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United States
Environmental Protection
Agency

Proceedings

Nanotechnology and the Environment: Applications and Implications Progress Review Workshop III

October 26-28, 2005
Arlington, VA

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Nanotechnology and the Environment: Applications and Implications Progress Review Workshop III

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U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

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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, developing a White Paper outlining Agency priorities and needs, coordinating extramural and intramural nanotechnology research, 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

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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, with representatives from Canada and Europe 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).

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U.S. EPA 2005 Nanotechnology Science To Achieve Results (STAR) Progress Review Workshop—Nanotechnology and the Environment III: Applications and Implications

Holiday Inn Rosslyn at Key Bridge
1900 N. Fort Myer Drive
Arlington, VA 22209

October 26 - 28, 2005

Executive Summary

OVERVIEW

The U.S. Environmental Protection Agency's (EPA) 2005 Nanotechnology Science To Achieve Results (STAR) Progress Review Workshop—Nanotechnology and the Environment III: Applications and Implications was held on October 26-28, 2005, in Arlington, Virginia. The workshop brought together approximately 150 researchers from academia and government to discuss ongoing research on nanotechnology and the environment. The focus for this year's meeting was applications and implications of nanotechnology. The workshop served as a stimulus for increased collaborations among the various researchers and included information to provide knowledge in the area of international nanotechnology research support.

Welcome and Introductory Remarks
William Farland, U.S. EPA

Dr. Farland noted that this workshop provides an important opportunity for EPA staff to interact with grantees and the academic community focusing on environmental applications and implications of nanotechnology. The workshop goals are to provide a stimulus for increased collaborations among the various researchers, improve knowledge of the environmental aspects of nanotechnology, and identify future research needs. EPA's role is to provide leadership on environmental applications and implications of nanotechnology.

The challenge is to identify how nanoscience can be used for beneficial environmental applications as well as to understand and predict the human health and ecological implications of nanoparticle releases to the environment. Nanotechnology applications can address existing environmental problems and prevent future problems in the areas of air and water quality, reduction of toxic compounds, and improved homeland security. Implications research is needed to assess nanomaterials in the environment and any possible risks that may be posed by nanotechnology. EPA has funded STAR nanotechnology research grants since 2001, beginning with applications and now focusing on implications. The newest request for STAR applications on nanomaterials is a joint release with the National Science Foundation (NSF), the National Institute of Environmental Health Sciences (NIEHS), and the National Institute for Occupational Safety and Health (NIOSH).

EPA faces regulatory challenges in the area of nanotechnology. The Agency is integrating its own science needs with those of other regulatory agencies through the Nanoscale Science, Engineering and Technology (NSET) Nanotechnology Environmental Health and Implications Workgroup. In EPA's first action related to nanomaterials, the Office of Pollution Prevention and Toxics has "permitted limited

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manufacture" under the Toxics Substances Control Act (TSCA) of a nanomaterial. More of these actions are likely to occur in the next few years.

PLENARY TALKS

Towards a National Nanotechnology Strategy for Canada
Paul Dufour, Privy Council Office, Government of Canada

The Canadian government has been investing heavily in overall research spending and has the highest per capita investment within the G-8 for support of the university research and research institutes. Investment specifically targeted to nanotechnology research is growing. Provincial governments in Canada also are supporting the development and commercialization of nanotechnology. NanoQuébec, which provides structuring and planning efforts in nanotechnology in Québec, is one example of the provincial Canadian focus on nanotechnology. Canada is working on a national nanotechnology strategy that will include research and development, innovation and commercialization, regulatory considerations, and education and engagement with the public. Regulations are an emerging issue, and a life cycle approach is needed as a guideline for assessing regulatory needs for the environmental management of nanotechnology. Sustained investments are necessary but will not be effective without a strategy that is national in scope, integrated, multidisciplinary, and internationally linked. Environmental, health, societal, and ethical issues associated with nanotechnology will be a core element of the Canadian strategy.

The strengths of the Canadian effort include talent in areas such as quantum computing and quantum devices, lab-on-a-chip and biodiagnostic devices, materials self-assembly, nanophotonics, and instrument development. Canadian universities and the Canadian National Research Council conduct leading-edge research, and the country has expertise in environment, agriculture, manufacturing, health, energy, communications, and security industries, which are prime areas of nanotechnology opportunities. Opportunities exist to collaborate with EPA, and Canada is pleased to work with the United States in the area of nanotechnology.

National Nanotechnology Initiative: The Long-Term View
Mihail Roco, NSF

The National Nanotechnology Initiative's (NNI) long-term vision is that the systematic control of matter on the nanoscale level will lead to a revolution in technology and industry. The NNI definition of nanotechnology involves technology that meets three criteria: (1) research and technology development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1 to 100 nanometer range; (2) creation and use of structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size; and (3) the ability to control or manipulate matter on the atomic scale. Four generations of nanostructures are predicted: passive nanostructures (already in existence), active nanostructures (active research and development presently in process), systems of nanosystems (by 2010), and molecular nanosystems (by 2015). The NSET Subcommittee of the National Science and Technology Council coordinates, plans, and implements the NNI, which has a current year funding of approximately $1 billion.

From 2001-2005, the elements of NNI included: funding fundamental research activities, examining long-term challenges, establishing centers and networks of excellence, developing a research infrastructure, beginning to address societal implications, and workforce education and training needs. Accomplishments include more than 3,000 active projects, more than 50 large nanotechnology research centers and networks, and education and outreach that began at the graduate education level and is expanding to the undergraduate and high school level, as well as K-12 informal science education.

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Collaborations and partnering are important. International dialogue on responsible nanotechnology research and development has begun through workshops and workgroups. In addition, for the immediate and continuing societal implications issues, long-term concerns must be addressed. An anticipatory and corrective approach in planning is needed that is both transforming and responsible in addressing societal implications for each major nanotechnology research and development program or project from the beginning. Risk governance of nanotechnology is becoming an increasing focus at the national and international levels.

An Overview of Canadian Nanomedicine Research Funding: The Canadian Institute of Health Research Vision
Eric Marcotte, Canadian Institute of Health Research

The Canadian Institute of Health Research (CIHR) is a virtual organization with networks of researchers aligned along common interests and themes. CIHR scientific directors remain at their host universities and collectively advise the Canadian Governing Council on research plans and budget allocations to support cross-disciplinary, internationally competitive health research in Canada. The Regenerative Medicine and Nanomedicine Initiative is one of three major strategic initiatives of CIHR and is co-led by the Institute of Neurosciences, Mental Health, and Addiction and the Institute of Genetics. Regenerative medicine and nanomedicine were combined because of similar research interests and allows for more funding options. Research topics include: nanotechnology gene therapy; stem cells; tissue engineering; rehabilitation sciences; and social, ethical, economic, environmental, and legal issues.

Dr. Marcotte highlighted two examples of research funded through the Regenerative Medicine and Nanomedicine Initiative. The first is a research project of Dr. Isabelle Brunette at Hôpital Maisonneuve-Rosemont that focuses on improved outcomes of corneal transplantation using femtosecond laser-assisted corneal posterior lameller transplantation with endolethelial enhancement. The second example is research in Dr. Warren Chan's laboratory at the University of Toronto on the use of quantum dots in tissue remodeling, early cancer diagnosis, and guidance during tumor detection with potential applications in stem cell research. Sixty percent of new discoveries from grants have been for nanomedicine projects. The nanomedicine grants and projects are in the following categories: drug delivery, biomaterials, clinical imaging/tools, and molecular imaging/tools. Funding has been increasing for nanomedicine projects. A new 2005 request for applications includes a call for projects that address the health, safety, and environmental risks of nanomedicine. CHIR strengths include strong ongoing funding support for nanomedicine, a commitment to multidisciplinary research, and close interagency collaboration.

Nanotechnology at EPA—An Update
Barbara Karn, U.S. EPA, on detail at Woodrow Wilson Center

EPA's research framework for nanotechnology and the environment involves applications and implications. Applications address existing environmental problems or prevent future problems. Implications address the interactions of nanomaterial with the environment and any possible risks that may be posed by nanotechnology. EPA's nanotechnology research program has six thrusts: (1) build and sustain a community of researchers in nanotechnology and the environment, including both applications and implications; (2) institutionalize nanotechnology within EPA's mission; (3) assure consideration of the environment and human health in governmental research programs related to nanotechnology; (4) work with industry to assure environmentally responsible development of nanotechnology and products containing nanomaterials; (5) provide leadership in international activities involving the environment, human health, and nanotechnology; and (6) provide education and outreach to the public to promote understanding of nanotechnology with respect to the environment and human health.

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Progress has been made in nanotoxicology research, the number of nanotechnology products available, and the amount of research funding for nanotechnology and the environment issues. Improvement is still needed in nanotechnology in sustainability research, life cycle studies, and public involvement. Dr. Karn shared information on her work at the Woodrow Wilson Center on "green" nanotechnology to make nanomaterials and nanoproducts "greenly" and to use nanotechnology to "green up" current processes. The focus of "green" nanotechnology includes understanding of the full life cycle of nanomaterials and nanoproducts, which is necessary for sustainability. The challenge is to use nanotechnology to help clean up past environmental damage, correct present environmental problems, prevent future environmental impacts, and help sustain the planet for future generations.

Nanotech: Rolling to Market
David Rejeski, Woodrow Wilson Center

A survey by *Small Times* magazine identified more than 1,600 companies involved in nanotechnology, with more than 700 products being produced. The question is how consumers will respond to nano-based products. Companies do not always advertise their involvement in nanotechnology because industry is not sure if nanotechnology is an asset or liability. Concerns exist over public reaction and governmental regulations. Scientists focus on the health and environmental risks of nanotechnology, but investors focus on consumer perception. Sixty to 70 percent of the public has never heard of nanotechnology. Once informed, the public is excited about the benefits of nanotechnology, but trust in either industry or government to manage nanotechnology risks is low, and gaps exist in the current regulatory system to address nanotechnology risks.

The area of green nanotechnology (Green Nano) has large potential benefits with low perceptual risks. Three areas include: "dark green"—nanotechnology applied directly to solve environmental problems; "light green"—nanotechnology providing environmental benefits for other applications; and "right green"—nano-based processes and products designed to have an environmentally low impact. Dr. Rejeski proposed the following to support a U.S. green nano-based program: (1) create at least one dedicated NSF/EPA-funded Center for Green Nano; (2) create a database of Green Nano research and researchers and make it available for investors; (3) ensure technology verification for nano-based products; (4) utilize a government procurement system to support Green Nano products on the market; and (5) focus Small Business Innovation Research (SBIR) grants on Green Nano.

Nanotechnology and Human Health Impact
Andrew Maynard, Woodrow Wilson Center

Many societal and environmental benefits are anticipated from nanotechnology projects and products, but there may be unanticipated roadblocks, including unexpected human health and environmental risks. Sustainable nanotechnology will depend on societal acceptance, minimizing risk, and maximizing the benefits of the technology. The foundation for a positive nanotechnology outcome is based on global partnerships and moving beyond the hype and confusion of this technology. Global implications require global cooperation and collaboration, including coordinated approaches to finding solutions.

Implications-focused research must be specific to materials, devices, and products. It is important to differentiate between nano-based materials and products presenting significant, marginal, or no potential risk. Information is available using similarity, analogy, and principles from research in areas of aerosol behavior, exposure control, general health effects, ultrafine hazards, and physicochemical significance of specific products such as asbestos and crystalline silica. Extrapolation used wisely can provide strategic direction. Integration of risk-based and applications-based research will be necessary to pre-empt and

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proactively minimize adverse health impact. Characterization is important for risk assessment. The complexity of many nanomaterials demands sophisticated characterization, frequently beyond what is typically applied to "macro" materials. Understanding implications to human health will require multiple disciplines working together.

Nanotechnology in the EU: Research Opportunities
Pilar Aguar, European Commission

This talk was focused on European health and safety nanotechnology research activities and noted that the European Commission is interested in fostering international cooperation and collaborations. The goal of the European approach is a European nanotechnology strategy that is integrated and responsible. The Commission has supported research and development and increased support for collaborative research and development into the potential impact of nanotechnology on human health and the environment. NANOSAFE and NANOFORUM are two examples of previous European projects related to the safety of nanoparticles. Current projects include NANOSAFE2, NANOTOX, and IMPART; these programs focus on the interaction of engineered nanoparticles with the environment and the living world. The upcoming program request includes a doubling of the overall budget with large increases proposed for nanosciences and nanotechnologies, with an emphasis on collaborative research, frontier capacity, human potential, and research capacity. The European Union's current Framework Programme for Research and Technological Development (and presumably the upcoming one also) is open to the world, with funding granted to participants from almost all countries.

