membrane immobilized Fe/Pd nanoparticles showed highly effective dechlorination of selected aromatics.

## Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature

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### Environmental Implication/Application

Chlorinated aromatics and aliphatics represent a class of commercially important but particularly toxic chemicals that enter the environment from manufacturing operations and user applications. This research project with nanostructured metals (Fe, Fe/Ni, Fe/Pd) immobilized in membrane phase is expected to have significant positive impact on pollution remediation through compact and flexible dechlorination technology development with high reaction rates at room temperature, significant reduction of metals usage, and improvement in water quality.

Three separate methodologies have been established and refined successfully for the synthesis and incorporation of nano-sized metals into thin-film polymeric matrices. These methods include: (1) direct membrane-phase Fe/Ni particle formation using a modified phase-inversion preparation of cellulose acetate; (2) *in situ* reduction of Fe and Ni or Pd ions captured by polyacrylics supported on microfiltration membrane through ion exchange/chelation; and (3) solution-phase synthesis of Fe and Fe/Ni nanoparticles followed by immobilization in a cellulose acetate thin-film under anaerobic conditions. Method #2 with metal chelating polyacrylic acids (PAA), for example, provided highly controlled nanoparticles formation and allows metal reuse because of recapture. In addition, to the rapid degradation (by Fe/Ni) of trichloroethylene (TCE) to ethane, complete dechlorination of chlorobiphenyls was achieved using milligram quantities immobilized Fe/Pd nanoparticles in membrane domain. The rapid and complete dechlorination of TCE and chloro-aromatics by milligram amount of bimetallic nanoparticles synthesis in a membrane domain is a highly significant development for both remediation and pollution prevention. Research dealing with highly improved reductive dechlorination techniques should lead to substantial improvement in environmental quality.



## Dendritic Nanoscale Chelating Agents: Synthesis, Characterization, Molecular Modeling and Environmental Applications

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### Abstract

Dendrimers are monodisperse and highly branched nanostructures with controlled composition and architecture. Poly(amidoamine) (PAMAM) dendrimers possess functional nitrogen and amide groups arranged in regular “branched upon branched” patterns. This high density of nitrogen ligands enclosed within a nanoscale container makes PAMAM dendrimers particularly attractive as high-capacity chelating agents for toxic metal ions [Cu(II)], electron transfer mediators [Fe(II)], redox active metal clusters [FeS], and metal clusters with catalytic properties [Pt(II)]. PAMAM dendrimers also can be functionalized with surface groups that make them soluble in appropriate media or bind onto appropriate surfaces. This research project explores the fundamental science of metal ion uptake by PAMAM dendrimers in aqueous solutions and assesses the extent to which this fundamental knowledge can be used to develop: (1) high-capacity and reusable chelating agents for industrial and environmental separations; and (2) FeS laden nanoparticles with enhanced reactivity, selectivity, and longevity for reductive detoxification of perchloroethylene (PCE) in aqueous solutions and subsurface formations.

To achieve these objectives, an integrated project is proposed that combines: (1) materials synthesis and characterization; (2) bench-scale measurements of metal ion [Cu(II), Fe(II), Co(II), Ni(II), Cd(II), and Ag(I)] uptake by PAMAM dendrimers in aqueous solutions; (3) x-ray absorption spectroscopic (XAS) investigations of metal ion-PAMAM dendrimer complexes in aqueous solutions; (4) bench-scale measurements and spectroscopic investigations of the reduction of PCE by water soluble FeS-PAMAM dendrimer nanocomposites and solid particles coated with FeS-PAMAM dendrimer nanocomposites; and (5) molecular modeling of (a) metal ion uptake by PAMAM dendrimers in aqueous solutions; and (b) PCE reductive dechlorination by FeS clusters.

The successful completion of this research is expected to result in: (1) more effective functional materials for recovering precious metal ions [e.g., Ag (I)] and toxic metal ions [e.g., Cu (II)] from industrial wastewater solutions by low-cost, membrane-based processes (e.g., ultrafiltration); and (2) more effective reactive media for reductive detoxification of PCE in aqueous solutions and subsurface formations.

## **Dendritic Nanoscale Chelating Agents: Synthesis, Characterization, Molecular Modeling, and Environmental Applications**

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### **Environmental Implication/Application**

Clean water is essential to human health. It also is a critical feedstock in a variety of key industries including the electronics, pharmaceutical, and food industries. The world is facing formidable challenges in meeting rising demands of clean water when the available supplies of surface water and groundwater are steadily decreasing due to increasing pollution. The ability to design and synthesize water-soluble dendrimer-based functional nanostructures with: (1) metal ion chelating functional groups; (2) redox active metal ions and clusters; (3) catalytically active metal ions and clusters; (4) hydrophobic cavities; and (5) bioactive active agents to provide new and unprecedented opportunities for developing a new generation of efficient, cost-effective, and environmentally acceptable functional materials for water treatment processes. The Dendrimer Enhanced Filtration (DEF) process (Diallo MS, U.S. Patent Pending) exploits these unique properties of dendrimers and other dendritic polymers to develop a new generation of water purification technologies. The DEF process is structured around three unit operations: (1) a reaction unit; (2) a clean water recovery unit; and (3) a dendrimer recovery unit. In the reaction unit, contaminated water is mixed with a solution of functionalized dendritic polymers to carry out the specific reactions of interest, including metal ion chelation, organic solubilization, contaminant oxidation-reduction, contaminant hydrolysis, and microbial/viral disinfection. Following completion of the reaction, the resulting solution is passed through a filtration membrane (Filtration Unit) to recover the clean water. The contaminant laden dendrimer solutions are subsequently sent to the Reactive Filtration Unit to recover and recycle the functionalized dendritic polymers. The key novel feature of the proposed DEF process is the combination of dendritic polymers with multiple chemical functionalities with the well-established technology of nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). This allows the development of a new generation of water treatment processes that are flexible, reconfigurable, and scalable. The flexibility of DEF is illustrated by its modular design approach. DEF systems will be designed to be “hardware invariant” and thus reconfigurable in most cases by simply changing the “dendrimer formulation” and “dendrimer recovery system” for the targeted contaminants. Finally, because DEF is a membrane process, it is a fully scalable process. Thus, DEF could be used to develop small mobile membrane-based water treatment systems as well as larger and fixed treatment systems.

## Synthesis, Characterization, and Manipulation of {FeS-PAMAM} Dendrimer Nanocomposites

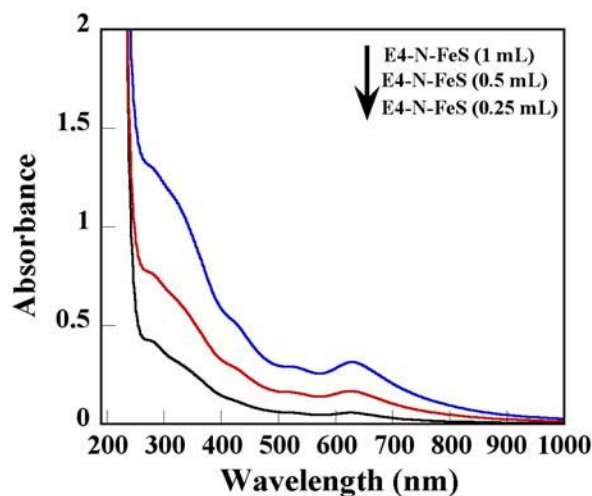
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### Abstract

Nanoparticles have received great scientific and technological interest in environmental remediation. It is expected that nano-sized FeS particles have much higher reactivity than FeS-based minerals because of their higher surface area. Dendrimers are a novel class of polymers with a spherical shape and narrow size-distribution that are used as templates to form monodispersed dendrimer nanocomposites containing metal sulfides. In this research study, FeS nanoparticles were synthesized using generation 4 polyamidoamine (PAMAM) dendrimers with amine (E4.NH<sub>2</sub>), hydroxyl (E4.N(Gly)OH), and carboxyl (E4.SAH) terminal groups as templates. These {FeS-PAMAM} nanocomposites were characterized by ultraviolet (UV)-Vis spectroscopy, zeta potential measurements, transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy dispersive spectroscopy (EDS).

*Synthesis and Characterization of Nanocomposites.* Upon addition of sulfide anions to the Fe(II)-PAMAM complexes, monodisperse {FeS} DNC particles form as a result of homogenous nucleation and simultaneous cluster growth. Figure 1 shows the UV-Vis spectra of {FeS-E4.NH<sub>2</sub>} nanocomposites in aqueous solution.



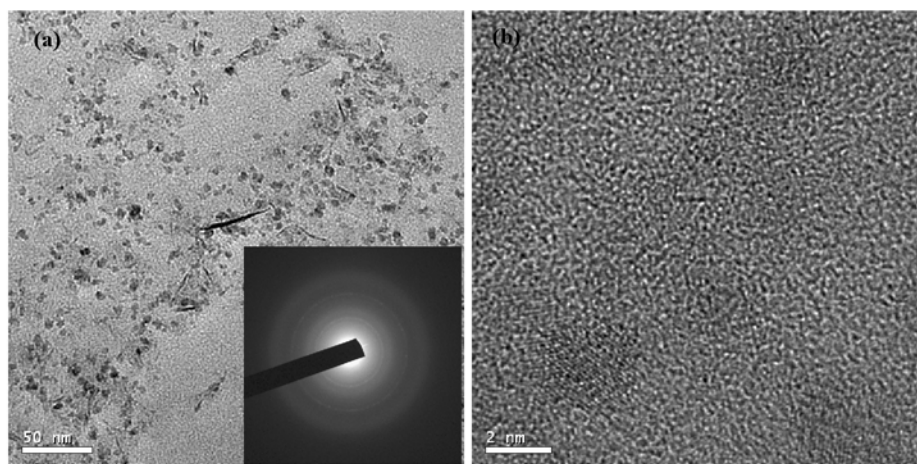
**Figure 1.** UV-Vis Spectra of FeS-E4.NH<sub>2</sub> nanocomposites containing different amount of FeS nano-particles.

In the presence of {FeS} nanocomposites, a strong buildup in absorbance at 250-1,000 nm is observed in the spectra, indicating the formation of FeS clusters. The peak at 630 nm may be attributed to interparticle interactions. In the case of {FeS-E4.N(Gly)OH} nanocomposites after the formation of FeS nano-domains, a prominent broad band develops at 250-800 nm as well as another one at 610 nm. With the increase of the {FeS} concentration, the intensity of these bands increases. The UV-Vis spectra of {FeS-E4.SAH} nanocomposites are quite different from those of {FeS-E4.NH<sub>2</sub>} and {FeS-E4.N(Gly)OH}. The absorbance profile of {FeS-E4.SAH} nanocomposites is quite similar to the template E4.SAH dendrimer in the low molar concentration range. When the FeS amount is increased, a broad band profile at 250-1,000 nm also can be observed. The sensitivity of FeS clusters to oxidation makes the exact assignment of the peaks in the UV-Vis

spectra difficult. All of the {FeS-PAMAM} nanocomposites are quite stable and soluble under anaerobic conditions.

Surface charge of {FeS-PAMAM} nanocomposites was determined by zeta-potential measurements. All of the {FeS-PAMAM} nanocomposites have the same polarity as the PAMAM templates. It was found that although the zeta potential values are fairly similar, the morphologies of {FeS-E4.NH<sub>2</sub>} prepared from different iron (II) salts are different, as demonstrated by TEM.

Figure 2 shows the TEM images of {FeS-E4.NH<sub>2</sub>} nanocomposites. It is clear that the formed particles are dominantly spherical with a diameter of  $d = 4\text{--}6$  nm. Only a small portion of needle-shaped nanocrystals can be found in the TEM images (Figure 2a). High-resolution TEM image confirms the polycrystalline nature of the particles (see Figure 2b). SAED pattern (inset of Figure 2a), which is composed of rings and bright dots, further verifies the polycrystalline phase of the formed FeS-E4.NH<sub>2</sub> nanocrystals. It is interesting to note that the morphology of FeS-E4.NH<sub>2</sub> nanocomposites can be tuned by varying the different anions from predominantly round-shaped {FeS-E4.NH<sub>2</sub>} nanocomposite particles to a needle-like shape with the length of 15-32 nm and diameter of about 2 nm. The composition of the FeS-PAMAM nanocomposites has been confirmed by EDS.

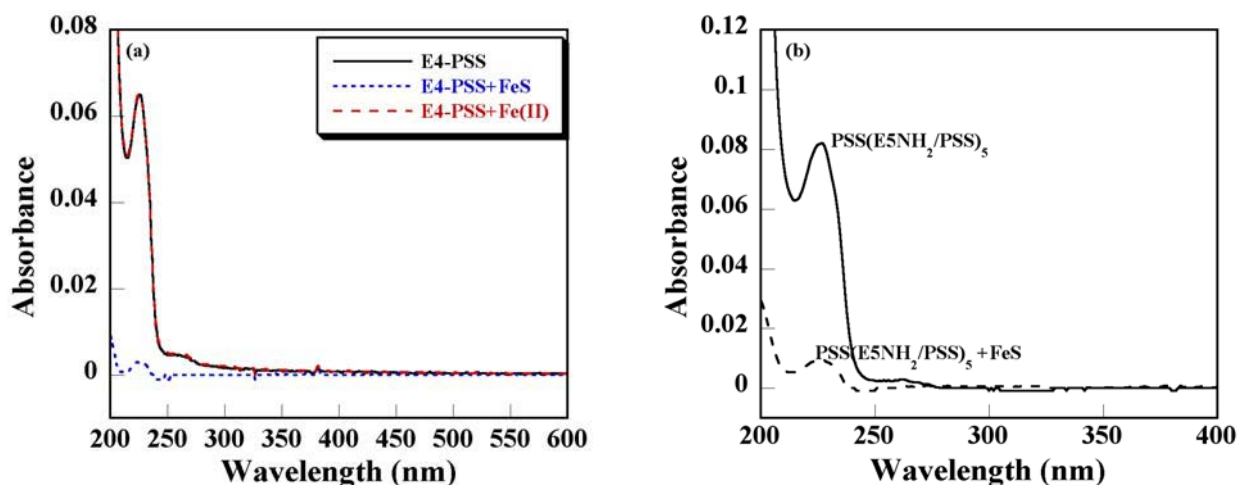


**Figure 2.** TEM images of {FeS-E4.NH<sub>2</sub>} (Sample ID: 3xys89-3) nanocomposites. (a) low magnification TEM image; Inset: SAED pattern; (b) high-resolution TEM image showing individual nanocomposite particles.