Natural Sciences and Engineering Research Council of Canada (NSERC) Nano Innovation Platform
Peter Grutter, National SERC Nano Innovation Platform

The NSERC Nano Innovation Platform (NanoIP) is a multidisciplinary, national network of university researchers from many fields of science and engineering created to accelerate and intensify research and education of high-quality personnel in nanoscience and nanotechnology in Canada. The objectives of NanoIP are to: develop and implement a national strategy with stakeholders; facilitate and build local nanotechnology communities; support a few high-risk projects at high funding levels; and increase the budget for nanotechnology in Canada. NanoIP award selections are based on quality, innovation, and the need for funds. An international refereeing and selection committee selects recipients. The overall goal is for a better understanding of the basic physicochemical properties of nanomaterials and nanoparticles. Fundamental understanding of nanomaterials is needed before toxicology and environmental studies can be generalized. The NanoIP awards assist in providing the foundation to investigate nanomaterial and nanoparticle toxicology and environmental and biological impact. A systematic coordinated approach is necessary, as this task is complex, time consuming, and expensive.

Health Canada Overview: Foresight Activities
David Blakey, Health Canada

Health Canada is the federal department responsible for helping the people of Canada maintain and improve their health. Its mission and activities are accomplished through partnerships. The existing tools for managing the risks related to nanotechnology include legislation and regulation. There are policies and guidelines that are under development and review. Life cycle management is needed to address the various exposure potentials of nanotechnology. Research is needed on the toxicology of nanotechnology as well as detection and monitoring tools. Gaps exist in the knowledge of toxicity and *in vivo* effects, exposure routes, and bioaccumulation potential. EPA and Health Canada have a collaborative effort to investigate the toxicological properties of metallic iron nanoparticles. Further discoveries and understanding of fundamental properties of nanomatter hold promise for beneficial new materials and

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applications; therefore, it is imperative to consider potential health effects to ensure that commercialization of innovations occurs while minimizing risks and building public confidence and acceptance. Risk research must be adequately funded, early in the process, and in balance with innovation investments. International cooperation is important to address these needs.

International Aspects of Nanotechnology
Celia Merzbacher, Executive Office of the President

Nanotechnology research activities and funding amounts invested around the world are increasing. Nanotechnology is advanced both through collaboration and healthy competition. Collaborations are increasing through continued interaction, policies that support collaboration, educational programs, the scientific need, and advantages of collaboration.

The development of standards is an important international effort in nanotechnology. Standards can aid research and development, support commerce and trade, and protect human health and the environment. The United States sets standards differently than other countries. The National Technology Transfer and Advancement Act of 1995 requires U.S. governmental agencies to use voluntary, consensus standards in lieu of government-unique standards, except where it is inconsistent with law or impractical to accomplish. The American National Standards Institute (ANSI) is the nonprofit organization that administers and coordinates the U.S. voluntary standardization and conformity assessment system with a mission to enhance the global competitiveness of U.S. business and improve the U.S. quality of life. The ANSI Nanotechnology Standards Panel provides: a forum for interested parties to define needs; facilitates development and adoption of standards responsive to identified needs; and acts as a liaison with other national, regional, and international nanotechnology standards efforts to create identical, or harmonize existing, standards.

International trade is an area that is now becoming a focus for nanotechnology. Preliminary discussions on an international level relate to export control, the Wassenaar Agreement, and visas. The Organisation of Economic Co-operation and Development (OECD) has nano-related activity, and these activities can be influential in trade issues.

NIOSH Nanotechnology Research Program
Vladmir Murashov, NIOSH

The NIOSH Nanotechnology Initiative addresses the implications and applications of nanotechnology in the workplace through a research program, a research center, and extramural program support. The NIOSH Nanotechnology Safety and Health Research Program presently funds five nanotechnology research projects. The NIOSH Nanotechnology Research Center is a virtual center that aims to identify critical issues, develop a strategic plan to address issues, fund new nanotechnology projects, and disseminate information gained. One focus for the center is the development of a Web-based nano-information library (http://www.cdc.gov/niosh/topics/nanotech/NIL.html). In addition, NIOSH has research supplement projects focusing on toxicity of nanoparticles as well as an extramural program that funds nanotechnology research. NIOSH has partnered with EPA to fund projects related to occupational health. Collaborative programs provide an opportunity to leverage resources, and NIOSH has established a number of collaborative programs with a wide range of academic, industrial and government partners. The outreach occurs through conferences, a Web site, current intelligence bulletins, and safety recommendations. Dr. Murashov encouraged participants to sign up for *Focus on Nanotechnology* at http://www.cdc.gov/niosh/topics/nanotech/focus.html, which highlights occupational and health applications and implications research.

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NSF Perspective
Cynthia Ekstein, NSF

NSF is the principal source of federal funding for university-based fundamental engineering research, providing more than 42 percent of the total federal support in this area. NSF supports fundamental research on engineering systems, devices and materials, and their underpinning processes and methodologies. Nanoscale engineering received the largest funding for NSF Engineering activities in FY05. This funding supported four areas: Nanoscale Interdisciplinary Research Teams, Nanoscale Science and Engineering Centers, nanoscale exploratory research, and nanotechnology undergraduate education. Collaborative RFAs have been issued for nanotoxicology research with EPA, NIOSH, and NIEHS. NSF recognizes the importance of an understanding of nanotechnology by the public and the U.S. workforce. NSF has selected the University of California, Santa Barbara, and Arizona State University to create two new Centers for Nanotechnology in Society. These centers will support research and education on nanotechnology and social change, as well as educational and public outreach activities and international collaborations.

REMARKS

Dr. Karn thanked participants for attending the workshop, particularly colleagues from Europe and Canada. The workshop provided an opportunity to build the research community, allowing participants to hear aspects of nanotechnology and the environment outside of their disciplines. EPA funds a broad range of research projects in applications and implications, and meetings such as this workshop allow for communication across a wide range of disciplines.

RESEARCH PROJECT PRESENTATIONS

AEROSOL

U.S. EPA STAR Grantees

Elemental Composition of Freshly Nucleated Particles
Murray Johnston, University of Delaware

The objective of this project is to develop a method for real-time sampling and analysis of individual airborne nanoparticles in the 5 to 20 nm diameter range. Airborne particles are associated with societal implications related to human health concerns 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.

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LIFE-CYCLE ANALYSIS

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Evaluating the Impacts of Nanotechnology via Thermodynamic and Life-Cycle Analysis
Bhavik Bakshi, Ohio State University

New data, tools, and techniques are needed to evaluate the life cycle environmental and economic aspects of nanomanufacturing to encourage sensible engineering decisions and policy. The objectives of this research are to develop life cycle inventory data of nanomanufacturing, perform life-cycle analysis (LCA) of nanotechnology and traditional processes and products, and then perform thermodynamic LCA and test hypotheses for evaluating life cycle impact with limited information. This research will combine data from the laboratory, LCA databases, and economic models through a multiscale LCA and test thermodynamics-based hypotheses for evaluating life cycle impact of emerging technologies. This project will develop techniques for gaining insight into the life cycle impact of emerging technologies and provide a tool for LCA and economic analysis of polymer nanocomposites. The expected benefits of the research include identifying and managing risk in research, development, and commercialization of nanomanufacturing; minimizing irrational optimism or unfounded fear about nanotechnology; and balancing harm to the environment and human health with economic feasibility.

GREEN MANUFACTURING

U.S. EPA STAR Grantees

Graft Polymerization as a Route To Control Nanofiltration Membrane Surface Properties
James Kilduff, Rensselaer Polytechnic Institute

This project will develop new nanofiltration membranes by modifying the surface structure of commercial membranes at the molecular level via UV-assisted graft polymerization of hydrophilic monomers using their patented method. The objective is to transfer major successful developments from biotechnology applications to environmental protection. New materials will be developed that offer high flux compared to commercial membranes (by improving membrane porosity), enhanced rejection of inorganic anions and ionizable organic compounds (by controlling membrane pore size distribution and surface charge), and enhanced ability to resist fouling by natural organic matter (NOM) by reducing adhesion. Researchers seek to understand the characteristics of NOM accumulated on membrane surfaces both in terms of resistance to flow (which can influence the cost of membrane processes) and its affects on the transport and rejection of charged solutes. Results from this project will provide new approaches to develop membrane materials that have superior performance characteristics in terms of both enhanced rejection of charged contaminants and resistance to fouling by NOM. The research also will expand our understanding of the role of membrane charge and NOM fouling layers on solute rejection by nanofiltration processes. The proposed materials and processes will provide new options for controlling risks from contaminants of water supplies to protect human health and improve the performance of membrane treatment technologies, while reducing associated costs.

Development of Nanocrystalline Zeolite Materials as Environmental Catalysts
Sarah Larsen, University of Iowa

The objective of this research project is to develop nanometer-sized zeolites as environmental catalysts. Nanocrystalline zeolites possess very large internal and external surface areas that can be exploited for many different applications. This research project demonstrated that zeolite particle size can be system-

atically tuned in the nanometer range by varying reaction conditions. The nanocrystalline zeolites can be functionalized to control their properties and used as building blocks for hierarchical zeolite structures, such as fibers, films, and hollow zeolites. The most recent work of the project has been to exploit these materials for environmental applications. Environmental applications for nanocrytalline zeolites and hierarchical structures include adsorption of volatile organic chemicals such as toluene from aqueous or gaseous solutions and the potential for selective catalytic reduction of NO_2 with hydrocarbons on nanocrystalline Y zeolites.

Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications
Manjusri Misra, Michigan State University (Lawrence Drzal, PI)

This research project seeks to replace 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. The goal of this research is to replace conventional petroleum-based clay-reinforced polymers with biodegradable plastics. The approach used was to toughen poly(hydroxybutyrate) (PHB) to improve impact properties; however, the modulus and consequently the stiffness of the material was reduced. To counteract this, nanoclay platelets were introduced to improve the stiffness to some extent. A new research approach is being used to address the main drawbacks of PHB and explore the nucleating effect of expanded graphite nanoplatelets on PHB. Expanded graphite nanoplatelets (xGnP) act as efficient nucleating agents for PHB. PHB crystallizes faster in the presence of xGnP, a behavior desirable for dynamic processing conditions. The effects of xGnP on the crystallization behavior and morphology of PHB provide a foundation for further investigations of PHB/xGnP systems, with the objective of obtaining advanced bionano-composites with controllable thermal and mechanical properties.

Ecocomposites Reinforced With Cellulose Nanoparticles: An Alternative to Existing Petroleum-Based Polymer Composites
William Winter, Syracuse University

The objective of this project is to explore the preparation, characterization, and formulation of cellulose nanoparticles into nanocomposites. The project also examined other substances, such as chitin nanocrystal preparation and derivatives. Further work in characterizing the effects of cellulose-graft-PCL and PHA composites is in progress. A challenge will be the scale up of the composite extrusion and compounding processes. Scale-up batches as large as 400 grams have been prepared. Challenges include separation of particles from acid, with experiments underway on acid recycling and minimization of reaggregation of particles. Biodegradation studies are another component of the research. Biodegradable particulates to replace glass fiber, and other nonbiodegradable inorganics in composites can provide environmental benefits. Cellulose-based materials have the potential to be used to generate wholly biodegradable nanocomposites, and commercialization discussions are underway with several companies.

Nanostructured Microemulsions as Alternative Solvents to VOCs in Cleaning Technologies and Vegetable Oil Extraction
Anuradee Witthayapanyanon and Linh Do, University of Oklahoma (David Sabatini, PI)

The objective of this project is to develop surfactant-based aqueous solvents to replace organic solvents in cleaning processes and vegetable oil extraction. Linker-based formulation rivals the performance of perchloroethylene, an organic solvent. For textile cleaning, linker-based and extended surfactant-based micro-emulsion as a pretreatment system can remove at least 50 to 85 percent of hydrophobic stains from fabric. In addition, the project has demonstrated low interfacial tension for vegetable oils with extended

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surfactants, and surfactant enhanced oil extraction achieves 86 to 92 percent recovery of peanut oil. The results to date are encouraging for the possible use of surfactant-based microemulsions as organic solvent replacements. Future work for the project includes studying the synergism of a combination of extended surfactant and linkers and the detergency mechanisms. Extraction efficiency of olive oil and soybean oil and the effect of pH on vegetable oils extraction also will be examined. Additional research is needed on the quality of oil extracted by the surfactant-enhanced vegetable oil extraction technique.