*Fabrication of Multilayer Structures.* To fabricate {FeS} nanocomposite films, either nanocomposites were deposited or preassembled multilayers of PAMAM/poly(styrenesulfonate) (PSS) were employed as matrices to facilitate the binding of Fe(II) ions. Polyelectrolyte multilayers are useful matrixes to confine inorganic nanoparticles, because the mass transfer of the nanoparticles within the multilayers is significantly limited as compared with the solution synthesis, thus overgrowth and aggregation of nanoparticles can be prevented.

The conditions for layer assembly of PAMAM/PSS multilayers were optimized by varying the deposition parameters (molecular weight of PSS, adsorption time, dendrimer generation, and dendrimer terminal groups). The formed nanoparticulate films were characterized by UV-Vis spectrometry and x-ray Photoelectron Spectroscopy (XPS).

The absorption peak at 227 nm was used to monitor the growth of PSS multilayers. It is clear that after each layer buildup of PAMAM, regular removal of PSS also is observed. E5.NH<sub>2</sub>/PSS multilayers release less PSS than E4.NH<sub>2</sub>/PSS multilayers. In addition, we found that higher Mw of PSS facilitates the multilayer construction and that longer PSS adsorption times and short PAMAM adsorption times decreased the PSS removal. Construction of E4.N(Gly)OH/PSS multilayers was unsuccessful. Structure and composition of the PAMAM/PSS multilayers did not change considerably during storage at 4 °C within 10 days. Figure 3 shows the UV-Vis Spectra of PAMAM/PSS multilayers before and after nanoparticle formation. An interesting observation is that after the formation of FeS nanoparticles, the absorbance of PSS at 227 nm decreases significantly (see Figures 3a and 3b). The FeS nanoparticulate films were not stable for more than 10 days' storage at 4 °C, probably due to partial oxidation of FeS because of exposure to air during UV-Vis measurements. XPS spectroscopy was used to confirm the composition of FeS nanoparticulate films.



**Figure 3.** (a) UV-Vis spectra of (E4/PSS)<sub>5</sub> multilayers before complexation with iron ions (solid line), complexed with Fe(II) ions (dashed line), and formation of FeS nanoparticulate films (dotted line). (b) UV-Vis spectra of (E5/PSS)<sub>5</sub> multilayers (solid line) and the respective FeS nanoparticulate films (dashed line) using (E5/PSS)<sub>5</sub> multilayers as matrixes.

*Nanocomposite Deposition Onto Silica Gel.* Preliminary experiments to deposit {FeS} nanocomposites onto mesoporous silica gels also has been conducted. Preliminary zeta-potential measurements show that the surface charge of silica gels was successfully reversed from negative to positive, indicating the formation of coating by the {FeS} nanocomposites.

*Conclusion.* Uniform {FeS} nanoparticles have been successfully synthesized using surface-modified PAMAM dendrimers as templates. The formed nanocomposite particles were found to be polycrystalline by high-resolution TEM and SAED. The nanoparticle morphology can be varied from spherical to rod-like using different anions. The UV-Vis absorbance spectra increase in the 250-1,000 nm range is proportional to the amount of FeS nanoparticles present. {FeS} nanoparticles displayed different absorbance profiles when PAMAMs of different termini were used as a template. Zeta potential measurements indicated that the formed {FeS-PAMAM} nanocomposites have the same polarity as the dendrimer templates. To deposit FeS nanoparticulate films onto substrates, PAMAM/PSS multilayers were constructed by the layer-by-layer self-assembly method, and these preassembled multilayers were used as host matrices to prepare {FeS} nanoparticles. The formed FeS nanoparticulate films exhibited less absorbance than the corresponding PAMAM/PSS multilayers. x-ray spectroscopy qualitatively confirms the presence of both iron and sulfur elements. In addition, deposition of {FeS-PAMAM} onto mesoporous silica gels also was confirmed by zeta-potential measurements, showing reversal of surface charge after the deposition of {FeS} nanocomposites.

## **Hollow and Nanoporous Iron Particles**

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### **Abstract**

Hollow iron spheres with micro- and nano-scale pores were prepared using template-directed synthesis. Iron nanoparticles were deposited on the surfaces of polymeric resin by reductive precipitation. The resin was subsequently removed by heat treatment. Pores ranging in size from nanometers (~80 percent, <100 nm) to several micrometers were observed on the shell. Specific surface area of the resulting iron spheres (0.4 mm dia.) was 2,100 m<sup>2</sup>/kg, that is 1,250 times bigger than the theoretical specific surface area of solid iron particles at the same size. Tests further suggested that the iron spheres are effective for the reduction of several common environmental pollutants, including azo dyes and chlorinated aliphatic compounds. Surface area normalized rate for the reduction of trichloroethene was 17 percent higher than that of conventional microscale iron particles. The reaction rate per unit of iron mass was approximately 1,461 times higher than that of solid iron particles at the same size. The nanoporous iron has broad potential in groundwater remediation and industrial waste treatment.

## Developing Functional Fe<sup>0</sup>-Based Nanoparticles for *In Situ* Degradation of DNAPL Chlorinated Organic Solvents

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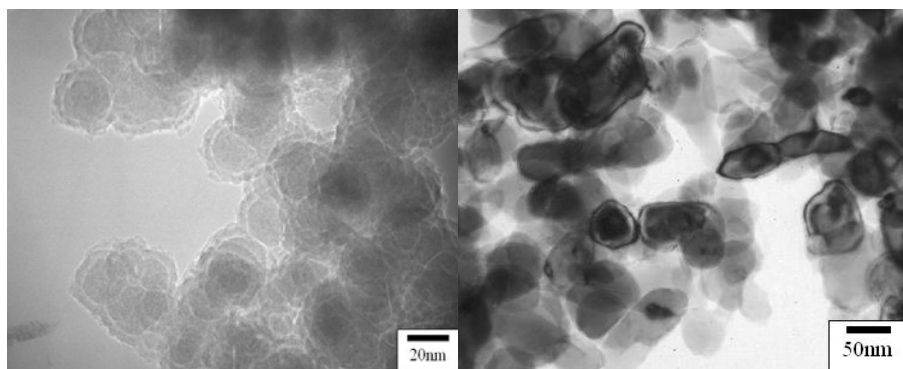
### Abstract

Dense non-aqueous phase liquids (DNAPLs) in the subsurface remain an important and costly environmental liability. DNAPL serves as a continuous long-term source of groundwater contamination. This project integrates several basic science fields to advance a particle-based strategy for *in situ* DNAPL degradation by providing targeted delivery of reactive particles directly to the DNAPL.

Over the past decade, laboratory and field studies have demonstrated that zero-valent iron and bimetallic colloids (Fe/Pd) can rapidly transform dissolved chlorinated organic solvents into nontoxic compounds.<sup>1</sup> This emerging technology also has the potential to address DNAPL contamination, a vexing contamination problem. The objective of this research is to develop and test reactive nanoscale particles for *in situ* delivery to, and degradation of, chlorinated solvents that are present as DNAPLs in the subsurface. The hypothesis under consideration is that the surfaces of reactive Fe<sup>0</sup>-based nanoparticles can be modified with amphiphilic block copolymers to maintain a stable suspension of the particles in water for transport in a porous matrix, as well as create an affinity for the water-DNAPL interface. Delivering reactive particles directly to the surface of the DNAPL-water interface will decompose the pollutant into benign materials, reduce the migration of pollutant during treatment, and reduce the time needed to remove residual pollution by other means, such as natural attenuation.

Research in the first year of the project has focused on: (1) identifying suitable Fe<sup>0</sup> nanoparticles and understanding the properties that control their reactivity with trichloroethylene (TCE); (2) synthesizing amphiphilic polymer blocks and attaching these blocks to SiO<sub>2</sub> nanoparticles; and (3) evaluating the properties of the resulting polymer-modified functional nanoparticles, including their hydrodynamic radius, stability, TCE-water partitioning behavior, and mobility in a porous matrix.

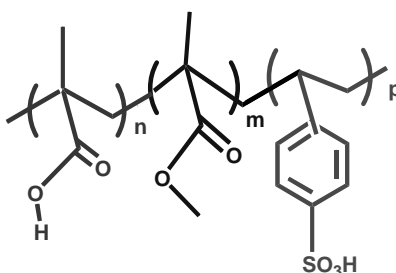
The TCE reaction rates, pathways, and efficiency of two types of nanoscale Fe<sup>0</sup> particles were measured in batch reactors; particles were synthesized from sodium borohydride reduction of ferrous iron (Fe/B), and commercially available particles (RNIP) were synthesized from the gas phase reduction of Fe-oxides in H<sub>2</sub>. Particle characterization indicated many similarities between the particles, but several distinct differences between the particle types were found. TEM micrographs of the particles evaluated are given in Figure 1(a,b). Both particle types showed a core-shell morphology. RNIP particles had an Fe<sup>0</sup> core and a magnetite (Fe<sub>3</sub>O<sub>4</sub>) shell. No other Fe-oxides were detected. Electron diffraction indicated that the core of the Fe/B (borohydride reduced particles) contains α-Fe<sup>0</sup>; however, early reports on metallic nanoparticles made from borohydride reduction of dissolved iron identified these particles as a Fe-B alloy rather than pure α-Fe<sup>0</sup>.<sup>2,3</sup> The boron content measured in these particles was approximately 4 wt percent, which is nearly 18 mol percent. Boron precipitated on the outer shell of the particles (as borate) accounts for approximately 0.2-1 wt percent, so the remaining boron is most likely present as a Fe-B alloy as previously suggested, or as distinct phases of Fe<sup>0</sup> and B<sup>0</sup>. No Fe-oxides could be detected on Fe/B, also suggesting that the shell may be a boron-oxide (borate) rather than a Fe-oxide. The effect of boron on the reactivity of these particles remains unclear.



**Figure 1.** (a) Borohydride reduction methods. (b) H<sub>2</sub> reduction method.

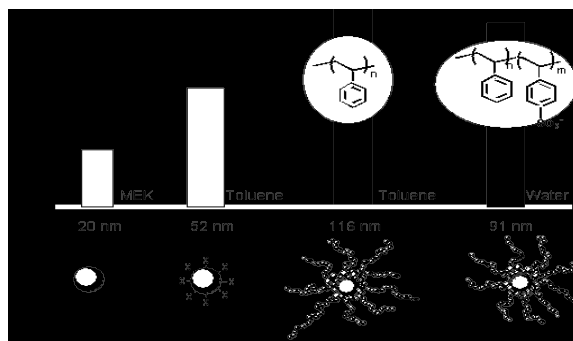
Reactivity was determined under iron limited (high [TCE]) and excess iron (low [TCE]) conditions, and with and without added H<sub>2</sub>. The reactivity and efficiency of the two particle types were very different and strongly influenced by the oxide shell properties and the presence of boron.<sup>4</sup> For example, the main reaction products using Fe/B were primarily saturated (e.g., ethane, butane), but the reaction products using RNIP were primarily unsaturated (e.g., acetylene, ethene). A concentration dependence on the TCE reaction rate and product distribution was observed. The addition of H<sub>2</sub> to the reactor headspace increased the reactivity of Fe/B, and these particles were able to use externally supplied H<sub>2</sub> to reduce TCE, suggesting that these particles are catalytic. RNIP particles did not display this behavior. The ability of Fe/B to catalyze the hydrodehalogenation of TCE may be because they are a Fe-B alloy rather than pure Fe<sup>0</sup>.

This research project involved synthesizing amphiphilic polymer blocks, grafting polymers to SiO<sub>2</sub> nanoparticles, and evaluating the properties of the resulting polymer-modified functional nanoparticles. Atom Transfer Radical Polymerization (ATRP) was used to synthesize tailored block copolymers for hybrid nanoparticles.<sup>5,6</sup> Concerning the synthesis of Fe<sup>0</sup> nanomaterials, a technique was developed for building hydrophobic-hydrophilic hybrids that consist of a short anchoring poly(methacrylic acid) block, a hydrophobic PMMA protective shell, and a hydrophilic SPSt outer block (see Figure 2). Polystyrene and poly(methyl methacrylate) have been identified as good candidates for the hydrophobic blocks. Sulfonated polystyrene has excellent water solubility and makes a good hydrophilic block. Additional methods for grafting polymers to Fe<sup>0</sup> are under investigation. ATRP also was used to synthesize particles (d<sub>p</sub>~100 nm) with an inorganic core (SiO<sub>2</sub>), and an amphiphilic polymer shell has been synthesized (see Figure 3). The particles were water soluble, formed stable suspensions, and partition to the TCE (DNAPL)-water interface. Bench-scale transport studies demonstrate that the nanoparticles are readily transported through a saturated porous matrix, suggesting that they will be transportable in the subsurface.



**Figure 2.** Hydrophobic-hydrophilic triblock copolymers containing a short anchoring group.





**Figure 3.** Polymer decorated SiO<sub>2</sub> nanoparticles.

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## Developing Functional Fe(0)-Based Nanoparticles for *In Situ* Degradation of DNAPL Chlorinated Organic Solvents

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### Environmental Implication/Application

Groundwater contamination by chlorinated organic solvents poses a significant health hazard. Dense non-aqueous phase liquid (DNAPL) present at these sites acts as a long-term source. Remediation is costly and poses significant technical challenges.<sup>1</sup> This project develops and evaluates a new class of affinity-targeted nanoscale remediation agents for efficient *in situ* remediation of DNAPL source areas in aquifers. By locating and maintaining reactive nanoiron particles at the DNAPL-water interface, fewer particles will be required and more efficient DNAPL remediation is possible relative to other methods (e.g., surfactant and alcohol flooding, bio-augmentation, and chemical oxidation). Even though the benefits of mass removal from a source zone in meeting regulatory goals are controversial, reducing entrapped DNAPL mass will lower the longevity of the source and reduce mass flux. This can mitigate future human and ecological exposure risk and the duration and cost of treatment.<sup>2</sup> Additional advantages of *in situ* treatment with nanoiron include the ability to provide significant DNAPL mass reduction without generating secondary waste streams and exposure pathways, the ability to control the delivery distance (e.g., selective placement of subsurface treatment zones), and the ability to provide residual treatment capacity to mitigate mass flux from diffusion-controlled low permeability zones. Nanoiron also has the potential for lower initial capital and life-cycle costs compared to other source zone treatments. Realizing these benefits, however, requires a fundamental understanding of the factors affecting the migration and distribution of nanoiron in the naturally heterogeneous subsurface.

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## A Bioengineering Approach to Nanoparticle-Based Environmental Remediation

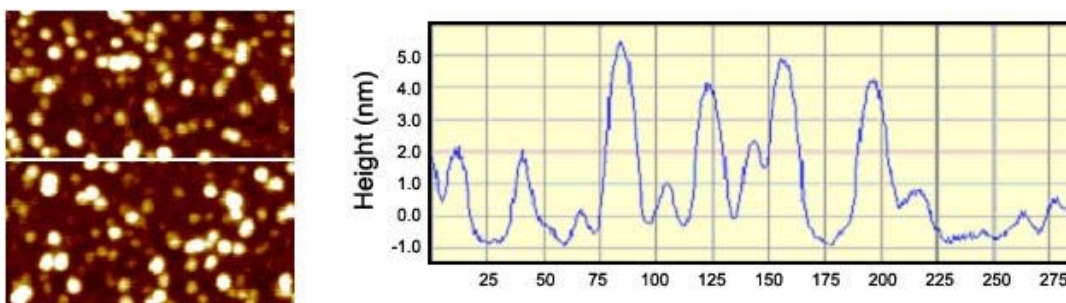
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### Abstract

Research has investigated the potential use of ferritin, and ferritin-derived compounds, as templates to synthesize nanomaterials and to use these materials as substrates for environmental degradation processes. Specifically, recent research has developed a synthetic route for the assembly of supported nano-metal oxide particles by assembling them in the biological protein ferritin and then removing the protein shell. This methodology has been further exploited to allow production of nanometallic particles of homogeneous size. Also, the fundamental chemistry of ferritin-derived systems and their activity for the remediation of toxic metals in the presence and absence of light have been investigated recently.

*Horse Spleen Ferritin (HS-Fn) as a Precursor to Supported Metal Oxide and Metallic Nanoparticles.* Figure 1 shows a Tapping Mode™ AFM image of ferrihydrite nanoparticles prepared by ultraviolet (UV)-ozone treatment of 2,500 Fe loaded ferritin dispersed on an SiO<sub>2</sub> substrate. The accompanying cross-section shows the full range of height values to be 6.5 nm, with a root-mean-square (RMS) roughness (standard deviation of the height about the average value) of 1.46 nm. The peak-to-valley height differences for the large features in the cross-section are in the 4-6 nm range. The lateral full widths at half maximum (FWHM) of the individual particles are several times larger than the heights due to tip convolution effects.

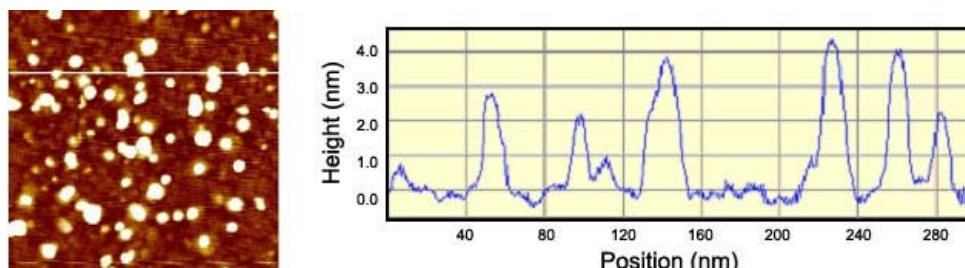


**Figure 1.** AFM Tapping Mode™ micrographs (top view) of FeOOH nanoparticles prepared by UV-ozone treatment of 2,500 Fe loaded ferritin for 60 mins at 100 °C under oxygen (< 5psi); section analysis.

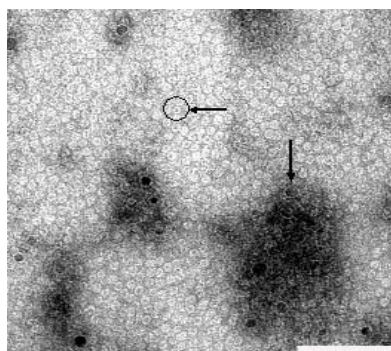
Reduction of the ferrihydrite nanoparticles to the Fe metal was conducted in a reaction cell coupled to the ultra-high vacuum (UHV) chamber. The sample was then transferred directly into the UHV chamber where X-Ray Photoelectron Spectroscopy (XPS) was conducted. The AFM image of these particular particles (see Figure 2) shows a similar morphology to the particles prior to reduction. Again, the peak-to-valley height differences for the large features in the cross-section are in the 4-6 nm range, and in this case the RMS roughness is 1.47.

*Formation of Reactive Cu Nanoparticles Encapsulated Within the Protein Cage of Ferritin.* The photolysis of Cu(II) in the presence of iron oxide-mineralized ferritin and a sacrificial reductant such as citrate or tartrate resulted in the formation of a wine-red color after 1 hour. Control reactions photolyzed in the absence of Cu(II), tartrate/citrate, or iron oxide mineralized ferritin, did not change color over the same period. No reaction was observed when solutions were left in the dark or in the presence of the unmineralized (apo) ferritin. In addition, Fe(II) alone was not observed to spontaneously reduce Cu(II) in deaerated solutions. Ex-

amination of the photolysis products by transmission electron microscopy (TEM) revealed electron-dense spherical particles (see Figure 3), with the Cu(II):ferritin ratio serving as the major determinant of particle size. Histograms of particle sizes were fit to Gaussian distributions. Higher Cu(II):ferritin ratios led to larger particle sizes, with loadings of 250, 500, 1,000, and 2,000 leading to average particle diameters of  $4.5 \pm 0.8$ ,  $9.7 \pm 4.2$ ,  $12.7 \pm 3.6$ , and  $31.4 \pm 10.1$  nm, respectively. The reactivity of these nano-Cu particles will be investigated with regard to environmental remediation reactions.



**Figure 2.** AFM Tapping Mode™ micrographs (top view) of iron nanoparticles prepared by heating 2,500 Fe loaded FeOOH nanoparticles in a reducing environment; section analysis.

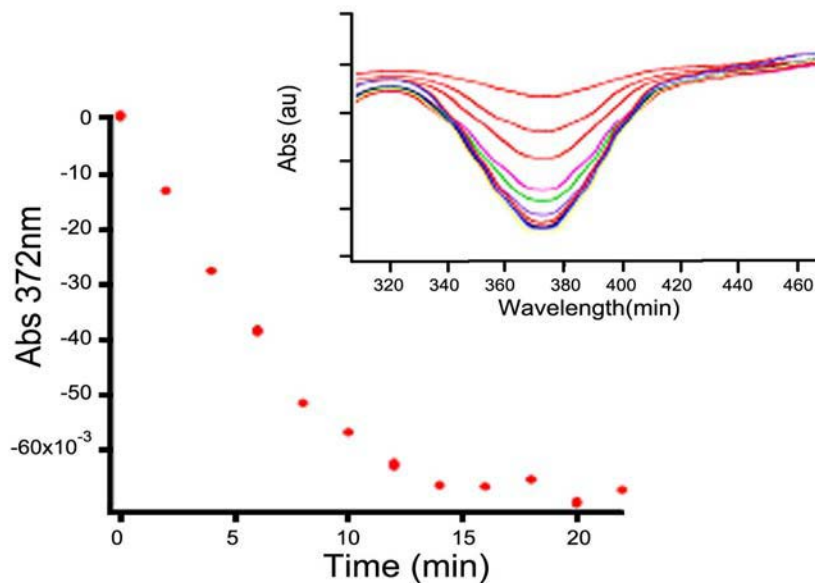


**Figure 3.** Metallic Cu particles grown within ferritin.

*Formation of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> Nanoparticles Within the Protein Cage of Ferritin.* Mineralization of mammalian ferritin using high oxidation state transition metal ions as starting materials can be achieved using a photoreduction process. The Fn cages with Fe-oxhydroxide and Ti-oxhydroxide nanoparticles have been mineralized successfully, in a spatially selective manner, and the resultant nanoparticles within the protein cages were encapsulated. The composite materials, synthesized in this way, have particle sizes that are highly monodisperse. This represents a new synthetic approach to the formation of protein encapsulated metal oxyhydroxide materials in the nanoscale size regime.

Photolysis of a solution of Fe(III) or Ti(IV) citrate in the presence of the apo-ferritin cage results in the formation of small amounts of Fe(II) and Ti(III), respectively. In the presence of oxygen, these reoxidize and hydrolyze to form nanoparticles within the protein cage. The Fe reaction could be monitored spectroscopically by the development of the ligand-to-metal charge transfer absorbance characteristic of Fe(III)-oxo polymers. When the reaction was performed in the absence of the protein cages, the development of the color was clearly associated with the formation of a rust colored precipitate. When Ti(IV)citrate was used as a starting material, there was no change in color during the photolysis reaction. In the presence of the protein cages, the reaction solution remained homogeneous, but in control reactions in the absence of the protein cage, a white precipitate

formed as the photolysis proceeded. If the photolysis was performed under inert atmosphere, the characteristic purple color of d1 Ti(III) species could be observed. The Ti-oxyhydroxide material was tested for its ability to catalyze the photoreduction of  $\text{CrO}_4^{2-}$  under Xe-arc lamp illumination (see Figure 4). This material exhibited a catalytic behavior similar to that observed previously for  $\text{Fe}_2\text{O}_3$ -ferritin.



**Figure 4.** The plot shows the loss of Cr(VI) (reflected in the loss of absorbance at 372 nm) from solution as the Ti-oxyhydroxide catalyzes its reduction to Cr(III) in the presence of light.

## A Bioengineering Approach to Nanoparticle-Based Environmental Remediation

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### Environmental Implication/Application

This research project is a multidisciplinary effort to develop a firm understanding of the properties of nano-size metal oxide compounds within the protein shell (or cage) of the iron storage protein, ferritin (spherical with a 120 D diameter). Prior to this research effort, these systems were relatively unexplored in terms of their potential use in remediation processes or as a method for synthesis of nano-scale particles of metal compounds. The entire system, consisting of the inorganic core material and protein shell, provides opportunities for the development of new catalysts for beneficial environmental chemistry by manipulating the composition and size of the core material, as well as chemically functionalizing the surrounding protein shell. The bioengineering approach proposed here has allowed us to investigate the reactivity of a variety of metal oxides (with a primary emphasis on iron oxyhydroxide), with variable nano-dimensions that may have great potential benefits to chemical and photochemical remediation schemes. Both the thermal chemistry and photochemistry of the particles toward the redox chemistry of toxic metals have been probed. The nanomaterials used in this research are ubiquitous components of soils, aquatic systems, and related environments, and have found uses in remediation strategies, but not at the nano-scale. Furthermore, results have demonstrated the ability to reduce the metal oxide core of ferritin to yield nano-sized zero-valent metal particles. Hence, our bioengineering approach yields a synthetic route to well-defined, nano-metal particles for environmental chemistry. At least one prior impediment to fully investigating and ultimately testing the utility of nano-structures has been the difficulty that their preparation and stabilization presents. The bioengineering approach has addressed this issue and has helped circumvent these difficulties in an environmentally benign and biodegradable system. The low band gap energy of most Fe(III) bearing iron oxides allows them to harness a significant amount of the solar spectrum to carry out photochemical processes. Because of its attractive semiconductor properties and low cost, iron oxides have been investigated as photocatalysts for the degradation of environmental toxins (e.g., chlorocarbons and metals). Their potential use, however, is limited due to their undergoing photoreduction (i.e, conversion of Fe(III) to Fe(II)), resulting in the deterioration of the catalytic particle. In this study, the nano-catalyst is encapsulated by a protein cage that stabilizes the iron oxide against photoreduction. Ferritin is engineered by nature to convert Fe(II) to Fe(III) so a hypothesis has been that any Fe(II) produced by photoreduction will be rapidly converted back to Fe(III) in the presence of O<sub>2</sub>. This stabilization by the protein shell will be a significant advantage over, for example, a free-standing iron oxide particle photocatalyst. While the protein cage stabilizes the core, its presence still allows the iron oxide core to drive important environmental chemistry. In our laboratory, for example, photoexcited ferritin mediates the rapid reduction of toxic Cr(VI) to the immobile Cr(III) species.

## **Section 5. Treatment**

Cost-effective treatment of pollutants poses a challenge for EPA and others in the development of effective risk management strategies. EPA supports research that addresses new treatment approaches that are more effective in reducing contaminant levels and more cost effective than currently available techniques. A variety of pollutants at different concentrations requiring removal may exist at contaminated sites, in groundwater, or in process fluids. Nanotechnology offers the possibility of more effective treatment of gases, soil, and water due to the higher surface to volume ratios of nanomaterials. In addition, collection and separation mechanisms may be more effective due to unique physical properties at the nanoscale. Specific control and design of materials at the molecular level may impart increased affinity, capacity, and selectivity for pollutants.