REMEDIATION

U.S. EPA STAR Grantees

Dendritic Nanoscale Chelating Agents: Synthesis, Characterization, Modeling and Environmental Applications
Mamadou Diallo, California Institute of Technology

This project explores the fundamental science of metal ion uptake by poly(amidoamine) (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 tetrachloroethylene (PCE) in aqueous solutions and subsurface formations. The overall results of this research suggest that dendritic nanoscale chelating agents provide unprecedented opportunities for developing a new generation of efficient and cost-effective high capacity and recyclable chelating agents and FeS dendrimer nanocomposites to treat water contaminated by toxic metal ions and redox active solutes. The research has led to a patent for recovery of metal ions from aqueous solutions by dendrimer-enhanced filtration. The system is modular, flexible, and scalable for nanofiltration, ultra-filtration, and microfiltration. Comparatively lower operating pressure, energy consumption, and loss of ligands can be achieved with dendrimer-enhanced ultrafiltration to recover metal ions from contaminated water.

Developing Functional Fe(0)-Based Nanoparticles for* In Situ *Degradation of DNAPL Chlorinated Organic Solvents
Gregory Lowry, Carnegie Mellon University

The objective of this project 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^0-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 to 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 2 years of the project has focused on: (1) identifying suitable Fe^0 nanoparticles and understanding the properties that control their reactivity with TCE; (2) synthesizing and characterizing amphiphilic block copolymer-modified nano-iron; and (3) evaluating the DNAPL-targeting and transport properties of the resulting polymer-modified functional nanoparticles.

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Nanostructured Catalytic Materials for NO_x Reduction Using Combinatorial Methodologies
Selim Senkan, University of California, Los Angeles

The objective of this project is to integrate combinatorial catalysis methodologies with nanostructured materials processing for the discovery, optimization, and better understanding of new, active, and stable catalytic materials for the reduction of NO_x under lean-burn conditions. These objectives will be accomplished by systematically exploring a large number of different combinations of metals and nanostructured metal oxide supports. Libraries of catalytic materials were prepared by individually impregnating five support materials of Al_2O_3, CeO_2, SiO_2, TiO_2, and Y-ZrO_2 with salt solutions of 42 elements from the periodic table, resulting in five different metal loadings. These support materials were chosen because of their durability in harsh engine exhaust conditions. Catalytic materials were then tested for their NO reduction activities using array channel microreactors and mass spectrometry. The test conditions realistically simulated the actual engine-out conditions, thereby rendering the findings immediately relevant to automobile exhaust treatment catalysis. These systematic investigations led to the discovery of Pt/TiO_2 and Pt/SiO_2 as the most significant materials, both of which exhibited superior performances, reducing the levels of NO by 25 percent and 20 percent, respectively.

A Bioengineering Approach to Nanoparticle-Based Environmental Remediation
Daniel Strongin, Temple University

The objective of this project is to develop a bioengineering approach that can be used to create nano-size catalytic materials as the basis for new remediation strategies. The project will assess the potential use of ferritin, and ferritin-derived compounds, as catalysts in environmental degradation processes. The ferritin system has the advantage of being environmentally benign and biodegradable. The research focuses on: (1) the development of a bioengineered synthesis of a variety of homogeneous nano-sized metal and metal oxide particles; (2) the determination of the electronic properties of the nanoparticles and their reduced forms (i.e., the base metal) as a function of size; and (3) a determination of the reactivity of the particles toward beneficial environmental chemistry, as a function of size and electronic structure. The ultimate goal is to develop new nano-sized materials based on ferritin that may serve as catalysts in (photo)chemical degradation processes of common contaminants. The research is expected to provide significant insight into the dependence of electronic structure and reactivity on chemical composition of nanoparticles.

Nanoscale Bimetallic Particle for* In Situ *Remediation
Wei-xian Zhang, Lehigh University

The primary goal of this research is to continue the research and development of the nanoscale bimetallic particle technology for *in situ* remedial applications. The objectives of the project include: (1) optimization and scale-up of the synthetic method(s) to facilitate the rapid and cost-effective production of nanoparticles for large-scale field applications; (2) extension of the technology by expanding the scope of amenable contaminants to include perchlorate and toxic metals (e.g., Cr(VI)); and (3) investigation of transport, reactions, and long-term performance with various chlorinated organic compounds and heavy metal ions.

Transformation of Halogenated PBTs With Nanoscale Bimetallic Particles
Wei-xian Zhang, Lehigh University

The objective of this research is to develop nanoscale bimetallic particles (e.g., Fe-Pd) with sizes in the range of 1-100 nm for treatment of hydrophobic, persistent, bioaccumulative toxic compounds (PBTs). Nanoparticles have higher contaminant availability and higher reactivity towards PBTs. State-of-the-art

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techniques of nanomaterial synthesis will be exploited to create novel materials for PBT treatment. The synthesized nanoparticles will be systematically assessed for the rate and extent of PBT degradation. The model compounds selected for this research include: polychlorinated biphenyls (PCBs), hexachlorocyclo-hexanes (HCHs), chlorinated benzenes, and phenols. Transport and reactions of the iron nanoparticles in porous media will be studied in laboratory soil columns. Fluorescent tagging methods will be used for detailed microscopic analysis of particle transport and deposition in porous media.

Nanostructured Catalysts for Environmental Remediation of Chlorinated Compounds
Yunfeng Lu, Tulane University

The use of zero-valent iron for *in situ* remediation of chlorinated compounds may be used more effectively by minimizing aggregation and improving mobility during *in situ* remediation. The objective of this research project is to design mesoporous supports for nanoscale iron catalysts with controlled functionalities to allow catalyst partitioning to the organic/aqueous/interfacial regions. The principles of surfactant self-assembly can be used to create structured mesoporous supports. The goals for continuing and future work include: (1) generating iron containing silica nanoparticles; (2) functionalizing silicas with hydrophobic/hydrophilic ligands to control catalyst mobility and partitioning characteristics; (3) evaluating catalytic activity towards TCE breakdown using static experiments; (4) developing a novel microcapillary video-microscopy based technique to visualize contaminant droplet and catalyst particle characteristics during *in situ* remediation; and (5) performing column experiments to measure the efficacy of contaminant break-down during *in situ* remediation.

Synthesis and Application of a New Class of Stabilized Nanoscale Iron Particles for Rapid Destruction of Chlorinated Hydrocarbons in Soil and Groundwater
Dongye Zhao, Auburn University

The goal of this research is to develop a cost-effective, *in situ* remediation technology that employs a new class of dispersed iron-based nanoparticles for the rapid destruction of chlorinated hydrocarbons in soil and groundwater. The specific objectives are to: (1) synthesize a new class of stabilized iron-based nano-particles using low-cost and "green" stabilizers such as starches and celluloses; (2) test the effectiveness of the stabilized nanoparticles for dechlorination of select contaminants (TCE and PCBs) in soil and ground-water; and (3) test the feasibility of an *in situ* remediation process that is based on the nanoparticles. The preliminary data showed that a water-soluble or sodium carboxymethyl cellulose (CMC) can serve as the dispersant to stabilize palladized iron (Fe-Pd) nanoparticles. Compared to nonstabilized Fe-Pd particles, the stabilized nanoparticles displayed markedly improved physical stability, soil dispersibility, chemical reactivity, and reactive longevity. Column tests showed that the stabilized nanoparticles can readily disperse in a loamy-sand soil and then be recovered completely. Batch dechlorination tests demonstrated that the CMC-stabilized nanoparticles degraded TCE 29 times faster than nonstabilized counterparts based on the pseudo first-order rate constant.

Nanostructured Membranes for Filtration, Disinfection, and Remediation of Aqueous and Gaseous Systems
Svetlana Zivanoic, University of Tennessee (Kevin Kit, PI)

The objectives of this research project are to: (1) develop electrospun nanofiber chitosan membranes to treat aqueous and gaseous solutions through filtration, disinfection, and metal binding; (2) understand the electrospinning process for chitosan to control membrane structure; (3) investigate the effect of membrane structure on filtration, disinfection, and metal binding; and (4) optimize performance/efficiency of chitosan membranes. The central hypothesis for the research is that the degree to which these nanofiber chitosan membranes effectively filter contaminants, kill microbes, and bind harmful metals will be

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optimized by minimizing the size of the electrospun fibers and maximizing the available chitosan surface area. The results of this research could provide a new nanostructured system for the treatment and remediation of aqueous and gaseous environments with improved efficiency over current filtration technologies. The goal is that microorganisms are removed via filtration and killed on contact. The multiple functions that these chitosan membranes will serve (removal, destruction, and immobilization of toxic species) could make them cost-effective replacements for multiple treatment systems presently in use. Environmental advantages include the fact that chitosan is biodegradable and no organic solvents are required for processing.

SENSORS

U.S. EPA STAR Grantees

Metal Biosensors: Development and Environmental Testing
Anne Anderson, Utah State University

Cells of a soil-borne pseudomonad respond differentially to the toxic metals copper and cadmium. The objective of this research project is to develop and test biosensors and DNA arrays that will detect copper or cadmium and indicate the bioavailability of these metals to a bacterium. Constructs have been made and responses are beginning to be determined; however, it will be important to identify specific metal promoters. Bioinformatics and proteomics can be used to investigate genes as candidates for a biosensor method. Project research has demonstrated that some metal complexes can be detected by pseudomonads. Genomic studies demonstrated that a subset of the genome is sensitive to the presence of metals and that some genes not predicted by bioinformatics show a change in gene expression as a result of the presence of cadmium or copper. Future work will include testing new Lux fusions for specificity and sensitivity, investigating the role of polyphosphate for understanding the phenomenon of stasis induced by cadmium exposure, investigating the use of specific RNA/DNA hybridizations to determine altered gene expression, and testing the effects of copper citrate, cadmium citrate, and other complexes with bioassays and physical measurements.

Nanosensors for Detection of Aquatic Toxins
Robert Gawley, University of Arkansas

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. Saxitoxin is a marine toxin that is difficult to detect. The standard chemical assay method is a mouse bioassay with an analytical goal of 1 μm. This project's objective is to utilize fluorescence sensing to detect saxitoxin and other marine toxins. Selecting the correct fluorophore for use in detection is a challenge. The present work is focused on mimicking the natural action of saxitoxin by placing a sensor inside a large dendrimer, allowing the saxitoxin to diffuse to the core, and then measuring the fluorescence response. The first attempt was a coumarin sensor anchored in the dendrimer nanoenvironment. Coumarin is not a good fluorophore in this case because the shellfish extract has an absorbance at the same wavelength as the coumarin. A longer wavelength fluorophore is needed, and research has begun on a visible chromophore, boron dipyrrin. Future work will examine incorporation of a visible fluorophore into the dendrimer, testing of an improved peptide for binding, and evaluation of the fluorescence response with shellfish extracts.

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Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS (CυMOS) Transistors
Edwin Kan, Cornell University

An ideal microsensor for autonomously monitoring chemical and molecular environmental hazards in both water and air should simultaneously have high sensitivity, high selectivity, large dynamic range, low manufacturing cost, simple calibration/reset protocols, long lifetime, field reconfigurability, and low power consumption. The objective of this research project is to develop a silicon-based neuron MOS transistor with a novel extended floating-gate structure that permits molecular and chemical sensing. Project work has improved the fluidic integration for molecule-blocking pores to obtain more reliable transient and small signal information and allow for better cleaning. Accomplishments include totally CυMOS integrated FET devices with extended floating gates for chemical sensing. The floating-gate structure for electron-tunneling operations provides more degrees of freedom for sensing, and CυMOS-integration enables detailed control circuits. Project work has demonstrated that universal sensor arrays can be constructed to have specificity that allows for pH sensing, pressure sensing, and photodetection using different coatings on the sensor. Future work will focus on designing a nanoelectronic interface using C_{60} or nanotubes as the floating gate.

Compound Specific Imprinted Nanospheres for Optical Sensing
Barry Lavine, Oklahoma State University

The objective of this research project is to investigate the use of molecularly imprinted polymer particles as the basis of a sensitive and selective method for the detection of pharmaceuticals and other emerging organic contaminants. Such imprinted particles can be incorporated into hydrogel membranes. The project presently is focusing on theophylline. Theophylline-imprinted particles are suspended in polyvinyl alcohol hydrogel and exposed to varying concentrations of theophylline. In the absence of theophylline, the hydrogel is turbid because the refractive index of the particles is greater than the refractive index of the hydrogel. In the presence of aqueous theophylline, the polymer will swell. The increased water content in the particles causes a decrease in particle refractive index, bringing them closer to the refractive index of the hydrogel. This leads to a decrease in membrane turbidity, which is proportional to theophylline concentration in the solution. Changes in the swelling of the theophylline-imprinted particles are monitored using surface plasmon resonance spectroscopy.

Carbon Nanotube Self-Assembly in a VOCs Monitoring Platform
Somnath 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 com plex 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. The project has used three different ways to make carbon nanotubes, including catalytic arc, catalytic laser ablation, and catalytic chemical vapor deposition. Catalysis for single-walled nanotubes is more difficult than for multi-walled nanotubes. GC columns coated with carbon nanotubes are able to do the same type of separation as traditional GC columns, and results exhibit classical chromatography features. Nanotube synthesis is a balancing act of catalyst, residence time, and the precursor used. Thickness levels are not consistent along the length of the column, and this phenomenon needs further investigation.

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Advanced Nanosensors for Continuous Monitoring of Heavy Metals
Omowunmi Sadik, State University of New York, Binghamton

The objective of this research project is to incorporate novel, colloidal-metal nanoparticles into a bed of electrically conducting polymers, and then use these for the development of nanosensors. The highlight of efforts during the second year of the project was the development of a Pd synthetic approach that was tested as an environmental catalyst for the conversion of Cr(VI) to Cr(III). One of the synthetic nano-structured materials developed under the project was tested as an environmental catalyst for the conversion of higher valent to low valent Cr in soil and water samples. The real sample application of the Pd nanoparticles-sulfur mixture tested using soil samples produced more than 92 percent conversion in the presence of Pd-NPs/S within 1 hour. In contrast, only 33 percent of the same concentration was converted to Cr(III) in the absence of Pd-NPs/S. This represents a greater than 500-fold improvement in conversion rate compared to current microbial approaches. This work offers a new and safe application of nanotechnology for the reduction of high oxidation state heavy metal pollutants.

Ultrasensitive Pathogen Quantification in Drinking Water Using High Piezoelectric PMN-PT Microcantilevers
Wan Shih, Drexel University

The objective of this research project is to develop highly piezoelectric microcantilever arrays for *in situ*, rapid, simultaneous multiple pathogen quantification in source water with the ability to detect pathogens using electrical means with unprecedented sensitivity (10^{-15} g). The short-term goals for the second year of the project were to: (1) examine *in situ*, direct detection of various waterborne pathogens, including *Escherichia coli* 0157:H7 and *Salmonella typhimurium* using PZT cantilevers with antibodies immobilized on various surfaces, such as gold and titanium; and (2) use the highly reactive PMN-PT precursor powder developed by the researchers to fabricate PMN-PT freestanding films by tape casting and use the freestanding PMN-PT films. Research results have shown sensitive *Escherichia coli 0157:H* and *Salmonella* detection. Smaller cantilevers lead to increased detection sensitivity. Another advancement has been the development of a microcantilever array. Both the material and sensors are patented. Real-time detection has been achieved through the use of the arrays with a flow cell. In this system, no adjustment is needed because there are no background values to subtract. This method was used for detection of *Bacillus anthracis* spores and proteins such as prostrate specific antigen. The portable system includes an electrical unit, sensor, and flow cell. Future work involves development of array piezoelectric microcantilever sensors to allow for protein detection at the unprecedented pg/mL levels and single-cell bacteria detection.

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 field-effect transistors (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 arrays are built from the bottom up with the channel material exposed. Because of the ability to use ink jet printing, the cost is relatively low. Sensitivity of the arrays is a challenge. Often a tradeoff occurs between sensitivity and stability. Using functional groups to make parts of an array specific can enhance sensitivity without the need for larger arrays. Nonlinearity as a result of sample drift over time is a challenge. Progress has been made on sensor integration, including developing methods for dealing with drift. The challenge continues to be the optimization of structure and process flow, particularly in terms of stability, reliability, and fluid compatibility. Future project work will focus on the

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development of fluid-compatible derivatives and deployment for testing of environmentally relevant analytes.

A Nanocontact Sensor for Heavy Metal Ion Detection
Nongjian Tao, Arizona State University

The objective of this research project is to develop a high-performance and low-cost sensor for the initial onsite screening of surface and groundwater that will provide early warning and prevention of heavy metal ion pollution. The highly integrated sensor will consist of arrays of different nanojunctions, including nanocontacts, molecular junctions, and polymer nanojunctions, for simultaneous detection of a range of different chemical species. Recent project work has focused on the use of peptides as molecular probes. Protein molecules are good at recognizing other molecules, and combinatorial chemistry can provide tools for construction of molecular probes. Results of aniline functionalized with peptides showed that the peptides chosen had high affinity for the metal ion and provided sensor specificity. Characterization by Fourier Transform Infrared Spectroscopy (FTIR) revealed that the peptide structure is in polymer film. Results from tests of the nanojunction metal ion sensors found the ability to detect copper as low as 4 ppt and nickel as low as 22.5 ppt. The sensors are reusable approximately nine times for metal ion detection. Using the nanojunction sensors to analyze drinking water from Tempe, Arizona, showed agreement with analysis by atomic absorption spectroscopy.

Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring
Joseph Wang, Arizona State University

The project goal is to create a novel microfluidic device for rapidly, continuously, and economically monitoring different classes of priority pollutants. The laboratory-on-a-chip concept provides opportunities to meet this goal, but integration of functional elements is required. A protocol for rapid screening and fingerprint identification of phenols was developed that uses microchip flow-injection analysis for fast screening and early detection of total phenolic compounds and then allows for switching to the fingerprint mode. Screening is rapid, 5 to 10 seconds, and individual fingerprinting occurs within 2 to 3 minutes, with the ability to switch between total and individual protocols quickly. Progress was made on the macro-to-micro interface through incorporation of a Sharp microchip inlet to facilitate electrokinetic loading of samples directly into the separation microchannel. Integrating additional sample-handling capabilities and incorporating various nanomaterials can further enhance such microsystems. The electrocatalytic activity and resistance to surface fouling of carbon nanotube materials provides improved sensitivity, stability, and resolution compared to common carbon-electrode detectors.

Conducting-Polymer Nanowire Immunosensors Array for Microbial Pathogens
Ashok Mulchandani, University of California, Riverside

Waterborne pathogens are responsible for 90 percent of waterborne disease outbreaks in the United States, but 50 percent of outbreaks have no causative agents identified because of inadequacy of detection methods. The objective of this project is to develop a novel technique for the fabrication of antibody-functionalized nanowires that are individually addressable and scalable to high-density immunosensor arrays for label-free, real-time, rapid, sensitive and cost-effective detection. Silicon nanowire and carbon nanotube FETs have challenges, and conducting polymers may be useful to meet these challenges. Aspects of conducting polymers that are favorable include conductivity that can be reversibly modulated more than 15 orders of magnitude and the ability for electrochemical synthesis. Benign conditions enable the direct deposition of conducting-polymer materials with embedded bioreceptors in one step. This project's future work includes demonstrating the ability to grow biologically functionalized nanowires of

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controlled dimension and obtaining an understanding of sensor sensitivity and selectivity, with the goal of fabricating and evaluating a nanowire immunosensor array for multiple viruses.

Canadian Grantees

Exploring the Impact of a Nanostructure's Size and Shape on Cellular Uptake, Clearance, and Metabolism
Warren Chan, University of Toronto

Novel discoveries on molecular differences between diseased and healthy cells and tissues and developments of nanotechnology probes and tools are transforming the way we treat and diagnose disease. Biological molecules provide a means to direct nanostructures to a diseased site where the nanostructure can be optically, electrically, or magnetically lit up or treat the diseased site. A key to this hybrid research field is the ability to engineer nanostructures with defined properties. Essentially, a nanostructure provides a system that has custom-tunable function based on its size and shape. Recently, the use of such nanostructures for cell, tissue, and animal imaging and therapeutic applications for the early detection and treatment of cancer has been demonstrated. The interface of these two fields has prompted several important questions, such as: Are the nanostructure's toxic? How does a cell process these nanostructures? What is the fate and clearance of these nanostructures? Are these processes related to the dimensional or surface chemical characteristics of the nanostructures? These fundamental questions must be answered before nanostructures become useful for clinical applications. Dr. Chan's presentation included a discussion on the techniques and research results in elucidating these fundamental questions. The size and shape-dependent uptake of the nanostructures in cell cultures and in animals using model nanostructures also was discussed. The results from these studies provide guidance for the design of nanostructures for biomedical applications.

TREATMENT

U.S. EPA STAR Grantees

Applications of Nanoscale Tunable Biopolymers for Heavy Metal Remediation
Ashok Mulchandani, University of California, Riverside

Heavy metal accumulation in soil leads to water contamination and biomagnification. Conventional approaches are often inadequate in reducing the concentrations to satisfy sub-ppb regulatory limits. The advantages of nanoscale biopolymers derived from biological building blocks include: easy production by engineered bacteria; they are environmentally friendly (i.e., they are biodegradable and contain no hazardous compounds); they can be engineered for specific metal recognition and binding; and they can be reversibly precipitated by change in temperature. The objective of this research was to design a new generation of elastin-like protein (ELP) biopolymers with enhanced metal binding affinity and selectivity for water and soil remediation. ELP biopolymer with enhanced metal binding affinity and selectivity was designed successfully. The work of the project provided a novel, environmentally friendly, and green engineering method for removal of heavy metal from water and soil.

Synthesis, Characterization, and Catalytic Studies of Transition Metal Carbide Nanoparticles as Environmental Nanocatalysts
Ismat Shah, University of Delaware

Current regulations based on the 1990 Clean Air Act Amendments (CAAA) require vehicle NO_x emissions to be less than 0.6 g/mile with 100,000 hours duration. In 2007, further reduction in NO_x

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emissions, below 0.2 g/mile, is mandated. Because of the limited availability of the platinum (Pt)-group metals, an alternative catalyst is required. The objective of this research project is 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_x. Transition metal carbides are known to have catalytic properties similar to Pt-group metals, and WC (Tungsten Carbide), in particular, has been used in isomerization reactions as a replacement for Pt. The research project demonstrated that WC nanoparticles effectively reduce NO_x, and WC composition and structure determine the conversion efficiency. In pure NO_x, catalyst oxidation occurs at temperatures of 500 ºC and beyond. CO addition can add to the conversion efficiency and stability of the catalyst. Further stabilization is needed through the addition of O or N.

A Novel Approach To Prevent Biocide Leaching
Patricia Heiden, Michigan Technological University

Newer wood preservative formulations are formulated without chromium and arsenic to reduce negative environmental impact; however, because of this, the preservatives are more likely to leach to the environment. This research project is based on a hypothesis that increased biocide loss leads to decreased longevity of wood products, leading to increased biocide use, which increases stress on sensitive environments. The objectives of this research project are to "fix" biocides into nanoparticles to provide a stable, controlled situation that could reduce or prevent leaching. The biocide release is controlled through the nanoparticles' matrix hydrophobicity. The expected result of the research is to increase wood product lifetime using less biocide. Wood treatment systems using nanoparticles and conventional preservatives will be compared. The key tasks will be to: (1) verify equivalent loading in wood; (2) perform leaching studies; and (3) examine the biological efficacy of the different treatments compared to untreated wood.

FATE/TRANSPORT

U.S. EPA STAR Grantees

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

The 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 estuarine 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.

A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol
Vicki Grassian, University of Iowa

Manufactured nanoparticles may become suspended in air during production, distribution, use and disposal, and become a component of the tropospheric aerosol and thus the air we breathe. The objectives

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of this research are to: (1) characterize a variety of manufactured nanomaterials in terms of their size, shape, bulk and surface properties (metal, oxide and semiconductor nanoparticles); (2) determine if engineered nanomaterials are particularly deleterious to health compared to particles from combustion processes that have been more extensively studied; and (3) evaluate the relative health effects caused by different surface coatings on the nanoparticle. This research focused on one of the smallest commercially available nanoparticles, 5 nm TiO_2. These particles are pure anatase, and their surfaces are truncated by surface hydroxyl groups and adsorbed water under ambient conditions (i.e., there are no surface coatings present from manufacturing). The particle surfaces can be modified by adsorption, and thus the impact of coatings can be studied in future experiments. The particles form an aerosol using a nebulizer. The particles aggregate and form an aggregate size of approximately 100 nm as determined from TEM and SMPS. Sub-chronic inhalation exposure to TiO_2 nanoparticles caused an increase in the number of activated macrophages; however, mice recovered after 3 weeks post exposure. No signs of pathological changes in BAL fluid or in lung tissue were found in this study.