## NO<sub>x</sub> Reduction With Transition Metal Carbide Nanoparticles

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### Abstract

This research project deals with exploring the possibility of using alternative catalytic materials, transition metal carbides (TMC) and oxycarbides (defined as oxygen-modified carbides), to replace platinum (Pt)-group metals for the reduction of NO<sub>x</sub>. The carbides and oxycarbides of Groups 4-6 early transition metals are characterized by many unique and intriguing catalytic properties. The catalytic properties of TMC and transition metal oxycarbides (TMOC) have been the subject of many investigations in the fields of catalysis and surface science. From the catalysis literature, it is now well established that the catalytic properties of TMC and TMOC often show strong similarities to those of the more expensive Pt-group metals (Ru, Rh, Ir, Pd, and Pt). In the past few years, several surface science groups have performed fundamental investigations of the catalytic properties of TMC and TMOC. For example, our research group has performed extensive studies aimed at directly comparing the chemical reactivity of carbide surfaces with that of Pt-group metals. The results provided conclusive evidence that the decomposition of a variety of hydrocarbon molecules on TMC occurs via reaction mechanisms that are characteristic of Pt, Rh, and Pd. Furthermore, comparative studies have been performed on the decomposition of NO on the bulk surfaces of molybdenum (Mo) and tungsten (W) carbides and oxycarbides. Preliminary results clearly demonstrate that carbides and oxycarbides of Mo and W are very efficient in the conversion of the toxic NO pollutants into the harmless N<sub>2</sub> molecules, with catalytic activity and selectivity being similar or better than those of the expensive Pt-group metals.

*Decomposition of NO on Carbide Modified W(111) Surface.* It is relatively easier to study the decomposition pathways of NO on carbide modified single crystal W surfaces. This study will be extended to include the WC and WOC nanoparticles. The decomposition pathways are investigated using a combination of temperature programmed desorption, auger electron spectroscopy, high-resolution electron energy loss spectroscopy, and soft x-ray photoelectron spectroscopy. All of these surfaces exhibit high activity toward the decomposition of NO, and the only N-containing products are N<sub>2</sub> and N<sub>2</sub>O. Furthermore, all three surfaces preferentially produce N<sub>2</sub> over N<sub>2</sub>O from the decomposition of NO. Oxygen atoms, produced from the decomposition of NO, react with carbide surfaces to produce gas-phase CO at high temperatures. In addition, the results demonstrate that cycles of alternate NO/hydrocarbon treatments can regenerate the carbide overlayer on W(111), and the regenerated C/W(111) surface remains active in the decomposition of NO.

*EXAFS Study of the Nanoparticles.* Extended X-ray Absorption Fine Structure (EXAFS) analysis shows the nearest neighbor coordination in materials. These studies are important because WC surfaces have catalytic behavior for NO decomposition similar to that of Pt. If the same electronic structure and local chemistry in the WC nanoparticles are observed as in the bulk surfaces, their catalytic properties can be correlated. Previously, it was reported that the synthesis process can be modified to obtain desired surfaces. EXAFS is used to compare the local chemistry of the nanoparticles with that of bulk surfaces. Figure 1a shows the comparison of the W K-edge oscillation for the nanoparticle film, with spectra from the bulk and theory (FEFF). Figure 1b shows the edge oscillations of the nanoparticles and the bulk only. The similarity on the structure is readily observable, indicating that the local chemistry of the nanoparticles is similar to that of the bulk; therefore, catalytic properties of the nanoparticles should be similar to that of the bulk.

*NO<sub>x</sub> Decomposition With WC<sub>x</sub> Nanoparticles.* Preliminary experiments to study NO<sub>x</sub> decomposition with WC<sub>x</sub> nanoparticles were conducted in an in-line reactor. The reactor setup is shown in Figure 2. The temperature of the reactor can be controlled from RT to 1,000 °C. Currently, only the nitrogen column in the gas chromatograph (GC) is being used. This will be expanded to include the NO column very shortly. A mixture of 1 percent NO with He is used as the test gas. Flow rates are adjusted by using mass flow controllers. A base line for the experiment is obtained by passing the gas mixture through the reactor, without any catalyst. The

base line is shown in Figure 2. With the addition of the catalyst, the direct decomposition of  $\text{NO}_x$  occurs according to the reaction:  $\text{NO}_x \rightarrow \text{N}_2 + \text{O}_2$ .

The  $\text{N}_2$  signal is detected by GC. Figure 2 shows the increase in the  $\text{N}_2$  signal intensity as a function of the reactor temperature. The decomposition reaction starts to occur at temperatures above 200 °C, increases rapidly up to about 500 °C, and becomes constant beyond 500 °C. We think that the leveling off is a result of the loss of some carbon form of the nanocatalyst. The next set of experiments includes the addition of hydrocarbon to the feed gas. This will not only imitate the automobile exhaust better, it also will stabilize the carbon concentration in the nanoparticles and enhance the activity further with the temperature.

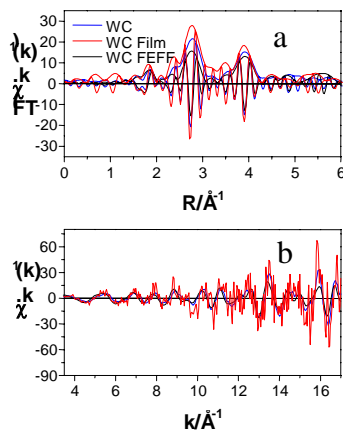


Figure 1. EXAF results comparing the nanoparticles, bulk and theoretical spectra.

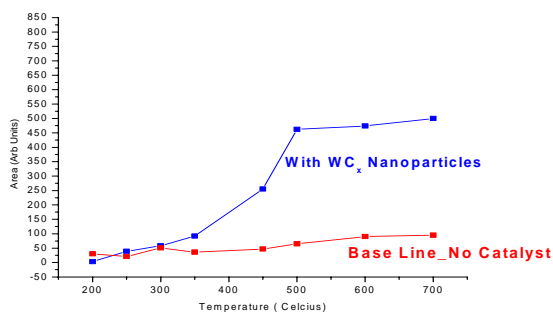


Figure 2.  $\text{NO}_x$  decomposition with and without the catalyst.

## NO<sub>x</sub> Reduction With Transition Metal Carbide Nanoparticles

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### Environmental Implication/Application

One of the major environmental pollution sources is from automobile exhaust, which causes smog and acid rain. Since 1975, the automobile manufacturers have taken a variety of steps to reduce the level of harmful emission gases, including NO<sub>x</sub>, CO, and unburned hydrocarbons (HC). At present, the emission levels of these gases can be reduced by catalytic reactions in the catalytic converter via the following chemical reactions: CO + O<sub>2</sub> -> CO<sub>2</sub>, CO Oxidation; HC + O<sub>2</sub> -> CO<sub>2</sub> + H<sub>2</sub>O, HC Oxidation; NO<sub>x</sub> + HC -> N<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub>, NO<sub>x</sub> Reduction by HC; NO<sub>x</sub> + CO -> N<sub>2</sub> + CO<sub>2</sub>, NO<sub>x</sub> Reduction by CO. In these reactions, the harmful pollutants are converted into relatively harmless molecules such as CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. These reactions occur inside the automobile catalytic converters in the presence of catalysts, which consist of mixtures of platinum-group metals, such as rhodium (Rh), platinum (Pt), and palladium (Pd). Due to their limited natural abundance in the Earth's crust, the platinum-group metals are among the most expensive elements. For example, the current price for a troy ounce of Rh is about \$2,500, which is about three times more expensive than gold. For the reason of cost effectiveness, the Pt-group metals in the catalytic converter are always kept at a minimum amount, as long as it is sufficient to reduce the emission levels to meet the government regulations.

Recently, the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB) have defined specific future targets for the reduction of emission gases of NO<sub>x</sub>, CO, and HC. For example, the target emission levels for the 1997-2003 Ultra Low Emission Vehicle (ULEV) are 0.04, 1.7, and 0.2 g/mile of HC, CO, and NO<sub>x</sub>, respectively. An even more stringent target, set by the 2004 ULEV2 Act, requires that the level of NO<sub>x</sub> be further reduced to 0.05 g/mile. The current catalytic converter technology is able to reach the 1997-2003 targets. However, it is insufficient to achieve a further decrease, by a factor of four, in the level of NO<sub>x</sub> by the year 2004. Although one of the obvious solutions is to increase the concentrations of the Pt-group metals in the catalytic converter, the cost effectiveness would eventually become a major issue for automobile manufacturers and catalyst vendors.

This research project attempts to explore the possibility of using alternative catalytic materials, transition metal carbides and oxycarbides (defined as oxygen-modified carbides), to replace Pt-group metals for the reduction of NO<sub>x</sub>. The carbides and oxycarbides of Groups 4-6 early transition metals are characterized by many unique and intriguing catalytic properties. Ever since the landmark paper by Levy and Boudart regarding the Pt-like properties of tungsten carbides, the catalytic properties of transition metal carbides (TMC) and oxycarbides (TMOC) have been the subject of many investigations in the fields of catalysis and surface science. From the catalysis literature, it is now well established that the catalytic properties of TMC and TMOC often show strong similarities to those of the more expensive Pt-group metals (Ru, Rh, Ir, Pd, and Pt). In the past few years, several surface science groups have performed fundamental investigations of the catalytic properties of TMC and TMOC. For example, our research group has performed extensive studies aimed at directly comparing the chemical reactivity of carbide surfaces with that of Pt-group metals. The results provided conclusive evidence that the decomposition of a variety of hydrocarbon molecules on TMC occurs via reaction mechanisms that are characteristic of Pt, Rh, and Pd. Furthermore, comparative studies were performed on the decomposition of NO on the bulk surfaces of Mo and W carbides and oxycarbides. Preliminary results clearly demonstrate that carbides and oxycarbides of Mo and W are very efficient in the conversion of the toxic NO pollutants into the harmless N<sub>2</sub> molecules, with catalytic activity and selectivity being similar or better than those of the expensive Pt-group metals. Nanoparticles of TMC and TMOC offer the means of obtaining the phase and crystal surface required for efficient NO reduction. If successful, the replacement of Pt-group metals by TMC or TMOC nanoparticles would offer enormous economic incentives for the effective reduction of NO<sub>x</sub>. More importantly, it might offer one of the more realistic ways to achieve the NO<sub>x</sub> emission level, 0.05 g/mile, because of the prohibitively high price of the Pt-group metal catalysts.

## Simultaneous Environmental Monitoring and Purification Through Smart Particles

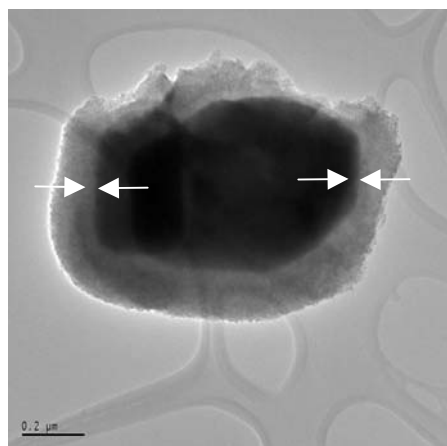
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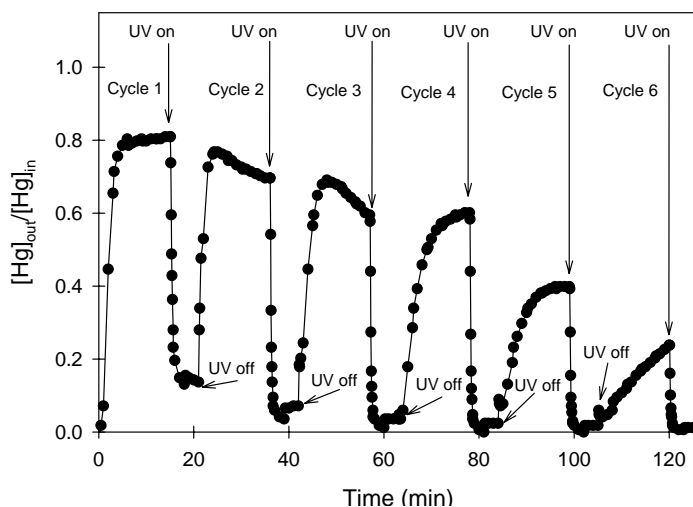
### Abstract

This research project has resulted in the development of two multifunctional composite materials. The first composite material consists of a hard magnetic core, an intermediate silica layer, and a photocatalytic titania shell (7.7 nm primary particle size). Figure 1 shows a TEM micrograph of the material (the region between the white arrows is the silica layer). The high surface area titania shell is responsible for photocatalytic oxidation of pollutants when illuminated by ultraviolet (UV) light. Under an external magnetic field as in the newly designed MAPR (Magnetically Agitated Photocatalytic Reactor), the composite can be magnetically fluidized, thus providing enhanced mixing with pollutants to be treated and enhanced exposure to UV light. The resultant advantage is improved pollutant destruction. An additional advantage is the retrieval of the material from the treated air or water media. The novel composite has been demonstrated to outperform the benchmark Degussa P25 in the destruction of phenol in laboratory tests.

The project team also has developed a silica-titania composite that possesses synergistic photocatalytic oxidation and adsorption. The nanostructured silica substrates provides high surface area, but the nanosized titania particles are responsible for photocatalytic oxidation of pollutants. Excellent removal of elemental mercury vapor has been demonstrated. A unique feature of the novel composite is that the adsorption improves over time as shown in Figure 2. Based on the mechanisms identified, the team has developed a second generation composite that has extraordinary mercury removal capability without the excitation of UV light.



**Figure 1.** TEM micrograph of titania/silica/magnet composite.



**Figure 2.** Fractional  $\text{Hg}^0$  concentration at reactor outlet (showing improved adsorption over time).

## **Simultaneous Environmental Monitoring and Purification Through Smart Particles**

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### **Environmental Implication/Application**

Photocatalytic TiO<sub>2</sub> nanoparticles have been well recognized for their superior ability to oxidize pollutants. However, its separation from treated water has been a serious limitation. Unintentional release of nanoparticles into the environment also causes concerns due to their potential toxicity. Mass transfer limitation for TiO<sub>2</sub> nanoparticles coated on tubes or beads is another constraint of the current TiO<sub>2</sub> technology. The multifunctional magnetic silica-titania composite material developed by the University of Florida has overcome these limitations and brings several advantages to the environment. Magnetic fluidization of the material allows its enhanced mixing with pollutants to be treated and enhanced by exposure to a light source. Pollutant destruction kinetics is improved, thus reducing the amount and energy required for pollutant treatment. Its movement can be well adjusted and confined to a prescribed space using a controlled magnetic field. Retrieval of the material from treated air or water media also can be accomplished easily by magnetic separation. By incorporating silica, photo-dissociation of the magnetic core, which commonly occurs with other magnetic materials, does not exist anymore. This prevents introduction of heavy metals into water and reduces unnecessary consumption of materials. In short, the magnetic silica-titania based nanotechnology enables us to improve environmental quality with less consumption of materials and energy.

In parallel, a nanostructured silica-titania composite has been developed that possesses synergistic photocatalytic oxidation and adsorption capabilities. The nanostructured silica provides high surface area for adsorbing pollutants as a concentrator while the nanosized TiO<sub>2</sub> particles can photocatalytically oxidize pollutants. The synergistic combination allows a reduced energy requirement as the light source only needs to be provided. This material has been successfully tested for removing elemental mercury vapor in air. The material changes its color as oxidized mercury accumulates on the material. The change of material color provides a convenient tool to identify the state of the material. The concentrated accumulation of oxidized mercury can be recycled by heat treatment or vacuum treatment. The recycle reduces demand of mercury from mining, which is known to yield significant environmental damages. The silica-titania composite is regenerated in the meantime. The regeneration prolongs the lifetime of the material, thus reducing the required amount of material to be supplied. Furthermore, no hazardous waste is generated by this technology, which is in contrast to current carbon-based technology. Hazardous waste disposal of mercury-loaded carbon is costly and may have a long-term environmental impact. During the research, a unique feature of improved adsorption over time has been observed, which has never been reported before. The mechanism of this feature has been identified, which led to the development of a second generation composite. The benefit of this new material is its independence from ultraviolet light, thus reducing the energy requirement.

## **Nanoscale Biopolymers With Tunable Properties for Improved Decontamination and Recycling of Heavy Metals**

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### **Abstract**

Heavy metal ions are major sources for pollution of the biosphere, and they are usually found as co-contaminants in many Superfund sites. Current technologies are inadequate to reduce metal concentrations to acceptable standards and to separate these heavy metals from a waste mixture for potential recycling. The goal of this project is to develop a technology utilizing nanoscale metal-binding biopolymers with customizable properties for the differential sequestration and recovery of different heavy metals in a mixed-metal waste. Tunable biopolymers based on elastin-like polypeptides (ELP) will be generated to demonstrate this feasibility by specifically incorporating different metal binding domains into ELP biopolymers with dramatically different transition temperatures. Initial feasibility studies will utilize two different ELP building blocks containing either polyhistidine or synthetic phytochelatin as the metal-binding domain. Application of this technology for soil remediation also will be discussed. This technology serves as an example to provide an efficient and nontoxic solution to the removal and separation of heavy metal contamination.

## **Nanoscale Biopolymers With Tunable Properties for Improved Decontamination and Recycling of Heavy Metals**

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### **Environmental Implication/Application**

The biosynthetic approach is environmentally friendly and allows precise and independent control of the length, composition, and charge density of the interacting end blocks and metal-binding domains, thus allowing the flexibility in designing tunable biopolymers that can undergo transition from water-soluble into aggregate forms under a wide range of conditions. Such precise control is valuable to satisfy the needs of different process conditions. Compared to conventional chemical chelators or chelating polymers, the proposed biopolymers are environmentally friendly because no toxic chemical is required for their synthesis and regeneration can be achieved easily. This strategy, if successful, will provide a low-cost and environmentally benign technology for heavy metal removal.

## **Use of Ozonation in Combination With Nanocrystalline Ceramic Membranes for Controlling Disinfection By-Products**

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### **Environmental Implication/Application**

The production of disinfection by-products (DBPs) during the disinfection process in drinking water is a very important issue since some DBPs, such as trihalomethanes (THMs), are carcinogenic or potentially carcinogenic. In addition, THMs in drinking water have been linked to miscarriages, premature births and low birth weight babies. Because of their greater perceived health risk, under Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule, which was promulgated in December 1998, the maximum contaminant level (MCL) for total THMs (TTHMs) was lowered from 100 µg/L to 80 µg/L, and that for the sum of five haloacetic acids (HAA5). The proposed Stage 2 regulations will further limit the levels of THMs and other DBPs. Therefore, novel ways to further remove DBP precursors to meet the more stringent regulations concerning DBPs must be developed.

This proposed ozonation/membrane process combines ozonation and membrane technology to control DBP precursors and raise the quality of treated water. Inactivation of pathogens in the residual stream, reduction of membrane fouling, and an increase in the efficiency of natural organic matter (NOM) destruction by ozone could be achieved in this process as well. If this proposed process is successfully developed, it will help drinking water treatment plants upgrade or retrofit their conventional system and comply with the Stage 2 D/DBP standards.



## **Section 6. Fate, Transport, and Transformation**

As nanotechnology progresses from research and development to commercialization and use, manufactured nanomaterials may be released into the environment. EPA is interested in determining the routes through which manufactured nanomaterials enter the environment and their modes of dispersion, interaction, and degradation within the environment: soil, water, atmosphere, and biosphere. Persistence and bioaccumulation/biomagnification are factors that offer guidance for determining whether substances are classified as hazardous. Although the short-term effects of a toxic nanomaterial may result from a single exposure, the long-term effects due to bioaccumulation and persistency may be more severe, ranging from lasting health problems to organ damage. Biomagnification, a side effect of bioaccumulation, is the amplification of the concentrations of nanomaterials in each successive step in the food chain. Keeping in mind the novel properties of nanomaterials, new or modified test methods, basic datasets for environmental fate/transport endpoints, and applications of new or existing air dispersion, soil transport, groundwater models may be needed.



## **Adsorption and Release of Contaminants Onto Engineered Nanoparticles**

*Mason B. Tomson  
Rice University, Houston, TX*

### **Abstract**

As nanotechnology develops into a mature industry, the environmental and health effects of its core materials become of increasing importance. This research project aims to evaluate the sorption and release of contaminants onto the surfaces of engineered nanoparticles. Specifically, four hypotheses will be tested in this research: (1) carbon nanostructures have a high capacity for sorption/desorption hysteresis with polynuclear aromatic hydrocarbons and other common organic contaminants; (2) the sorption capacity of inorganic nanomaterials for heavy metals is the same as the corresponding bulk crystals, when corrected for surface area; (3) the sorption of naturally occurring humic materials and surfactants to metal oxide and carbon nanomaterials will diminish the sorption capacity of heavy metals on oxides and increase the sorption of hydrocarbons on carbon nanomaterials; and (4) the transport of nanoparticles in soils, sediments, and porous media will be vastly greater than the corresponding colloids or bulk materials.

This project is motivated by the interest in collecting data needed for risk assessments of nanoparticle materials. It is never too early in an emerging technology to consider issues of environmental impact; for nanotechnology, sound technical data concerning the health risks and potential exposure of nanomaterials in water will allow nanomaterials to be targeted at the most appropriate applications. Such information also will allow environmental issues to factor in early into manufacturing development, leading to a greener and ultimately more economic industry. There is no existing technical literature that speaks to the issue of the environmental impacts of nanoengineered materials. However, related areas concerning contaminant sorption to minerals and clays, as well as the importance of particle-mediated transport to exposure calculations are quite relevant and have informed our thinking about this problem.

The introduction of a new class of materials into consumer products will require information about the potential behavior and risks that these systems pose to the environment and people. The high surface area of nanoparticles means that even weak sorption of contaminants to surfaces can introduce a significant new pathway for exposure, or removal, of molecular contaminants in biological systems. This research project provides the information needed to assess whether this risk is substantial for nanoparticles disposed of in groundwaters. It is expected that this research would yield the necessary parameters to understand the fate of engineered nanoparticles in the environment and to yield the necessary parameters for future development of risk assessment of the engineered nanoparticles. The research group has conducted the first groundwater contamination studies. Recently, a dual equilibrium desorption equation was developed and it has been considered by many consulting companies and regulatory agencies for adoption into their remediation scheme and regulatory guidelines.

## **Adsorption and Release of Contaminants Onto Engineered Nanoparticles**

*Mason B. Tomson  
Rice University, Houston, TX*

### **Environmental Implication/Application**

The introduction of a new class of materials into consumer products will require information about the potential behavior and risks these systems pose to the environment and people. The high surface area of nanoparticles means that even weak sorption of contaminants to surfaces can introduce a significant new pathway for exposure, or removal, of molecular contaminants in biological systems. This research project provides the information needed to assess whether this risk is substantial for nanoparticles disposed of in groundwaters. It is expected that this research would yield the necessary parameters to understand the fate of engineered nanoparticles in the environment and to yield the necessary parameters for future development of risk assessment of the engineered nanoparticles. The first groundwater contamination studies have been completed. Recently, a dual equilibrium desorption equation was developed, and it has been considered by many consulting companies and a regulatory agency for adoption into their remediation scheme and regulatory guideline.

## **Impacts of Manufactured Nanomaterials on Human Health and the Environment: A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol**

*Vicki H. Grassian*

*Department of Chemistry, University of Iowa, Iowa City, IA*

### **Abstract**

The goal of this research project is to determine the potential effects of manufactured nanomaterial aerosol on human health. Manufactured nanomaterials will be characterized using a wide variety of techniques and analysis methods, including surface spectroscopy so that both bulk and surfaces properties can be understood on a molecular level. Because a number of physical and chemical properties are size-dependent on nanometer length scales, it is important to fully characterize the nanoparticles used in these studies. These well-characterized particles will then be used for inhalation and exposure studies using laboratory animals. There will be additional characterization once the aerosol has been generated to determine if the particles aggregate or retain the size distribution determined prior to aerosol generation. Toxicology assessments of the animals will include murine acute pulmonary inflammation assay, murine subacute pulmonary toxicology evaluation, and murine microbial challenge host resistance evaluation to screen for acute and subchronic pulmonary effects.

## **Impacts of Manufactured Nanomaterials on Human Health and the Environment—A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol**

*Vicki H. Grassian, Patrick O'Shaughnessy, and Peter Thorne  
University of Iowa, Iowa City, IA*

### **Environmental Implication/Application**

In this work, the potential effects of manufactured nanomaterial aerosol on human health will be investigated. It is expected that these studies will help answer questions as to the potential impact of manufactured nanomaterial aerosol on human health as there is clearly a lack of information in this regard. Two important factors of the proposed activities are the comparison of the potential health effects of manufactured nanomaterials to other anthropogenic sources of ultrafine particles from combustion processes and the effect of surface coatings, from manufacturing and atmospheric processing, on the toxicity of these particles.

## Chemical and Biological Behavior of Carbon Nanotubes in Estuarine Sedimentary Systems

*P. Lee Ferguson*

*Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC*

### Abstract

The general objectives of the proposed research are to: (1) determine factors controlling the fate of single-walled carbon nanotubes (SWNTs) and their synthetic by-products in estuarine seawater, sediment, and sediment-ingesting organisms; (2) examine the impact of SWNTs and by-products on the disposition of model organic contaminants in estuarine sediments; (3) determine whether the presence of SWNTs and by-products in estuarine sediments affects the bioavailability of model organic contaminants to estuarine invertebrates; and (4) assess the toxicity of SWNTs and by-products to suspension- and deposit-feeding estuarine invertebrate models in seawater suspension alone, and/or in combination with estuarine sediments.

This research project will address these objectives through a series of experiments designed to provide a holistic picture of the behavior of SWNTs and their synthetic by-products on entry into the estuarine environment. These experiments will include tracing the fate and phase-association of  $^{14}\text{C}$ -SWNTs and by-products under simulated estuarine conditions and through ingestion by deposit-feeding organisms, batch sorption studies to examine the affinity of SWNTs for model hydrophobic organic contaminants (HOC) in the estuarine environment, laboratory-scale bioaccumulation experiments designed to test modulation of HOC bioavailability by co-occurring SWNTs in estuarine sediments, and dose-response experiments designed to test the potential for SWNTs and by-products to directly cause adverse effects on a sensitive estuarine infaunal invertebrate (the harpacticoid copepod, *Amphisascus tenuiremus*).

The proposed work will, for the first time, address the physical, chemical, and biological behavior of novel and emerging carbon nanotube materials under environmental conditions typical of estuaries. In total, this study will address not only the potential for SWNTs to be transported, accumulate, and cause direct deleterious effects within estuarine environments, but also the potential for linked effects on the biological and chemical behaviors of known priority pollutants common in estuarine sediments. This combined approach represents a novel way of addressing the environmental impact of an emerging synthetic nanomaterial and will thus provide the U.S. Environmental Protection Agency and the scientific community with an entirely new and highly relevant dataset for risk assessment of SWNT-derived contaminant discharge. Further, the work will generate new scientific knowledge related to the behavior of these highly novel nanomaterials under conditions not normally tested in the course of nanoscience research (e.g., nonmammalian biological systems, highly saline aqueous solutions, and complex sediment media). This knowledge may become useful in designing new nanoscale technologies in, for example, environmental engineering or “green” manufacturing techniques.

## **Chemical and Biological Behavior of Carbon Nanotubes in Estuarine Sedimentary Systems**

*P. Lee Ferguson*

*Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC*

### **Environmental Implication/Application**

This research project will illuminate the potential for commercially relevant single wall carbon nanotube (SWNT) material to adversely affect estuarine environments on intentional or inadvertent release. The physical, chemical, and biological behavior of these novel and emerging materials will be studied under environmental conditions typical of estuaries. Specifically, this study will provide information on the phase-behavior (physico-chemical partitioning) of SWNTs among estuarine water, colloidal suspension, and suspended/bedded sediments. The resulting data will be crucial for predicting/modeling the environmental fate, transport, and risk of these materials in impacted estuaries.