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

Regarding cadmium selenide (CdSe) quantum dots in soil and water, where bacterial interactions will occur, this project is addressing the following questions: (1) What are the biotic fates of CdSe QDs? (2) What are the effects of QDs on bacteria? (3) How do fates and effects depend on QD conjugation, QD size, environmental factors (light, pH, reduction potential, oxygenation), bacterial strain and growth habit (biofilm or planktonic)? Thus far, the results have facilitated a working conceptual model of strain-dependent quantum dot interactions with bacteria: external nonspecific labeling in which unconjugated QDs cannot passively diffuse into cells; specific binding and nonspecific uptake in which conjugates are recognized by receptors on the cell envelope and light-mediated membrane damage from oxygen free radicals facilitates transmembrane transport, allowing conjugated QDs less than 5 nm diameter to enter cells; and external breakdown and transmembrane diffusion of constituent metals, such that Cd^{2+} may be expelled; Se^{2-} may be expelled or oxidized to Se^0 and then retained or expelled; and Cd^{2+} and Se^{2-} may combine into nanoparticles and be expelled or retained. Specific results in support of this working model were generated from studies involving several bacterial strains, including *Bacillus subtilus*, *Eschericia coli*, and *Psuedomas* spp. The work to date includes: (1) a putative, conceptual model for how quantum dots interact with bacteria; (2) evidence to support several interaction mechanisms, including light-activated QD production of membrane-damaging free radicals, free radical-assisted transmembrane transport of conjugated QDs, and conjugated QD-mediated DNA damage, arresting cellular division; and (3) early evidence for intracellular QD assembly in biofilms and planktonic culture.

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

Little is known about the environmental fate of manufactured nanomaterials. Sorption is often the most important fate mechanism for environmental contaminants. This research project tests the following four hypotheses: (1) carbon nanostructures have a high capacity for sorption/desorption hysteresis with poly-nuclear 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) 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. In the first year of this project, the researchers successfully characterized the sorption/desorption behavior of

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both organic and inorganic contaminants to nanomaterials and the fate and transport of naphthalene (an organic contaminant) and colloidal C_{60} particles in soil column.

The Bioavailability, Toxicity, and Trophic Transfer of Manufactured ZnO Nanoparticles: A View From the Bottom
Paul Bertsch, University of Georgia

The objectives of this project are to evaluate the bioavailability and toxicity of manufactured zinc oxide nanoparticles to the model soil bacteria *Burkholderia cepacia* and the model detritivore *Caenorhabditis elegans*, as well as the ability of nanoparticles to be transferred from one trophic level to the next in a simple food chain consisting of pre-exposed *B. cepacia* and *C. elegans*. In addition, the project will evaluate the synergistic or antagonistic effects of zinc oxide nanoparticles on the toxicity of copper to *B. cepacia* and *C. elegans*. The project is based on the hypotheses that: (1) the bioavailability and toxicity of manufactured zinc oxide nanoparticles increase with decreasing particle size; (2) the toxicity of such nanoparticles is lower than an equivalent concentration of dissolved zinc ions; (3) the bioavailability and toxicity of zinc oxide nanoparticles introduced via trophic transfer differs from the bioavailability and toxicity of direct exposure; and (4) the nanoparticles alter the bioavailability and toxicity of dissolved metals.

Hysteretic Accumulation and Release of Nanomaterials in the Vadose Zone
Tohren Kibbey, University of Oklahoma

Any nanomaterial that is widely used will ultimately enter the environment. The vadose zone may provide either a sink for nanomaterials and prevent their spread throughout the environment, or it may act as a long-term contaminant source. The project objectives are to: (1) study the vadose zone accumulation and release of a wide range of manufactured nanomaterials, and (2) examine hysteretic interactions at air and water interfaces and specific mineral surfaces. The expected outcomes from this research include: (1) improved *a priori* assessment of manufactured nanomaterial mobility in the environment and associated risk; (2) indications about nanomaterial classes likely to accumulate in the vadose zone and roles of mineral surfaces, air/water interfacial areas, and wetting/drying history on accumulation; and (3) new information necessary to assess the role of vadose zone interactions in decreasing or increasing ultimate risk to human or environmental health.

Fate and Transformation of C_{60} Nanoparticles in Water Treatment Processes
Jaehong Kim, Georgia Institute of Technology

Carbon nanomaterials are hydrophobic and form water stable aggregates. Such aggregates impact nanomaterials entering water treatment processes. Treatment processes can include both oxidation and filtration. This research project will test three hypotheses. *Hypothesis 1:* When subjected to oxidation by commonly used oxidants and disinfectants such as ozone, ultraviolet (UV) light, free chlorine, and monochloramine, the unique electron-rich surface chemistry of nano-C60 will lead to various chemical transformations. *Hypothesis 2:* A unique, weakly negatively charged surface of nano-C60 will lead to unique electrostatic and hydrophobic interactions with metal hydroxide soluble complexes and precipitates in coagulation processes employing divalent metals, with polymeric membrane surfaces in membrane filtration processes, and with hydrophobic surfaces of activated carbon in adsorption processes. *Hypothesis 3:* A unique size characteristic of nano-C60 will lead to unique filtration characteristics when filtered through nanoporous membranes, and unique mass transfer and adsorption kinetics/equilibrium characteristics when adsorbed by activated carbon with varying pore size distributions.

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Fate and Transport of C_{60} Nanoparticles in Unsaturated and Saturated Soils
Kurt Pennell, Georgia Institute of Technology

The objectives of this research project are to: (1) investigate the fate and transport of C_{60} nanomaterials in water-saturated soils as a function of soil properties and systems parameters; (2) assess the effects of C_{60} nanomaterials on soil water retention, water flow, and transport in unsaturated soils; and (3) develop and evaluate a numerical simulator to describe C_{60} nanomaterial transport, retention, and release in subsurface systems. To understand the fate and transport of nanomaterials in water-saturated soils, experiments will be conducted in water-saturated clean porous media, natural soils, and in heterogeneous aquifer cells. To understand the fate and transport of nanomaterials in unsaturated soils requires investigation of solution and interfacial properties as well as pressure-saturation relationships and unsaturated hydraulic conductivity. A mathematical model of nanomaterial fate and transport in porous media will be developed. It is hypothesized that classical particle filtration theory will not be sufficient to accurately describe C60 nanoparticle retention and release. The goal will be to incorporate short-range hydrophobic and hydrate forces equations to improve the predictions of particle retention and release.

NSF Grantees

Cross-Media Transport, Transformation, and Fate of Carbonaceous Nanomaterials
Linsey Marr, Virginia Polytechnic Institute and State University

Nanoparticles released into the atmosphere undergo transformations that change the particles' size, chemical composition, and surface properties. When these "aged" particles later deposit onto the earth's surface, they may have very different fates in the aquatic and terrestrial environments compared to the "fresh" compounds. The objective of this research is to characterize the behavior of "fresh-unaltered" versus atmospherically "aged" nanomaterials in aquatic and terrestrial systems. The research approach is to quantify the rate of reaction of airborne carbonaceous nanomaterials (CNMs) with ozone, evaluate transport of "fresh" and atmospherically "aged" CNMs in porous media, and quantify adhesive and repulsive forces between CNMs and environmental surfaces. The expected benefits include prediction of the fate of CNMs in the environment and assessment of the potential for human exposure. Such knowledge could assist in overcoming barriers to the use of nanomaterials for environmental applications.

TOXICITY

U.S. EPA STAR Grantees

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

The objectives of this research project are to: (1) determine the short-term chronic toxicity of photocatalytic nanoparticles to aquatic organisms, including bacteria, algae, and daphniad; and (2) assess major factors affecting the ecotoxicity of photocatalytic nanoparticles. Among the target organisms studied were: bacteria (*Escherichia coli*), algae (*Selenastrum capricornutum*), and daphniad (*Ceriodaphnia dubia*). The small size, surface charge, photocatalysis properties, and chemical composition of nanoparticles are all factors that could lead to their toxicity. Results show that in the size range of 5 to 30 nm, there appeared to be no significant difference in toxic response to the photocatalytic nanoparticles, but more data are needed. Cell damage was observed in terms of lipid oxidation and cellular respiration. The dose-response information, exposure experiments, and toxicity studies of this research will provide information on the evaluation of ecological risk associated with nanoparticles, including mechanistic information on the effects of nanoparticles on trophically important aquatic organisms.

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Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity
Robert Hurt and Agnes Kane, Brown University

The project approach is to develop and test a model nanomaterial system with well-characterized, accessible, nanophase iron and to characterize and test complex, commercial multi-walled nanotubes in four forms—as produced, vendor purified, vendor purified and mechanically damaged, and vendor purified and oxidatively damaged. Toxicity assays include iron mobilization experiments, assessment of plasmid DNA single strand breaks, and macrophage viability and morphology. Results of the research show that carbon nanofibers containing surface nanophase iron exhibit key indicators of potential toxicity and that unpurified multi-walled nanotubes contain mobilizable, redox-active iron. Purification greatly reduces iron mobilization and DNA breaks, whereas mechanical grinding has no measurable effect though oxidation may re-expose some encapsulated iron. Future work will include investigation of cellular mechanisms of nanomaterial uptake, characterization of iron mobilization from a broad range of nanomaterials (additional multi-walled nanotubes, single-walled nanotubes, magnetic nanoparticles, and reference materials), assessment of Fe mobilization, and initiating work on nickel- and cobalt-containing carbon nanotubes and nanofibers.

The Fate, Transport, Transformation, and Toxicity of Manufactured
Responses of Lung Cells to Metals in Manufactured Nanoparticles
John Veranth, University of Utah

It is assumed that because of their high surface area, nanoparticles are likely to induce larger responses in cells than their micron-sized counterparts. In addition, it is hypothesized that the transition metals in nanoparticles induce pro-inflammatory cytokine production via reactive oxygen species production. The approach used in this research includes the physical characterization of commercially available metal oxide nanoparticles, *in vitro* cell culture screening assays, and *in vivo* studies to establish health relevance. Preliminary results of the *in vitro* assays used to date show that the metal oxide nanoparticles are not highly potent compared to micron-sized particles of the same compound or compared to positive controls that are representative of environmental particulate matter. More work is needed. Future work will involve quantitative real-time polymerase chain reaction to measure many gene messages simultaneously. Preliminary gene array studies can provide candidate genes to match to cell culture results.

Nanomaterials in Drinking Water
Paul Westerhoff, Arizona State University

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 first year of the project focused in part on methodological advances. This included demonstrating that commercial nanoparticles do not behave as discrete nanoparticles in aqueous systems, and aggregation of these materials results in particles less than 1 μm. This research has focused on metal oxide nanoparticles, and understanding how surface change (zeta potential) affects the removal of nanoparticles during simulated drinking water treatment.

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Microbial Impacts of Engineered Nanoparticles
Pedro Alvarez, William Marsh Rice University

Responsible usage of nanomaterials in commercial products and environmental applications and prudent management of the associated risks require an understanding of nanoparticle mobility, bioavailability, and ecotoxicology. This project will elucidate processes governing the transport and microbial impacts of two classes of catalytic nanomaterials in soil-water systems: fullerenes and metallic nanoparticles (e.g., TiO_2, ZnO, and Fe(0)). The specific tasks will be to: (1) characterize nanomaterials size, shape, functionality, reactivity, aggregation, deposition potential, and bioavailability; (2) screen nanomaterials of varying sizes and properties for bacterial activity; (3) discern bacterial physiologic characteristics that confer resistance (or susceptibility) to catalytic nanomaterials; (4) evaluate the potential for fullerene biotransformation by reference bacteria and fungi; and (5) assess the impact of simulated nanomaterial releases on microbial diversity and community structure. At the conclusion of this project, there will be an improved understanding of the chemical and physical factors that control nanoparticle mobility and bioavailability, and their impacts on microbial activities, diversity, and community structure. This will benefit risk assessment and management efforts, and may contribute indirectly to the development of nanotechnology-based disinfection and biofouling control strategies.

Role of Particle Agglomeration in Nanoparticle Toxicity
Lung-Chi Chen, New York University (Terry Gordon, PI)

This research project focuses on the hypothesized difference in the toxicity of fresh (predominantly singlet) versus aged (predominantly agglomerated) carbon nanoparticles. The objectives are to: (1) measure the agglomeration rate of several types of carbon nanoparticles; (2) identify whether agglomeration is affected by differing exposure conditions, including humidity and particle charge; and (3) compare the toxicity of singlet versus agglomerated particles in mice exposed via the inhalation route. The research will establish the agglomeration of freshly generated carbon nanoparticles at various distances (i.e., aging times) downstream from particle generation in a dynamic exposure system. In addition, mice will be exposed to nanoparticles at various stages of particle agglomeration and the lungs will be examined for injury and inflammation. Previous toxicological studies of nanoparticles will provide the basis for the research. These studies demonstrated that freshly formed nanoparticles produce lung injury and inflammation in mice, and the gene expression patterns were dramatically different than those produced by endotoxin and ozone.