In addition, this work will provide detailed and valuable information on the potential for adverse effects of these materials (possibly related to differential feeding selection or gut/feeding appendage fouling) on trophically important members of the estuarine food web. This work will be structured to address the relevance to the fate of priority pollutants in estuarine sediments impacted by SWNTs. Furthermore, this research will generate new scientific knowledge related to the behavior of these novel nanomaterials under estuarine conditions, which may prove useful in the design of new nanoscale technologies.



## Transformations of Biologically Conjugated CdSe Quantum Dots Released Into Water and Biofilms

Patricia A. Holden

Donald Bren School of Environmental Science and Management, University of California,  
Santa Barbara, CA

### Abstract

Semiconductor nanocrystals (quantum dots [QDs]) differ in important ways from bulk semiconductor materials. Their increased band gap means that they function as strong oxidizing and/or reducing agents, and their small size allows them to pass into living cells. Conjugation of biomolecules to the crystal surface can alter any or all of these properties. In preliminary experiments, it was observed that nucleobase-conjugated cadmium selenide (CdSe) QDs were actively taken up by soil and aquatic bacteria (e.g., *Bacillus subtilis* and *Escherichia coli*). Effects on microbial viability attributed to the presence of the QDs included slower doubling times, heavy metal sequestration, and “blebbing” of metals into the environment. In this project, these effects will be quantified using a variety of biologically conjugated QDs and an assortment of microbial species, monitoring the process of quantum dot uptake and breakdown, and characterizing the breakdown products that result from bacterial metabolism of these particles. Possible hazards to microbial populations with extrapolation to humans through contamination of soil and water with quantum dot breakdown products will be analyzed and quantified.

Bare, core-shell and biologically conjugated QDs will be studied. Abiotic breakdown kinetics and products in aqueous environments will be determined by inductively coupled plasma (ICP) spectrometry for QDs as a function of exposure to light, pH, and oxidizing or reducing conditions. In preliminary experiments, biologically conjugated QDs are easily taken up by *B. subtilis*, but the process is light and pH dependent. Some breakdown occurs inside and outside of cells. Working with *Pseudomonas aeruginosa* and *Staphylococcus aureus* to represent Cd-sensitive and Cd-resistant strains, population growth and fluorescence for pure liquid cultures previously exposed to QDs will be quantified. Conventional methods (shake flask, viable and direct counting over time) will be used to assess the effects of labeling on bacterial growth rates under high and low nutrient conditions. QD fluorescence will be monitored throughout, adjusting final results for the dilution effect of growing populations. Concentrations of Cd and Se will be assessed inside and outside cells, and membrane associations of whole QDs and breakdown products will be quantified. The relationship of QD release and breakdown to cell viability will be assessed. DNA damage in bacteria will be assessed by quantifying 8-oxoguanine, a product of oxidative DNA damage, by microscopy and a commercially available fluorescent label. These experiments will provide basic insight into cellular interactions with QDs. The potential for single base pair damage from whole QDs and breakdown products will be assessed using time-correlated single photon counting techniques. Because most bacteria exist as biofilms in nature, mono- and dual-species bacterial biofilms will be cultured under continuous flow conditions in a commercially available flow cell. Using digital photomicroscopy and computerized image analysis, the effects of QD labeling on biofilm growth will be assessed. Unsaturated biofilms also will be cultured on membranes to assess the effects of QD labeling on development under soil-like conditions and as a function of nutrient and water availability. Cryo-environmental scanning electron microscopy (ESEM) coupled with energy dispersive spectrometry (EDS) will be used to visualize ultrastructural QD associations. Biofilms cultured in the absence of QDs will be exposed under a range of experimental conditions and assessed over time for viability and QD content. For all biofilm experiments, QD effects on exopolymeric substances (EPS) can be quantified by gas chromatography-mass spectrometry of derivatized glycosyl residues, and DNA and protein content can be determined by standard fluorometric and colorimetric methods, respectively.

Finally, column studies, using packed porous media under saturated and unsaturated conditions, will be conducted to assess QD and Cd mobility as a function of bacterial colonization. Because EPS is expected to chelate Cd, whole QDs, Cd, Se, and biopolymers will be quantified in breakthrough experiments, followed by

sacrificial characterization of residual analytes. Overall, this research project is intended to provide a comprehensive investigation into bacterial-QD interactions, which is needed to understand the impact and fates of these nanoparticles in the environment.

## **Transformations of Biologically Conjugated CdSe Quantum Dots Released Into Water and Biofilm**

*Patricia A. Holden<sup>1</sup> and Jay L. Nadeau<sup>2</sup>*

*<sup>1</sup>Donald Bren School of Environmental Science and Management, University of California, Santa Barbara, CA; <sup>2</sup>McGill University, Montreal, Quebec, Canada*

### **Environmental Implication/Application**

Cadmium selenide (CdSe) quantum dots (QDs) are nanoscale semiconductors that have widespread applications in biotechnology and medicine. The broad applications of these particles in medical diagnostics and other settings brings into question their impacts on nontarget organisms in the natural environment. This project seeks to discover the fates of CdSe QDs under abiotic and biotic conditions characteristic of the natural environment. CdSe QDs are altered by solution chemistry as well as sunlight. CdSe QDs damage DNA, but by what mechanism? CdSe QDs are likely to affect bacteria in water and biofilms, which could have implications for how these particles are transferred to higher life forms. Very little is known regarding the fates of CdSe particles in the environment. This research project will seek to discover the physical and biological transformation of these particles and the effects, relative to dissolved Cd ions, on bacterial function. The results will be important for strategically planning the handling and disposal of CdSe QDs and their overall management, so that potential CdSe-mediated environmental degradation can be circumvented.

## Repercussion of Carbon-Based Manufactured Nanoparticles on Microbial Processes in Environmental Systems

*Ronald F. Turco, Bruce M. Applegate, and Timothy Filley  
Purdue University, West Lafayette, IN*

### Abstract

The use of nanotechnology has tremendous potential for economic growth and is a key feature of sustainable development. Despite the impending increase in industrial production and the certain releases of Carbon Based Manufactured Nanoparticles (CMNPs) to the environment, almost nothing is known about their environmental impact. To engage in a publicly transparent evaluation of risks and benefits, and to develop public policy and technology to manage potential risks, fundamental scientific environmental research must be completed. The goal of this research project is to provide fundamental information about the impact of CMNPs on water, soil, and subsurface ecosystems.

*Objective 1:* There will be a shift in the structure of soil microbial populations in systems exposed to CMNPs as the nanomaterial will exert pressure on the microbial population. The intrinsic features describing activity will be estimated in four ways, including: (1) drawing information from the ratio of key fatty acids taken from the phospholipid fatty acids fraction (PLFA) and relating it to a background status of the soil microbial populations; (2) using genetic approaches, for example, density gradient gel electrophoresis (DGGE) with both bacterial and fungal primers; (3) using enzyme assays for dehydrogenase, urease, and cellulase; and (4) respiring and trapping CO<sub>2</sub> to estimate aerobic activity in the presence of CMNPs.

*Objective 2:* The long-term fate of CMNPs in the environment and their entrance into soil and aquatic biogeochemical cycles mostly will be a function of the activity of the specific oxygenase, ligninase, laccase, and fenton systems resident in microbial populations. Using <sup>13</sup>C-fullerenes in soil microcosm studies outlined in Hypothesis 1, CMNP carbon will be tracked to determine how the soil microbial biomass responds to CMNPs. The degree to which CMNP carbon is assimilated into microbial biomass, or is converted to a form bound with soil carbon, also will be assessed. Additionally, various litter forms (wood and leaves) spiked with <sup>13</sup>C-labeled fullerene with aggressive decay fungi will be inoculated to assess the degree to which CMNP carbon is assimilated into fungal biomass or converted to functionalized forms (free and bound).

*Objective 3:* Water-borne CMNPs represent an, as yet, unassessed toxicological risk to aquatic organisms because of their capacity to physically interact with cell membranes, possibly causing harm to the cells. A lux-gfp based assay will be used to estimate the impact of CMNPs on the processes of respiration and growth, allowing development of the first CMNP structure-to-microbial function model. This objective will involve monitoring bacterial bioluminescence to evaluate the impact of CMNPs (amount or structure) on bacterial response in aqueous systems.

The expected results of this research project are very substantial. The knowledge gained from this research will be used by government and industry for developing public policy and technology for the management of any environmental risks from CMNPs. This research also can be integrated with educational programs and used to disseminate knowledge about the behavior of nanomaterials.

## **Repercussion of Carbon-Based Manufactured Nanoparticles on Microbial Processes in Environmental Systems**

*Ronald F. Turco, Bruce M. Applegate, and Timothy Filley  
Purdue University, West Lafayette, IN*

### **Environmental Implication/Application**

This research project will provide the scientific community with a method for assessing the toxicity of carbon-based manufactured nanoparticles. This project will result in fundamental information regarding the impact on soil, water, and subsurface ecosystems. In addition, this project will study the shift in the structure of microbial populations in systems exposed to these materials, and the resulting effect(s) mostly will be a function of the activity of specific enzyme systems within the microbial systems.

## **The Fate, Transport, Transformation, and Toxicity of Manufactured Nanomaterials in Drinking Water**

*Yongsheng Chen, Paul Westerhoff, John Crittenden, and David Capco  
Department of Civil and Environmental Engineering and Department of Biology,  
Arizona State University, Tempe, AZ*

### **Abstract**

Although the current market for nanomaterials is small and their concentration may not be high enough in the environment to cause human health or environmental problems, this market is increasing rapidly and the discharge of nanomaterials to the environment in the near future could be significant as manufacturing costs decrease and new applications are discovered. The accumulation of nanomaterials in cells may have significant environmental and human impacts. However, at present, very little is known about the fate, transport, transformation, and toxicity of these man-made nanomaterials in the environment.

The objectives of this project are to: (1) characterize the fundamental properties of nanomaterials in aquatic environments, (2) examine the interactions between nanomaterials and toxic organic pollutants and pathogens (viruses), (3) evaluate the removal efficiency of nanomaterials by drinking water unit processes, and (4) test the toxicity of nanomaterials in drinking water using a cell culture model system of the epithelium. This study considers the physical, chemical, and biological implications of nanomaterial fate and toxicity in systems that will provide insight into the potential for nanomaterials to be present and of health concern in finished drinking water.

The proposed work will provide fundamental information about the fate, transport, and transformation of nanomaterials in the drinking water resources and the first evidence that such nanomaterials can or cannot be removed by conventional drinking water treatment processes. An improved assessment will be developed for the potential exposure risks of nanomaterials in drinking water. This research would ultimately provide essential information that would support policy and decision-making regarding handling, disposal, and management of nanoscale materials in commerce, manufacturing, and the environment.

## **Section 7. Toxicology**

As nanotechnology progresses from research and development to commercialization and use, it is likely that manufactured nanomaterials and nanoproducts will be released into the environment. EPA is charged with protecting human health and the environment, as well as ensuring that the application of engineered nanotechnology products occur without unreasonable harm to human health or the environment. The unique features of manufactured nanomaterials and a lack of experience with these materials hinder the risk evaluation that is needed to inform decisions about pollution prevention, environmental clean-up and other control measures, including regulation. Beyond the usual concerns for most toxic materials, such as physical and chemical properties, uptake, distribution, absorption, and interactions with organs, the immune system and the environment, the adequacy of current toxicity tests for chemicals needs to be assessed to develop an effective approach for evaluating the toxicity of nanomaterials. To the extent that nanoparticles are redox active or elicit novel biological responses, these concerns need to be accounted for in toxicity testing to provide relevant information needed for risk assessment to inform decision making.





## Short-Term Chronic Toxicity of Photocatalytic Nanoparticles to Bacteria, Algae, and Zooplankton

Chin Pao Huang and Donald C. Phillips

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### Abstract

The unique physical and chemical properties of photocatalysts can stress the aquatic environment. This research project will evaluate the short-term chronic toxicity of photocatalytic nanoparticles to bacteria, algae, and daphnia. Properties such as particle size, location and level of the band gap energy, surface charge, and chemical composition are keys to the ecotoxicity of photocatalytic nanoparticles. Generally, as the particle size decreases, the toxicity of the photocatalysts increases and the band gap energy may shift toward the visible end of the light spectrum, making smaller photocatalysts more sensitive to visible light. Photocatalysts can exhibit oxidation or reduction reactions or both. Photooxidation and photoreduction can have significant impacts on microorganisms. Nanoparticles in the aqueous environment also can acquire surface charges, which can affect specific chemical interactions between the nanoparticles and the microorganisms of interest.

This research project will assess the short-term chronic toxicity of photocatalytic nanoparticles to selected aquatic microorganisms. Nanoparticles possessing photocatalytic or semiconducting properties, including infrared (IR) sensitive CdSe and MoS<sub>2</sub>, visible light sensitive GaP, CdS, and ultraviolet (UV) light sensitive TiO<sub>2</sub>, ZnO, and SnO<sub>2</sub> will be studied. Testing organisms will cover three trophic levels: bacteria, algae, and primary consumers (e.g., zooplankton). *Escherichia coli* and a mixed commercial bacterial culture, *Selenastrum capricornutum* (green algae) and *Ceriodaphnia dubia* (daphnia), will be selected as the testing organisms. The specific objectives are to determine: (1) the acute toxicity of photocatalytic nanoparticles to a mixed bacterial culture; (2) the short-term chronic toxicity of photocatalytic nanoparticles to a pure bacterial culture of *E. coli*; (3) the short-term chronic toxicity of photocatalytic nanoparticles to *C. dubia*; (4) the short-term chronic toxicity of photocatalytic nanoparticles to *S. capricornutum*; (5) the short-term chronic toxicity of copper(II) to *S. capricornutum* in the presence of photocatalytic nanoparticles; (6) the short-term chronic toxicity of chlorinated phenols to *E. coli* and *C. dubia* in the presence of photocatalytic nanoparticles; and (7) the short-term toxicity of photocatalytic nanoparticles to freshwater algal assemblages.