Structure-Function Relationships in Engineered Nanomaterial Toxicity
Vicki Colvin, William Marsh Rice University

The overarching objective of this project is to provide the first structure-function relationships for nanoparticle toxicology. The specific objectives of the research are to: (1) expand the characterization of nanoparticle structure in biological media; and (2) characterize the effects of nanoparticles on cell function. This data will be used to test the hypothesis that nanoparticle structure (e.g., size and shape) controls cytotoxicity directly. A secondary hypothesis is that of the four major materials parameters in engineered nanoparticles (size, shape, composition, and surface), surface will be the most important in governing cellular effects. These hypotheses will be tested in several major classes of nanoparticles. 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. Risk management will be improved with the information provided in this research, particularly in that structure-function relationships for several major classes of nanomaterials will be established.

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Uptake and Toxicity of Metallic Nanoparticles in Freshwater Fish
Nancy Denslow, University of Florida (David Barber, PI)

The objectives of this project are to: (1) determine if fish exposed to metallic nanoparticles exhibit different responses than those exposed to dissolved metals; (2) determine if changing particle properties alter biological responses to a given metal; and (3) evaluate an *in vitro* model of nanoparticle-induced gill toxicity for its ability to predict *in vivo* responses. This project will characterize nanoparticles (Al, Ag, Ni, and Ti) in terms of size distribution, surface area, agglomeration, and particle number. Zebrafish will be exposed to metallic nanoparticles and dissolved metals for 96 hours. The general toxicity, tissue histology, ATPase activity in gill, GSH, TBARS, and tissue metal count will be determined. Microarray experiments will be performed to determine pathways that are affected by exposures. Finally, an *in vitro* gill cell line will be developed to identify mechanisms of toxicity.

Cellular Uptake and Toxicity of Dendritic Nanomaterials: An Integrated Physicochemical and Toxicogenomics Study
Mamadou Diallo, California Institute of Technology

This project seeks to advance the fundamental understanding of the relationships between the interactions of ethylene diamine core poly(amidoamine) dendrimers with cell membranes and their vascular and ingestion toxicity. Physical-chemical surrogates and atomic force microscopy will be used to characterize the interactions of dendrimers with cell membranes. Molecular dynamics simulations will be used to determine the three-dimensional structures and physical-chemical properties of the dendrimers in aqueous solutions and to characterize their mechanisms of interactions with cell membrane bilayers. The research also will characterize the vascular and ingestion toxicity of dendrimers through *in vitro* measurements of cell viability and toxicogenomics studies of human endothelial and kidney cells.

Acute and Developmental Toxicity of Metal Oxide Nanoparticles in Fish and Frogs
Chris Theodorakis, Southern Illinois University

Nanoparticle exposure may be an ecological hazard that affects the survival, growth, development, egg hatchability, and metamorphosis of larger aquatic organisms such as fish and frogs. The objective of this project will be to determine the acute and chronic toxicity metal oxide nanoparticles (Fe_2O_3, ZnO, CuO, and TiO_2) in fathead minnows (*Pimephase promelas*) and African clawed frog (*Xenopus laevis*). The approach will be flow-through exposure, with nanoparticle suspension in water. The expected benefits are hazard identification of nanoparticles, which is necessary for ecological risk assessment of these particles at an early stage in the development of this technology.

<u>NanoIP-Canada Grantees</u>

Interactions Between Semiconductor Nanoparticles and Biomembranes and DNA
Jay Nadeau, McGill University

This project will quantify the interactions of QDs with cell membranes, cellular proteins, DNA, and whole cells with the goal of identifying the exact conditions under which the particles can damage cells. This will result in the design of simple tests for researchers to use that will predict the cellular toxicity of nano-sized materials based on physical properties such as size and fluorescence. Researchers also will determine whether specific classes of molecules, including DNA molecules, make QDs more reactive and hence more toxic, which will allow for recommendations for handling and disposing of these particles in biological experiments. The photophysics of QDs, particularly their size, redox potential (which depends not only on band gap, but on the presence of surface states) have a great influence on the interactions of

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these particles with biological cells and structures. Electron transfer processes should be sought as causes of selective uptake of specific sizes of QDs. Common biomolecules also can sensitize QDs, making them more photoreactive and able to damage cell membranes with or without Cd release. DNA damage, however, has so far only been seen when Cd is released in significant quantities.

Understanding the Light-Induced Cytotoxicity of Quantum Dots: A Cellular, Photophysical, and Mechanistic Approach
Francoise Winnik, Université de Montreal

QDs, nanometer-sized light emitting semiconductors, are emerging as a new class of fluorescent probes for *in vivo* and cellular imaging. Factors contributing to the safe use of QDs need to be established, as the large-scale manufacture and handling of QD and the number of patients and attending staff that could be exposed is considerable. The objectives of this research are to develop a methodology to monitor QD cytotoxicity via chemical and photochemical studies coupled with *in vitro* assessment of key cellular pathways, and confirm the relative importance of hypothesized mechanisms of QD cytotoxicity. Methods such as solution photophysics, cell imaging, and quantitative analysis of released toxic ions will be used to assess the effects of irradiation and QD composition on ions released and on cell death and to probe how bioconjugation and surface modification affect ion release, QD photophysics, and cellular pathways implicated in QD cytotoxicity. The overall goal is to explore if common properties of QD-cell interactions can be identified as useful predictors of QD-induced cytotoxicity.

Other Grantees

Assessment of the Environmental Impacts of Nanotechnology on Organisms and Ecosystems
Jean-Claude Bonzongo, University of Florida

The goal of this project is to develop an understanding of the potentially complex interplay between manufactured nanomaterials (MN) and the health of organisms and ecosystems. The research hypothesis is that chemical elements used in the production of MN could lead to environmental dysfunctions due to: (1) the potential toxicity of these elements and their derivatives; (2) the nanometer-sizes that make MN prone to biouptake/bioaccumulation; and (3) the large surface area that might lead MN to act as carriers/ deliverers of pollutants adsorbed onto them. To address this broad hypothesis, toxicological approaches at the organism level in combination with experimental investigations at the system level will be used. In addition, the bioaccumulation tendency of MN with contrasting chemical and physical properties will be theoretically assessed by molecular modeling, which will assess possible damage to the cell membranes caused by MN and test the ability of MN to cross cell membranes. The proposed combination of toxicological, biogeochemical, and modeling expertise in the assessment of the potential impacts of MN on biota and the environment is anticipated to advance discovery, as well as our understanding of the behavior, fate, and impact of MN in the environment. At the very least, the anticipated findings could provide arguments that would help avoid the dispersal of MN until more is known about their environmental implications.

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EXPOSURE

U.S. EPA STAR Grantees

Health Effects of Inhaled Nanomaterials
Ting Guo, University of California, Davis (Kent Pinkerton, PI)

Epidemiological and toxicological studies on the effects of particulate air pollution support the premise that ultrafine or nanosize particles cause pulmonary inflammation as well as systemic effects. This project will test the hypothesis that inhaled nanomaterials cause respiratory effects in the form of oxidative stress and inflammation. Such events will lead to release of pro-inflammatory cytokines as well as other mediators to induce cell proliferation and alterations in the normal cellular milieu of the airways and alveoli of the lungs. Researchers will test whether these health impacts of nanomaterials on the respiratory system are driven in large measure by: (1) particle size, (2) particle composition, and/or (3) trace contaminants associated with the manufacturing process of nanomaterials. The expected results from this research include: (1) characterization of aerosolized nanotubes, ultrafine TiO_2, and carbon black (CB) under environmentally relevant conditions found in the workplace; (2) the influence of uniquely distinct forms of nanotubes to produce health effects in the respiratory system; and (3) the impact of trace metals associated with nanotubes to enhance/cause health effects due to inhalation.

Nanomaterial Interactions With Skin
Nancy Monteiro-Riviere, North Carolina State University

The objective of this research is to assess the nature of interactions between manufactured nanoparticles and skin, focusing on dermal absorption and cutaneous toxicity issues. Multi-walled carbon nanotubes without chemical modification or adjuvant treatments are capable of entering the cells and eliciting a biological response. Project work demonstrated that FITC labeling allows for imaging of fullerene penetration through the epidermal layer and the dermis. Surfactants play a major role in penetration of fullerenes into the skin. Studies performed with quantum dots of two different sizes/shapes and with three different types of coatings showed that these nanoparticles can penetrate through the epidermal and dermal layers of the skin. Ongoing and future studies will assist in defining the structure-activity relationships of various nanomaterials. The results of this research provide insight into the nature of the potential hazard to nanomaterials and an initial estimate of dermal exposure parameters that can be used to design more definitive studies.

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? and (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. Investigators 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.

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Iron Oxide Nanoparticle-Induced Oxidative Stress and Inflammation
Hong Yang, University of Rochester (Alison Elder, PI)

Nanoparticles can evade normal clearance mechanisms in the lung, thus increasing the likelihood that they will come into contact with several cell types where they will cause oxidative stress and inflammation. The clearance evasion and, possibly, the interactions with cells can lead to translocation to extrapulmonary tissues. The objectives of this project are to: (1) compare oxidative stress and toxicity of nanoparticles; (2) measure pulmonary and cardiovascular effects following inhalation and intravenous exposures in rats; and (3) measure translocation to extrapulmonary sites. This project will provide dose-, size-, and composition-related toxicological information about nanoparticles and will explore their translocation to extra-pulmonary tissues. The insight gained regarding mechanisms of response to nanoparticles and their dis-position after exposure can be used to predict outcomes of human exposures in environmental, occupational, and therapeutic settings.

Mechanistic Dosimetry Models of Nanomaterial Deposition in the Respiratory Tract
Bahman Asgharian, CIIT Centers for Health Research

The goals of this project are to: (1) develop dosimetry models capable of calculating the retained dose in the lungs of humans and animals; and (2) assess risk to people from exposure to nanoparticles by interspecies data extrapolation. The objectives of this research are to: (1) study diffusive and convective mixing of nanoparticles; (2) extend existing models of particle deposition in the lungs of rats and humans to the size range of nanomaterial; and (3) validate the model by comparison with measurements. This research effort will result in: (1) deposition measurements of nanosized particles in casts of human and rat nasal upper respiratory tract (URT) airways; (2) semi-empirical relationships to predict nanomaterial deposition in the URT airways; (3) respiratory tract deposition models of nanoparticles and nanotubes in humans and rats; (4) measurements of regional and lobar deposition of nanomaterial in the heads and lungs of rats; and (5) a user-friendly software package to implement models and provide rapid simulation capability.

Chemical Fate, Biopersistence, and Toxicology of Inhaled Metal Oxide Nanoscale Materials
Jacob McDonald, Lovelace Respiratory Research Institute

This project will test the hypothesis that the biological disposition, persistence, and toxicity of metal oxides change with size (comparisons between nanoscale and micron size) and composition (comparison between SiO_2 and Al_2O_3) of metal oxide powders. Researchers will test the hypothesis that metal oxide particles that are manufactured in the nanoscale have: (1) longer biological persistence; and (2) increased pul-monary and systemic toxicity relative to the same metal oxides of larger sizes. The two primary research objectives are to: (1) determine biological disposition (translocation/elimination/persistence) by measure-ment of residual metal oxide in plasma and six target organs (lung, brain, liver, kidney, spleen, intestine); and (2) determine local (lung/respiratory tract) and systemic toxicity by measurements of sensitive biochemical markers of inflammation and oxidative stress in addition to histopathological analysis.

<u>NIOSH Grantees</u>

Assessment Methods for Nanoparticles in the Workplace
Patrick O'Shaughnessy, The University of Iowa

The primary objectives of this project are to: (1) provide the scientific community and practicing in-dustrial hygienists with verified instruments and methods for accurately accessing airborne levels of

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nanoparticles; and (2) assess the efficacy of respirator use for controlling nanoparticle exposures. Researchers plan to satisfy these objectives through a combination of laboratory and field-based studies centered on the following specific aims: (1) identify and evaluate methods to measure airborne nano-particle concentrations; (2) characterize nanoparticles using a complementary suite of techniques to assess their surface and bulk physical and chemical properties; and (3) determine the collection efficiency of commonly used respirator filters when challenged with nanoparticles.

Monitoring and Characterizing Airborne Carbon Nanotube Particles
Judy Xiong, New York University School of Medicine

The objective of this project is to develop a comprehensive, yet practical, method for sampling, quantifying, and characterizing carbon nanotubes (CNT) particles in air, which will be capable of: (1) classifying sampled particles into three categories (tubes, ropes, and non-tubular particles); (2) measuring the number concentrations and size distributions for each type; and (3) measuring the shape characters of CNTs (diameter, length, aspect ratio, and curvatures). Successful completion of this project will produce a validated method for sampling airborne CNTs in workplaces and a practical method using Atomic Force Microscopy (AFM) image analysis to classify sampled CNT particles by type, and to separately quantify and characterize each type. The expected benefits from this research are: (1) methods for determination of potential health risks caused by worker exposure to the various types of nanoparticles; (2) a foundation for development of field and personal sampling devices for CNTs; and (3) information that is essential for studies on potential toxicity, source attribution, and control efficacy of this new type of material.