As a result of the proposed study, it is expected that systematic information on the short-term chronic toxicity of photocatalytic nanoparticles to bacteria, algae, and daphnia, which covers three successive trophic levels in the ecosystem, will be established.

## Short-Term Chronic Toxicity of Photocatalytic Nanoparticles to Bacteria, Algae, and Zooplankton

*Chin Pao Huang*

*Department of Civil and Environmental Engineering, University of Delaware, Newark, DE*

### Environmental Implication/Application

This research project addresses four major nano-ecotoxicity issues: (1) the general ecotoxicity of nanoparticles, (2) the additional effect of photocatalysis of nanoparticles to aquatic organisms; (3) the ecotoxicity of organisms of three subsequent trophic levels; and (4) the response of the natural algal community to nanoparticles. Information obtained from this project will serve a wider purpose to both the regulatory and the scientific communities. Specifically, the information to be obtained in this research including the EC50, IC25, and IC50 values of various nanophotocatalysts for bacteria (e.g., *Escherichia coli*), green algae (e.g., *Selenastrum capricornutum*), and daphnia (e.g., *Ceriodaphnia dubia*) will be useful for assessing the general ecotoxicity of nanophotocatalysts. Because these three test organisms represent three successive trophic levels, the toxicity effect displayed by these selected organisms can be extrapolated readily to species of higher orders in trophic scale. Based on the feeding capacity and behavior of each organism and the information obtained in this research such as EC50 and IC50, it is possible to estimate with first approximation the tolerable amount of uptake of the corresponding nanoparticles by organisms of higher order in the trophic structure. The mutagenicity of photocatalysts to aquatic bacteria, exemplified by *E. coli* and to be assessed with direct DNA sequencing technique, will shed much light on the ecotoxicity of nanophotocatalysts at the molecular-biological level. The synergistic and antagonistic effects of photocatalytic nanoparticles, examined by copper toxicity to green algae and chlorinated phenols toxicity to daphnia, will greatly aid in a better understanding of the inter-species toxicity mechanisms. The response of the natural algal community to nanoparticles also will be assessed. Algal community is among the most sensitive to environmental contaminants. Overall, information obtained from this project will prove to be most useful to the design of toxicity mitigation strategy for photocatalytic nanoparticles in aquatic systems.

## Evaluation of Nanoparticles Interactions With Skin

Nancy Ann Monteiro-Riviere

Center for Chemical Toxicology Research and Pharmacokinetics, Department of Clinical Sciences,  
College of Veterinary Medicine, North Carolina State University, Raleigh NC

### Abstract

This research project proposes to address whether manufactured nanoparticles can gain access to the epidermis after topical exposure, the first step in a toxicological reaction. Exposure to metallic nanoparticles, whose physical properties would allow them to catalyze a number of biomolecular interactions, potentially could produce adverse toxicological effects. The difference between nanoparticles and “traditional” hazardous chemical exposure is that decontamination of nanoparticles would be significantly more difficult than chemicals, as solubilization or dilution, the two hallmarks of post-exposure decontamination, might be less efficacious for these solid structures.

The focus of this research project is to assess the nature of interaction between manufactured nanoparticles and the skin; including dermal absorption, cutaneous toxicity, as well as the ability to distribute to the skin after systemic exposure. The skin is a primary route of potential exposure to toxicants, including novel nanoparticles. However, there is no information on whether particles are absorbed across the stratum corneum barrier or whether systemically administered particles can accumulate in dermal tissue. Our laboratory has developed a well-validated humane alternative animal model that is predictive of *in vivo* human dermal absorption, which is ideally suited to assess both the dermal absorption of nanoparticles as well as their potential accumulation in skin after systemic exposure. These studies will utilize iron oxide nanocrystals, cadmium selenide nanocrystals, and carbon fullerene nanoparticles, which are representative of the broad spectrum of nanoparticles presently being used by industry. Eight particle types selected from these commercially relevant manufactured nanoparticles will be studied to allow assessment of size, shape, and composition on absorption, distribution, or toxicity to the skin. These data would provide a preliminary but relevant assessment of both systemic exposure after topical administration as well as cutaneous hazard after both topical or systemic exposure, the two essential components of any risk assessment. If carbon nanoparticles are accidentally modified or if exposure occurs before cleansing, they could have untoward consequences if they gain entry to tissues.

All studies will be conducted in three well-characterized *in vitro* skin models: human skin keratinocyte cell cultures, porcine skin flow-through diffusion cells, and the isolated perfused porcine skin flap (IPPSF). Nanoparticles will be applied topically in three exposure scenarios (neat, water, mineral oil) at two doses to assess potential dermal absorption in the diffusion cell studies and to assess cellular toxicity (light and electron microscopy, viability) and irritation (IL-8 release) in cell culture. Those particles that penetrate skin or cause direct irritation will be completely characterized in IPPSF studies, which have previously been shown to be predictive of *in vivo* absorption in humans. Similarly, to model nanoparticle uptake into skin after systemic exposure, nanoparticles will be infused into the arterial blood supply of the IPPSF to assess the ability to distribute out of the vasculature into the skin. Deposition of particles in epidermal tissue after both infusion and topical exposure will be evaluated using high-resolution electron microscopy.

Presently, there are minimal data available on the interaction between manufactured nanoparticles and biological tissues. The basic requirement for any risk assessment includes information on hazard (e.g., toxicity) and exposure (e.g., absorption). This research project focuses on the health effects of nanoparticle interactions with the skin. This integrated research program will generate data on the ability of nanoparticles to be toxic to keratinocytes as well as assess the ability of nanoparticles to either be absorbed into skin after topical exposure, or distribute into skin as would occur after systemic exposure by an alternate route of administration. At the conclusion of the research, the boundaries of a dermal risk assessment for manufactured nanoparticle exposure will be available.

## **Evaluation of Nanoparticles Interactions With Skin**

*Nancy Ann Monteiro-Riviere*

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College of Veterinary Medicine, North Carolina State University, Raleigh NC*

### **Environmental Implication/Application**

There is a serious lack of information about the human health and environmental implications of manufactured nanomaterials. The purpose of this research is to address this deficiency in the area of skin absorption and toxicity to set bounds for future risk assessments. It is anticipated that this research will generate data in three specific areas relative to assessing the potential health effects of manufactured nanomaterials to humans: (1) Are nanoparticles absorbed across the skin? (2) Are nanoparticles irritating to cultured human keratinocytes? (3) Can nanoparticles distribute into skin after systemic administration?

There has not been any systematic investigation into the factors that determine whether these phenomenon can occur. Should minimal absorption or toxicity be detected, then this finding can be interpreted based on our previous data with other chemicals. The results should provide insight into the nature of the potential hazard to nanoparticles and provide an initial estimate of dermal exposure parameters that can be used to design more definitive studies. For example, information would be available on what is an appropriate vehicle and what is a "high" dose?

## **Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity**

*Robert H. Hurt*

*Division of Engineering, Brown University, Providence, RI*

### **Abstract**

Tubular and fibrous materials play a very special role in emerging nanotechnologies, but may show asbestos-like toxicity in humans upon inhalation. For asbestos fibers, it is known that both surface-reactive transition metals and fibrous geometry are major determinants of toxicity. Most commercial nanotubes/fibers are complex materials containing transition metal catalysts or residues and exhibiting complex distributions of length and diameter, as well as variability in defect density and surface functional groups.

The objective the proposed project is to conduct a carefully designed parametric study of the physical and chemical factors that underlie nanofiber/tube toxicity, in which shape, size, purity, and redox activity are carefully isolated by special synthesis techniques developed at Brown University.

This project uses model carbon nanofibers and nanotubes synthesized by non-catalytic templating routes from high-purity liquid-phase precursors. This approach allows explicit control of size and shape, and the as-produced materials are essentially free of transition metal impurities. Subsequent metal doping of these pure nanocarbons is then carried out to assess directly the effects of redox-active metals. A panel of fibrous and tubular nanocarbons have been synthesized, post-processed, and characterized, and the following toxicologic endpoints are being determined over a range of doses: (1) phagocytosis; (2) cell toxicity; (3) induction of proinflammatory gene expression; and (4) genotoxicity. These short-term toxicologic assays will establish the toxicity of these nanomaterials relative to carcinogenic asbestos fibers and nontoxic titanium dioxide nanoparticles. The work is being extended to commercial carbon nanotube samples, where metal residues can be partially or wholly encapsulated by carbon and the bioavailability of nanophase metals as a function of material processing and oxidation becomes a key issue.

We hypothesize that reactive transition metal catalyst residues are important determinants of carbon nanofiber/tube toxicity. On the basis of the preliminary data, we predict that nanomaterials doped with transition metals will be more toxic than pure carbon nanomaterials. This mechanistic study will provide guidance for the manufacturing of nanomaterials with minimal human health impact (e.g., through catalyst selection, purification, and control of mechanical damage that gives access to encapsulated metals), while maintaining desirable material properties and functions.

## **Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity**

*Robert H. Hurt and Agnes B. Kane  
Division of Engineering, Brown University, Providence, RI*

### **Environmental Implication/Application**

This research project will characterize and document the potential health effects associated with exposure to carbon nanotubes and nanofibers. These materials are among the most promising new products of the U.S. nanotechnology initiative, but a better understanding of their potential toxicity is needed before widespread commercialization can occur.

Manufactured batches of carbon nanotubes and nanofibers are complex materials that typically contain a variety of carbon forms as well as inorganic catalyst residues that may be partially or wholly encapsulated by carbon. Many catalyst compositions include reduced forms of iron, which are already known to play an important role in the inhalation toxicity of asbestos.

The specific objective of this project is to understand the role of iron residues in the potential toxicity of carbon nanotubes to macrophage cells. This mechanistic project will determine if and how iron nanoparticles mediate toxicity, and will provide guidelines on the threshold allowable amounts of bioaccessible iron residue in commercial nanomaterials. The data will help define nanotube fabrication and purification procedures that ensure intrinsically safe products and thus protect nanotechnology workers, users, and the environment.

## **Section 8. Industrial Ecology**

As new nanomaterials are discovered and dynamic patterns of commercial and environmental opportunity and risk are observed, there is an important need for EPA to improve its ability to respond to these emerging opportunities and risks as early as possible. Information is needed to engage in efforts to encourage the early redesign of products and services and effectively prevent the impacts of these materials on human health and the environment. A multidisciplinary and coordinated policy approach, including an analysis of product life cycle impacts, along with a materials flow analysis, starting with the conversion of raw materials, manufacture, use, and disposal, is necessary to encourage a culture of stewardship in relationship to the development and application of emerging nanotechnologies and materials.





## **Societal Implications of Nanotechnology: Benefits and Costs**

*Earl R. Beaver*

*Institute for Sustainability, New York, NY; Practical Sustainability, LLC, Chesterfield, MO;  
and BRIDGES to Sustainability, Houston, TX*

### **Abstract**

As each new technology emerges, there are implications that often are unforeseen. Surprises tend to be at least 50 percent negative. Using tools such as “Total Benefit and Cost Assessment” provide mechanisms for identifying and examining the surprises in advance. This presentation will report the work done by Practical Sustainability, LLC, and BRIDGES to Sustainability™ to identify and prioritize the issues surrounding the realm of nanotechnology. The excitement, in particular the interest by the U.S. federal government, provides incentives for accelerating the growth of this field. Researchers actively involved in the field have no reason to raise red flags and, yet, the earlier those flags are raised, the more thoroughly they can be explored. The odds of problems can be reduced, the magnitude of problems can be reduced, and the benefits of new technology can be maximized.

## **Societal Implications of Nanotechnology: Benefits and Costs**

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and BRIDGES to Sustainability, Houston, TX*

### **Environmental Implication/Application**

The benefits of this research project are to: (1) contribute to the U.S. Environmental Protection Agency's goal of developing "theoretically consistent, empirically feasible, and policy relevant estimates of values for changes in ecological benefits (the products, services, and amenities provided by ecosystems, including non-use values) caused by environmental influences"; (2) identify candidate societal implications for developers to utilize in considering positive and negative potential implications of nanotechnology; and (3) offer a method for researchers to make product development decisions. One way to contribute to those goals is to develop improved methodologies for assessing the environmental costs and benefits of alternative actions, because cost-benefit analysis (Total Benefit and Cost Assessment) is so widely used as a framework for evaluating policy choices, setting priorities, and allocating resources. Critics of new technologies, for example, argue that regulatory agencies fail to address the most serious risks, and that identifying the costs and benefits of alternative actions will help steer them towards the initiatives that promise to accomplish the most good with the resources expended. Total Benefit and Cost Assessment also is championed as a way to avoid policies such as overly stringent regulations that impose major compliance costs but produce limited value and to ensure that only worthwhile projects are undertaken. Because the costs and benefits of policy and regulatory choices vary significantly, Total Benefit and Cost Assessment can help ensure that risks are regulated and desirable actions encouraged in comparable, fair ways. The approach here is to follow the successful abbreviated valuation methods developed within the past 4 years and applied to "harmless odors" and "eutrophication of waterways."

## **A Life-Cycle Assessment Approach for Evaluating Future Nanotechnology Applications**

*Shannon M. Lloyd and Lester B. Lave*

*Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA*

### **Abstract**

By reducing the energy and materials required to provide goods and services, nanotechnology has the potential to provide more appealing products while improving environmental performance and sustainability. However, while nanotechnology offers great potential, it is unlikely to be the first entirely benign technology. A technological push towards greater investment in nanotechnology without a commensurate consideration of the net environmental benefits will likely lead to cases where the nanotechnology substitute is environmentally inferior to the product or process replaced. Whether and how soon the promise of improved environmental quality could be realized depends on phrasing life-cycle questions during research and development and pursuing commercialization intelligently.

A framework will be presented for a quantitative analysis of the life-cycle implications of projected nanotechnology-based products. We use technology scenarios and prospective hybrid life-cycle assessment to estimate the economic and environmental life-cycle implications of two projected nanotechnology-based products. In the case of using nanocomposites in light-duty vehicle body panels, the ability to disperse nano-scale particles in polymers would reduce vehicle weight thereby improving fuel economy. In the case of nano-fabricated catalysts, the ability to position and stabilize platinum-group metal particles in automotive catalyst would reduce the amount of platinum-group metal required to meet emissions standards, thereby reducing mining and refining activities. For each application, a conventional product is compared to its nanotechnology-based substitute to assess whether the nanotechnology substitute can be cost effective and improve environmental quality.

## **A Life-Cycle Assessment Approach for Evaluating Future Nanotechnology Applications**

*Shannon M. Lloyd and Lester B. Lave*

*Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA*

### **Environmental Implication/Application**

Evaluating the sustainability, and environmental and human health implications of consumer goods and services requires analysis of material and energy usage, as well as environmental discharges associated with each life-cycle stage. This life-cycle analysis goes from extraction of raw materials, to production, use, and end-of-life. The importance of evaluating product performance over a product's entire life cycle can be illustrated by considering a possible nanotechnology application. Advances in nanotechnology are expected to offer increased understanding of, and control over, catalyst design and performance. For example, bottom-up assembly may be used to synthesize catalytically active sites by positioning atoms or molecules one-by-one, thereby utilizing materials more efficiently. This precise positioning would result in less material use during catalyst production and perhaps less energy use during catalyst use. However, because catalysts require large numbers of active sites, efficient methods for positioning atoms or molecules will be needed to ensure that any materials savings from production or energy savings during use are not offset by the energy required to synthesize active sites one-by-one.

Life-cycle assessment is a systematic, analytical process for assessing the inputs and outputs associated with each life-cycle stage of a product or process. Life-cycle assessment is typically used to estimate the resource and environmental implications associated with existing products. Changing a product to reduce its environmental impact after the product has been developed can cost orders of magnitude more than making the change during research and development. Our framework employs technology scenarios and prospective hybrid life-cycle assessment to estimate the economic and environmental life-cycle implications of projected nanotechnology-based products. Conventional products are compared to nanotechnology-based substitutes to assess whether the nanotechnology substitutes can be cost effective and improve environmental quality. By employing this framework, policy makers and industry can identify technology scenarios and employ prospective life-cycle assessment during early research and development to evaluate future nanotechnology-based products and emerging nanotechnologies. The ability to evaluate life-cycle implications of alternative courses of action during research and development improves the ability to evaluate tradeoffs, optimize products for all aspects of life-cycle performance, and make more strategic R&D choices. A more informed understanding of the commercial, societal, and technological possibilities and consequences will enable better decisions in regard to the selection, development, and commercialization of nanotechnology.

## **Appendix**



**U.S. EPA 2004 Nanotechnology Science To Achieve Results (STAR)  
Progress Review Workshop — Nanotechnology and the Environment II**

**Loews Philadelphia Hotel  
1200 Market Street  
Philadelphia, PA 19107**

**August 18 – 20, 2004**

**Agenda**

**Wednesday, August 18, 2004**

- 9:30 – 10:00 a.m.**      **Registration**
- Overview**
- 10:00 – 10:15 a.m.**      **Welcome – Stephen A. Lingle**  
Director, Environmental Engineering Research Division,  
U.S. EPA, ORD, NCER
- 10:15 – 10:40 a.m.**      **Overview of Nanotechnology—Responsible Research  
and Development of Nanotechnology**  
Mihail Roco, Chair, Nanoscale Science, Engineering and  
Technology (NSET)
- 10:40 – 11:05 a.m.**      **EPA’s Nanotechnology Program—Vision of How  
Nanotechnology Can Be Used To Protect, Inform,  
Manage, and Improve the Environment and How  
Harm From Nanotechnology Can Be Studied  
and Prevented**  
Barbara Karn, U.S. EPA, ORD, NCER, Washington, DC
- Plenary Talks**
- 11:05 – 11:35 a.m.**      ***Nanotechnology Applications for Environmental  
Sensors: Rapid and Precise Monitoring; Lab-on-a-Chip  
Devices; Real-Time Analyses; Remote, In Situ, and  
Continuous Devices***  
Nongjian Tao, Arizona State University
- 11:35 a.m. – 12:05 p.m.**      ***Nanotechnology Applications for Treatment:  
Cost-Effective and Rapid Technologies; Smart Materials  
or Active Surface Coatings***  
Wilfred Chen, University of California Riverside

12:05 – 12:35 p.m.	<i>Nanotechnology Applications for Remediation: Cost-Effective and Rapid Technologies; Removal of Contaminants From Soil, Ground Water, and Aqueous Environments</i> Gregory Wilson, The American Association for the Advancement of Science
12:35 – 1:35 p.m.	<b>Lunch</b>
1:35 – 2:05 p.m.	<i>Nanotechnology Applications for Green Manufacturing: Minimize Harmful Emissions and Generated Wastes; Reuse; Recycle; Benign Chemical Processes; Self-Assembly</i> Lawrence T. Drzal, Michigan State University
2:05 – 2:35 p.m.	<i>Nanotechnology Implications in the Environment and Human Health: Life Cycle Assessment, Ecosystem Health, Persistence, Toxicity, Fate and Transport, Bioavailability, Bioaccumulation/Biotransformation</i> Nora Savage, EPA, ORD, NCER, Washington, DC
	<b>Green Manufacturing</b> Barbara Karn, Chair
2:35 – 2:55 p.m.	<i>Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces</i> Kristen Fichthorn, The Pennsylvania State University
2:55 – 3:15 p.m.	<i>Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications</i> Lawrence T. Drzal, Michigan State University
3:15 – 3:35 p.m.	<i>Development of Nanocrystalline Zeolite Materials as Environmental Catalysts: From Environmentally Benign Synthesis to Emission Abatement</i> Sarah C. Larsen, University of Iowa
3:35 – 4:00 p.m.	<b>Break</b>
4:00 – 4:20 p.m.	<i>Plasmon-Sensitized TiO<sub>2</sub> Nanoparticles as a Novel Photocatalyst for Solar Applications</i> George Chumanov, Clemson University
4:20 – 4:40 p.m.	<i>Graft Polymerization as a Route To Control Nanofiltration Membrane Surface Properties To Manage Risk of EPA Candidate Contaminants and Reduce NOM Fouling</i> Georges Belfort, Rensselaer Polytechnic Institute
4:40 – 5:00 p.m.	<i>Ecocomposites Reinforced With Cellulose Nanoparticles: An Alternative to Existing Petroleum-Based Polymer Composites</i> William T. Winter, The State University of New York



- 5:00 – 5:20 p.m.**      **Break**
- Aerosols**  
Maria Rodriguez, Chair
- 5:20 – 5:40 p.m.**      *Elemental Composition of Freshly Nucleated Particles*  
Murray V. Johnston, University of Delaware
- 5:40 – 6:00 p.m.**      *Ion-Induced Nucleation of Atmospheric Aerosols*  
Peter H. McMurry, University of Minnesota
- 6:00 p.m.**              **Adjourn**

**Thursday, August 19, 2004**

- 8:40 a.m. – 1:50 p.m.**    **Sensors**  
Marti Otto, Chair
- 8:40 – 9:00 a.m.**      *Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for Carcinogenic Chromium (VI) and Arsenic (V)*  
William C. Trogler, University of California San Diego
- 9:00 – 9:20 a.m.**      *Nanosensors for Detection of Aquatic Toxins*  
Robert E. Gawley, University of Arkansas
- 9:20 – 9:40 a.m.**      *Micro-Integrated Sensing Systems by Controlled Self Assembly of Nanoparticles*  
Somenath Mitra, New Jersey Institute of Technology
- 9:40 – 10:00 a.m.**      *Advanced Nanosensors for Continuous Monitoring of Heavy Metals*  
Omowunmi Sadik, State University of New York Binghamton
- 10:00 – 10:20 a.m.**      *Metal Biosensors: Development and Environmental Testing*  
Anne J. Anderson, Utah State University
- 10:20 – 10:40 a.m.**      **Break**
- 10:40 – 11:00 a.m.**      *Compound Specific Imprinted Microspheres for Optical Sensing*  
Barry K. Lavine, Oklahoma State University
- 11:00 – 11:20 a.m.**      *Ultrasensitive Pathogen Quantification in Drinking Water Using Highly Piezoelectric PMN-PT Microcantilevers*  
Wan Y. Shih, Drexel University
- 11:20 – 11:40 a.m.**      *Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring*  
Joseph Wang, New Mexico State University

11:40 – 12:00 noon	<i>Low-Cost Organic Gas Sensors on Plastic for Distributed Environmental Monitoring</i> Vivek Subramanian, University of California Berkeley
12:00 – 12:20 p.m.	<i>The Silicon Olfactory Bulb: A Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS Transistors (CvMOS)</i> Edwin C. Kan, Cornell University
12:20 – 1:30 p.m.	<b>Lunch</b>
1:30 – 1:50 p.m.	<i>A Nanocontact Sensor for Heavy Metal Ion Detection</i> Nongjian Tao, Arizona State University
	<b>Remediation</b> Philip Sayre, Chair
1:50 – 2:10 p.m.	<i>Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature</i> Dibakar Bhattacharyya, University of Kentucky
2:10 – 2:30 p.m.	<i>Dendritic Nanoscale Chelating Agents: Synthesis, Characterization, Molecular Modeling, and Environmental Applications</i> Mamadou S. Diallo, California Institute of Technology
2:30 – 2:50 p.m.	<i>Synthesis, Characterization, and Manipulation of (FeS-PAMAM) Dendrimer Nanocomposites</i> Lajos Balogh, University of Michigan
2:50 – 3:10 p.m.	<i>Hollow and Nanoporous Iron Particles</i> Wei-Xian Zhang, Lehigh University
3:10 – 3:30 p.m.	<b>Break</b>
3:30 – 3:50 p.m.	<i>Developing Functional Fe<sup>0</sup>-Based Nanoparticles for In Situ Degradation of DNAPL Chlorinated Organic Solvents</i> Gregory V. Lowry, Carnegie Mellon University
3:50 – 4:10 p.m.	<b>A Bioengineering Approach to Nanoparticle-Based Environmental Remediation</b> Daniel R. Strongin, Temple University
	<b>Implications</b> Philip Sayre, Chair
4:10 – 4:30 p.m.	<i>Societal Implications of Nanotechnology: Benefits and Costs</i> Earl R. Beaver, Practical Sustainability, LLC

4:30 – 4:50 p.m. *A Life-Cycle Analysis Approach for Evaluating Future Nanotechnology Applications*  
Shannon Lloyd, Carnegie Mellon University

4:50 p.m. Adourn

**Friday, August 20, 2004**

**Treatment**  
Anita Street, Chair

8:40 – 9:00 a.m. *NO<sub>x</sub> Reduction With Transition Metal Carbide Nanoparticles*  
S. Ismat Shah, University of Delaware

9:00 – 9:20 a.m. *Simultaneous Environmental Monitoring and Purification Through Smart Particles*  
Wolfgang M. Sigmund, University of Florida

9:20 – 9:40 a.m. *Nanoscale Biopolymers With Tunable Properties for Improved Decontamination and Recycling of Heavy Metals*  
Wilfred Chen, University of CaliforniaRiverside

9:40 – 10:00 a.m. *Use of Ozonation in Combination With Nanocrystalline Ceramic Membranes for Controlling Disinfection By-Products*  
Simon Davies, Michigan State University

10:00 – 10:30 a.m. Break

**Fate, Transport, and Transformation**  
Kevin Dreher, Chair

10:30 – 10:40 a.m. *Absorption and Release of Contaminants Onto Engineered Nanoparticles*  
Mason Tomson, Rice University

10:40 – 10:50 a.m. *Impacts of Manufactured Nanomaterials on Human Health and the Environment: A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol*  
Vicki Grassian, University of Iowa

10:50 – 11:00 a.m. *Chemical and Biological Behavior of Carbon Nanotubes in Estuarine Sedimentary Systems*  
P. Lee Ferguson, University of South Carolina

11:00 – 11:10 a.m. *Transformations of Biologically Conjugated CdSe Quantum Dots Released Into Water and Biofilms*  
Patricia Holden, University of CaliforniaSanta Barbara

11:10 – 11:20 a.m.	<b><i>Repercussion of Carbon-Based Manufactured Nanoparticles on Microbial Processes in Environmental Systems</i></b> Ronald Turco, Purdue University
11:20 – 11:30 a.m.	<b><i>The Fate, Transport, Transformation, and Toxicity of Manufactured Nanomaterials in Drinking Water</i></b> Yongsheng Chen, Arizona State University
	<b>Toxicology</b> Kevin Dreher, Chair
11:30 – 11:40 a.m.	<b><i>Short-Term Chronic Toxicity of Photocatalytic Nanoparticles to Bacteria, Algae, and Zooplankton</i></b> Chin-Pao Huang, University of Delaware
11:40 – 11:50 a.m.	<b><i>Evaluation of Nanoparticles Interactions With Skin</i></b> Nancy Monteiro-Reviere, North Carolina State University
11:50 a.m. – 12:00 noon	<b><i>Physical and Chemical Determinants of Nanofiber/ Nanotube Toxicity</i></b> Robert Hurt, Brown University
12:00 – 12:30 p.m.	<b>Closing Remarks</b> Barbara Karn and Nora Savage, SEPA, ORD, NCER, Washington, DC
12:30 p.m.	<b>Adjourn</b>

**U.S. EPA 2004 Nanotechnology Science To Achieve Results (STAR)  
Progress Review Workshop — Nanotechnology and the Environment II**

**Loews Philadelphia Hotel  
1200 Market Street  
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**August 18 – 20, 2004**

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