NSF Grantees

Gene Expression Profiling of Single-Walled Carbon Nanotubes: A Unique Safety Assessment Approach
Mary Jane Cunningham, Houston Advanced Research Center

There is increasing concern about potential adverse effects of engineered nanoparticles on the environment and on human health. Engineered nanomaterials will be exposed to human cells *in vitro*, and their toxicity will be assessed using the innovative technology of high throughput gene expression microarrays. The four main objectives of this research project are to: (1) compile reproducible gene expression profiles of primary human lung cells exposed to SWNTs; (2) apply different tiers of computational analysis to determine if toxicity is present; (3) compare across biological tissues with previous data from human skin cells; and (4) lay the foundation for a "systems biology" approach for predictive toxicity by merging traditional risk assessment methods with new toxicogenomics computational methods.

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Section 1. 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 V. Johnston
University of Delaware, Newark, DE

Abstract

The main objective of this research project is to develop a method for real-time sampling and analysis of individual airborne nanoparticles in the 5-20 nm diameter range. The size range covered by this method is much smaller than existing single particle methods for chemical analysis. Because particles in this size range are close to their origin, chemical composition measurements should provide greater insight into particle formation mechanisms.

Nanoparticles will be classified by elemental composition using aerosol mass spectrometry. The aerosol will be drawn directly into a mass spectrometer where individual particles are analyzed in real time by laser ablation. To increase the sampling efficiency for particles in the 5-20 nm diameter range, a quadrupole ion guide will be used to focus particles into the ablation laser beam path. Quantitative measurements of elemental composition will be achieved by complete atomization and ionization of individual particles using a high energy laser pulse to create a nano-plasma. This method will be used to study a variety of particle formation processes. Although laboratory investigations are emphasized in this work, the instrumentation will be suitable for field experiments.

Nanometer diameter aerosol particles are important precursors of larger particles in the accumulation mode. There is growing evidence that ultrafine particles are toxic and that particle number can be an important indicator of human health. Controlling ultrafine particle concentrations requires an understanding of the gas phase condensation processes that lead to new particle formation. Measuring the elemental composition of individual, nanoparticles will help quantify the relative contributions of the various sources.

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Ion-Induced Nucleation of Atmospheric Aerosols

Peter H. McMurry and Fred Eisele
University of Minnesota, Minneapolis, MN

Abstract

The objective of this research project is to study the role of ion-induced nucleation as a mechanism for producing new nano-sized particles in the atmosphere. The researchers hypothesize that: (1) nucleation processes in different locations are driven by different gas phase species and can be homogeneous and/or ion-induced depending on time and locale; and (2) ion-induced nucleation events can be due to the growth of either positive or negative ions, and different gas phase species are responsible for bursts of intermediate and large positive and negative ions. The ultimate goal of this project is to develop experimentally verified models for the formation of ultrafine atmospheric particles by nucleation.

This study will include both laboratory and field research and will involve the measurement of ion mobility spectra (nominal ion sizes 0.4 to 15 nm) and ion composition. Ion composition will be measured by tandem mass spectrometry and will include measurements of both positive and negative ion composition during nucleation events, which has not been done before. A microphysical model will be developed to interpret the data. This model will attempt to reconcile observed time-dependent trends in ion mobility distributions and aerosol charge distributions.

Recent epidemiological research has suggested that, on a mass basis, ultrafine particles can be more harmful to human health than larger particles. Furthermore, ultrafine particles formed by nucleation can grow into cloud condensation nuclei that can impact on the earth's radiation balance. This project complements other ongoing research in the laboratories in which the homogeneous nucleation is being studied through reactions of neutral molecules in the atmosphere. The results of this study will be useful to modelers, who require experimentally verified models of microphysical processes to evaluate aerosol climatic effects, human exposure, and so on.

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Section 2. Life-Cycle Analysis

Life-cycle analysis (LCA) is an approach to evaluating the environmental consequences of a product from "cradle to grave." The assessment considers all stages along the life cycle of a compound, including production, use, recycling, and disposal. As new nanomaterials are discovered and commercial and environmental opportunities and risks 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 adverse 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.

Evaluating the Impacts of Nanotechnology via Thermodynamic and Life-Cycle Analysis

Bhavik R. Bakshi
Ohio State University, Columbus, OH

Abstract

The proposed research will develop original life cycle inventory data for the manufacture of polymer nanocomposites, test two new hypotheses for thermodynamics-based Life Cycle Assessment (LCA) and impact assessment with limited information, and develop a tool for exploring economic and environmental aspects of alternate manufacturing combinations for selected nanoproducts and conventional processes. The following hypotheses will be tested: (1) Among alternatives for making similar products, the one with a higher life cycle thermodynamic efficiency has a smaller life cycle impact; and (2) Emissions with a smaller life cycle thermodynamic efficiency have a larger ecotoxicological impact. The second law of thermodynamics and hierarchical systems theory support these hypotheses. Validating them, however, has been challenging.

Through collaboration with leading academic groups, industry, and a national laboratory, life cycle inventory data and modules will be developed for the synthesis and use of nanoclays and carbon nanofibers. These modules will be combined with life cycle information at different spatial scales, ranging from equipment to ecosystems, and used to perform multiscale or hybrid LCA of several potential products. Different scenarios for the manufacture, use, end of life, emissions and exposure of typical consumable and durable products, such as automotive body panels and food wrapping film, will be analyzed, along with estimates of uncertainty. Thermodynamic LCA will treat industrial and ecological systems as networks of energy flow and combine the features of systems ecology, LCA, and systems engineering. The proposed hypotheses will be tested in a statistical sound manner via several case studies.

LCA of nanotechnology is essential for guiding and managing risk in research, development, and commercialization, while preventing irrational optimism or unfounded fear of this emerging field. However, it presents formidable obstacles because data and knowledge about resource consumption, and emissions and their impact are either unknown or not readily available. This work will lay the foundation for LCA of polymer nanocomposites and other emerging technologies. Validation of the first hypothesis will provide useful insight about nano versus traditional technologies, while the second hypothesis will provide a proxy for the ecotoxicological impact of the emissions. These hypotheses will be useful for nano and other emerging technologies before detailed emissions data and ecotoxicological studies are available. As more information about manufacturing, emissions and their impact becomes available, it will be incorporated in the proposed studies and tool.

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Section 3. 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.

Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

Sarah Larsen
University of Iowa, Iowa City, IA

Abstract

This project involves the development of nanometer-sized zeolites and zeolite nanostructures as environmental catalysts. Zeolites, which are widely used in applications in separations and catalysis, are aluminosilicate molecular sieves with pores of molecular dimensions. Recently, there has been a great deal of interest in the synthesis of nanocrystalline zeolites (zeolites with crystal sizes of 100 nm or less) and their unique properties relative to conventional micron-sized zeolite crystals. Nanocrystalline zeolites possess very large internal and external surface areas that can be exploited for many different applications. For example, nanocrystalline silicalite with a crystal size of 20 nm has an external surface area of approximately 175 m^2/g (approximately 30 percent of the total surface area on the external surface). For comparison, the external surface area of a 1 micron silicalite crystal is approximately 2 m^2/g, which accounts for less than 1 percent of the total surface area. A key feature of nanocrystalline zeolites is that the external surface can be utilized as a reactive or sorbtive surface resulting in materials with a wide variety of physical and chemical characteristics. In principal, bifunctional zeolite materials can be designed in which the external and internal surfaces have different functions.

Nanocrystalline ZSM-5, silicalite (purely siliceous form of ZSM-5), and Y zeolites have been synthesized in the researcher's laboratory with discrete crystal sizes as small as 15 nm. Hollow zeolite structures also have been prepared using zeolite nanocrystals as seeds and mesoporous silica as a template and silica source for zeolite growth. First, mesoporous silica is coated with nanocrystalline zeolite seeds. Then, the coated mesoporous silica is subjected to a hydrothermal treatment in an autoclave. During the hydrothermal treatment, the zeolite crystals grow larger using the mesoporous silica as the silicon source for crystal growth. Hollow zeolite structures with controlled porosity have many potential applications in diverse areas, including drug delivery, chemical storage, chemical sensors, and catalysis.

Applications of nanocrystalline zeolites in environmental protection will be discussed. In particular, the increased adsorption capacity of nanocrystalline zeolites for volatile organic compounds such as toluene has been demonstrated. In addition, unique reactivity of nanocrystalline NaY for the selective catalytic reduction of NO_2 with reductants such as propylene or urea has been investigated with Fourier Transform Infrared (FTIR) spectroscopy. In the absence of oxygen and water, selective catalytic reduction of NO_2 with propylene at low temperatures (473 K) resulted in the complete reduction of NO_2 to N_2 and O_2. Nanocrystalline NaY zeolite exhibits enhanced deNO_x at low temperature (T = 473 K) compared to commercial NaY zeolite, as shown by an FTIR study on the selective catalytic reduction of NO_2 with urea. Silanol groups and extraframework aluminum species on the external surface of nanocrystalline NaY were found to be responsible for the higher selective catalytic reduction (SCR) reaction rate and decreased formation of undesired products relative to commercial NaY zeolite. Isotopic labeling coupled with infrared analysis indicates that N-N bond formation involves both a N-atom originating from NO_2 and a N-atom originating from urea. Nanocrystalline alkali zeolites can be visualized as new catalytic materials that have NO_x storage capacity in the internal pores and high reactivity on the external surface. This is the first clear example in the literature demonstrating that the increased external surface area (up to ~40 percent of the total surface area) of nanocrystalline zeolites can be utilized as a reactive surface with unique active sites for catalysis.

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Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

Sarah Larsen
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, the ability to 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_x Emissions Abatement

The emission of NO_x and N_2O from stationary and automotive sources, such as power plants and lean-burn engines, is a major environmental pollution issue. NO_x leads to the production of ground-level ozone and acid rain, and N_2O is a greenhouse gas. The catalytic reduction of nitrogen oxides to N_2 is an important environmental challenge for scientists and engineers. Recently, the selective catalytic reduction of NO_x and N_2O 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_x and N_2O shows promise for applications to lean-burn gasoline and diesel engines where noble-metal three-way catalysts are not effective at reducing NO_x in the presence of excess oxygen. The SCR activity of nanocrystalline zeolites, such as NaY, has been investigated.

Adsorption of Volatile Organic Compounds (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 the researcher's 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 applications in particular chemical environments. For example, nanocrystalline ZSM-5 has been functionalized with octamethylsilane such that the hydrophobicity was dramatically increased. The functionalized zeolites will then be evaluated for the adsorption of toluene in aqueous solution.

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

William T. Winter
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.

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Nanostructured Microemulsions as Alternative Solvents to VOCs in Cleaning Technologies and Vegetable Oil Extraction

David Sabatini, Anuradee Witthayapanyanon, and Linh Do
University of Oklahoma, Norman, OK

Abstract

Introduction

Volatile organic compounds (VOCs), such as percholoroethylene (perc), hexane, and chloroform, have been widely used as conventional solvents in cleaning technologies and vegetable oil extraction. These organic solvents are classified as hazardous and probable carcinogenic substances. Although environmental contamination and health risks occur when using organic solvents in numerous operations, these organic solvents are still used due to their ready availability and a high cleaning efficiency. Therefore, the goal of this research is to find aqueous-based surfactant microemulsions that can replace VOC solvents with environmentally friendly systems.

Microemulsions contain nano-sized aggregates that can be used as extracting entities at the nanoscale level. This project uses nanoscale microemulsion environments as receptors for oily soils. Microemulsions play a key role in solvent replacement because of the ultralow interfacial tension (IFT) and ultrahigh solubilization properties of these systems. This project is focused on textile cleaning process and vegetable oil extraction applications.

Aqueous-Based Microemulsion for Textile Cleaning Process

In the textile cleaning process, long chain alkanes and highly hydrophobic oils (e.g., hexadecane and motor oil) were studied. Based on the hydrophobic nature of these oils, a special cleaning process, such as dry cleaning, is required to remove hydrophobic oily soils from stained fabrics. However, the solvent emission and energy consumption during dry cleaning operation create environmental concerns. An alternative to dry cleaning is wet cleaning. Wet cleaning uses water and nonpolluting detergents instead of hazardous solvents that can be used with computer-controlled washing and drying machines. Wet cleaning is more environmentally friendly than dry cleaning while still maintaining the same cleaning efficiency. Therefore, in this project, the researchers have developed aqueous-based microemulsions for cleaning oily soils with more environmentally friendly systems that can be applied to wet cleaning technology, thereby, replacing volatile organic solvents for textile cleaning application.

First of all, microemulsion with target oils (hexadecane and motor oil) were forumlated. The researchers hypothesized that the ultralow IFT and ultrahigh solubilization properties of middle phase microemulsion will provide the best solvency for textile cleaning. In addition, the use of hydrophilic/lipophilic linkers improved the formulations. The newly produced alkyl propoxylated sulfate surfactants, known as extended surfactants (surfactants with “internal” linkers), have desirable properties for this application. The detergency of an organic solvent system (perc), conventional surfactant (sodium dioctyl sulfosuccinate, Aerosol-OT) with and without linkers, extended surfactant, and commercial detergent were compared as shown in Figure 1.

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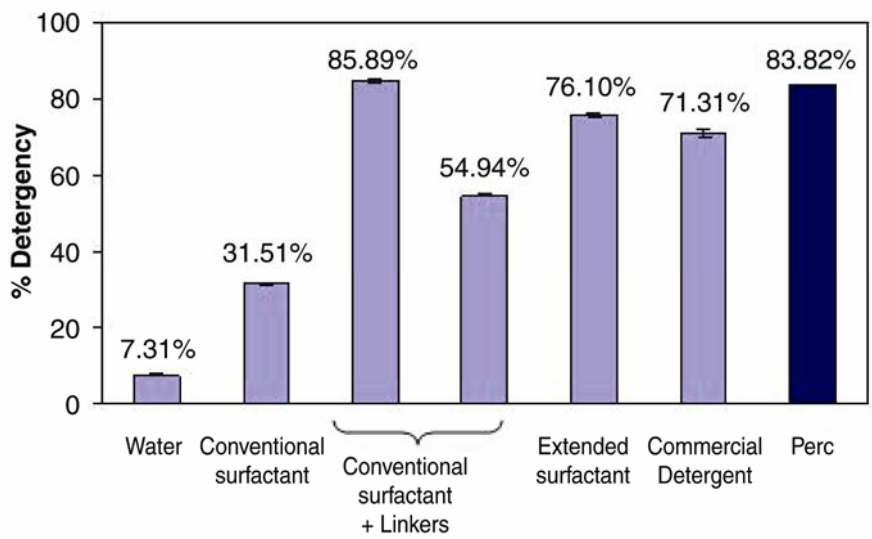

Figure 1. Detergency performance of a different pretreatment system.

The results showed that motor oil stains are not easily removed by a conventional surfactant (31.51 percent oil removal). However, as a pretreatment system, linker-based and extended surfactant-based microemulsion can remove at least 50 percent to 85 percent of motor oil stain from 65/35 polyester/cotton-type fabric. In addition, the use of extended surfactant show a synergism in formulating less complex surfactant formulations while still showing high detergency performance. Furthermore, the removal efficiency of hexadecane and motor oil from textiles, using our aqueous-based microemulsion formulations, is higher than using conventional pre-treatment organic solvent and commercial cleaner systems (84.89 percent versus 83.82 percent). The results to date are very encouraging for using surfactant-based microemulsions as organic solvent replacements.

Aqueous Extended-Surfactant-Based Method for Edible Oil Extraction

Edible oils are obtained from oilseed by either hexane extraction or the combination of mechanical pressing and hexane extraction. In 2001, the U.S. Environmental Protection Agency promulgated regulations on hexane emission due to growing environmental concern. The goal of this project is to formulate environmentally friendly surfactant-based formulations that maintain the simplicity of operation and reduce energy consumption while maintaining performance. For a surfactant system to be used in vegetable oil extraction, ultralow interfacial tension is the most desirable property because it promotes both roll-up and snap-off mechanisms of the oil from the seed. A number of conventional surfactant systems have been evaluated but could not achieve low IFT at ambient temperature and without the addition of co-oils and/or alcohols. The newly produced extended-surfactants, with hydrophobic and hydrophilic "linkers" inserted between the head and tail parts of a surfactant molecule, have been able to achieve ultralow interfacial tension with a wide range of edible oils. To their knowledge, the researchers are the first to achieve this result, which shows great promise for use in edible oil extraction. Figure 2 shows the IFT results of the conventional surfactant Aerosol-OT versus the extended-surfactant C12-14PO-2EOSO_4Na with canola oil, and IFTs of C12-14PO-2EOSO_4Na with various types of vegetable oils, namely canola, soybean, corn, and peanut oil.

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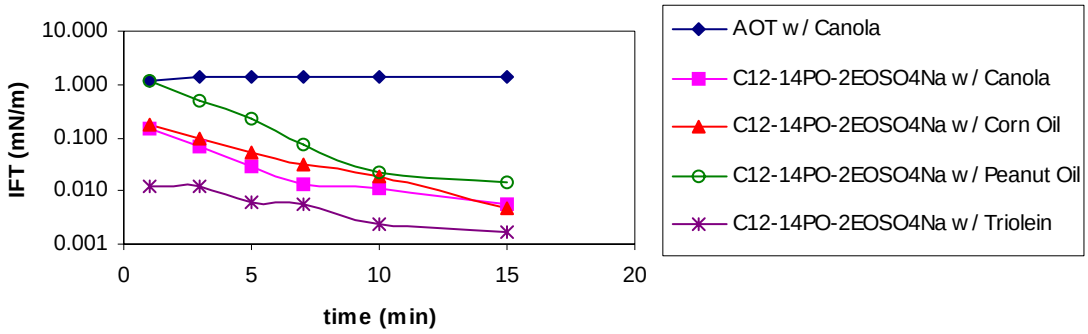

Figure 2. IFT Measurement of conventional surfactant and extended-surfactant with vegetable oils.

Figure 3 shows the results of oil extracted by using the aqueous extended-surfactant-based formulation versus aqueous enzymatic (1) and hexane methods. At low concentrations, ambient temperature and no additives, extended-surfactant systems show 90 percent of oil yield, which is very competitive with hexane-based and aqueous enzymatic methods. In addition, extended-surfactants are able to produce ultralow IFT with a wide range of edible oils; therefore, it is expected these techniques can be used as a universal method such like hexane.

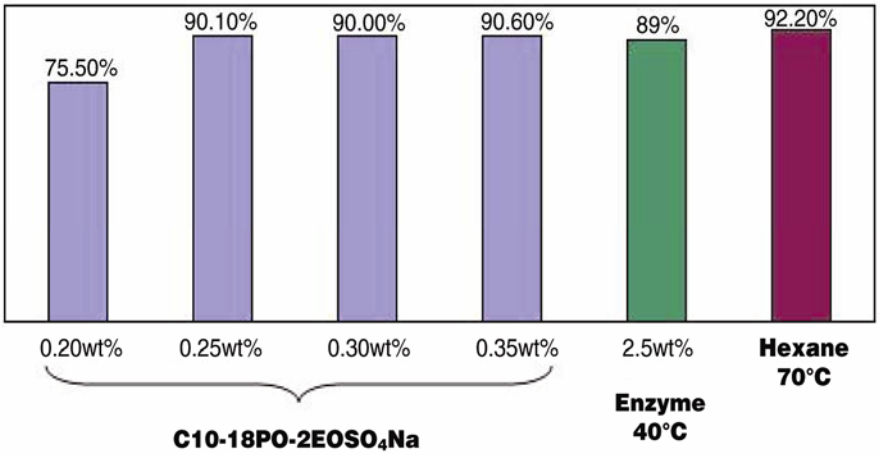

Figure 3. Percentage of peanut oil extracted.

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Success Stories

Nanostructured microemulsions as alternative solvents to VOCs in cleaning technologies and vegetable oil extraction. Recipient of JSD's Outstanding Paper Award for 2003.

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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.

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

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[3]University of Michigan, Ann Arbor, MI

Abstract

Dendrimers are highly branched nanostructures with controlled composition and architecture. Poly(amido-amine) (PAMAM) dendrimers that possess functional nitrogen and amide groups are arranged in regular "branched upon branched" patterns. Their high density of nitrogen ligands, along with the possibility of attaching functional groups such as primary amine, carboxylate, hydroxyl, etc., to PAMAM dendrimers, can result in a substantial increase in binding capacity for transition metal ions [e.g., Cu(II), Ag(I), Fe(III), etc.]. The well-defined molecular compositions, sizes, and shapes of PAMAM dendrimers have also made them particularly attractive as: (1) scaffolds for paramagnetic metal ions in magnetic resonance imaging; and (2) templates for the synthesis of metal-bearing nanoparticles with tunable electronic, optical, catalytic, and biologic activity.

This 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 tetrachloroethylene (PCE) in aqueous solutions and subsurface formations.

The overall results of this research suggest that dendritic nanoscale chelating agents provide unprecedented opportunities for developing a new generation of efficient and cost-effective high capacity/recyclable chelating agents and FeS dendrimer nanocomposites for treatment of water contaminated by toxic metal ions and redox active solutes.

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

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Abstract

Introduction

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 subsurface DNAPL.

Over the past decade, laboratory and field studies have demonstrated that zerovalent iron and bimetallic colloids (Fe/Pd) can rapidly transform dissolved chlorinated organic solvents into nontoxic compounds.[1-3] This emerging technology also has the potential to address DNAPL contamination. 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^0-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 2 years of the project has focused on: (1) identifying suitable Fe^0 nanoparticles and understanding the properties that control their reactivity with trichloroethylene (TCE); (2) synthesizing and characterizing amphiphilic block copolymer-modified nanoiron; and (3) evaluating the DNAPL-targeting and transport properties of the resulting polymer-modified functional nanoparticles.

Results and Discussion

Identifying suitable Fe^0 nanoparticles and understanding the properties that control their reactivity with TCE. The TCE reaction rates, pathways, and efficiency of two types of nanoscale Fe^0 particles were measured in batch reactors. The two types of nanoscale Fe^0 particles were synthesized from sodium borohydride reduction of ferrous iron Fe(B) and commercially available particles (RNIP) synthesized from the gas phase reduction of Fe-oxides in H_2. 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 provided in Figure 1(a,b). Both particle types showed a core-shell morphology. RNIP particles were crystalline and had an Fe^0 core and a magnetite (Fe_3O_4) shell. No other Fe-oxides were detected. Fe(B) (borohydride reduced particles) were amorphous α-Fe^0, and contained 4-5 wt percent boron (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 FeB_x alloy.[2,3]

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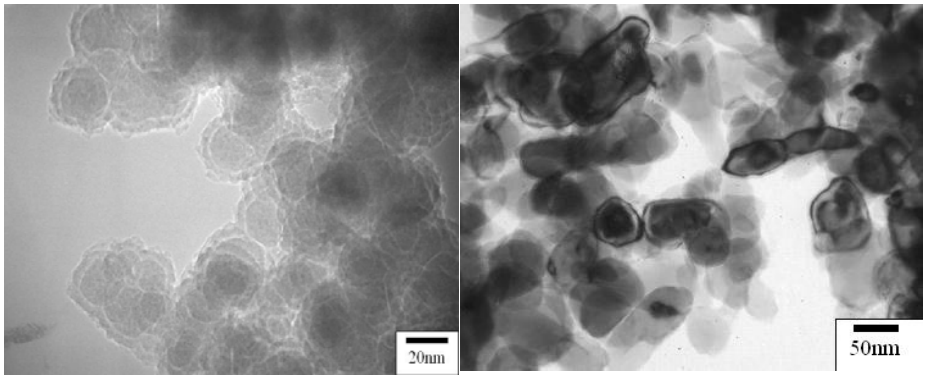

a) b)

Figure 1. (a) Fe(B); (b) RNIP.

Reactivity was determined under iron limited (high [TCE]) and excess iron (low [TCE]) conditions, and with and without added H_2. 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. For example, the main reaction products using Fe(B) were primarily saturated (e.g., ethane, butane), while the reaction products using RNIP were primarily unsaturated (e.g., acetylene, ethane).[2] A concentration dependence on the TCE reaction rate and product distribution was observed. Few chlorinated intermediated products were observed for either particle. The addition of H_2 to the reactor headspace increased the reactivity of Fe(B), and these particles were able to use externally supplied H_2 to reduce TCE, indicating that these particles are catalytic. RNIP particles did not display this behavior. The ability of Fe(B) to catalyze the hydrodehalogenation of TCE is attributed to their amorphous structure rather than the presence of boron in the structure.[3] All of the boron in Fe(B) is released during reaction with water and TCE, which may be problematic if boron degrades water quality or has human or ecotoxicity.

Synthesis and TCE/water partitioning of amphiphilic block copolymer-modified nanoiron. Atom Transfer Radical Polymerization (ATRP) was used to synthesize tailored block copolymers for hybrid nanoparticles.[4-6] Concerning the synthesis of Fe^0 nanomaterials, a technique was developed for building hydrophobic-hydrophilic hybrids that consist of a short anchoring poly(methacrylic acid) block, a hydrophobic poly(methylmethacrylate) protective shell, and a hydrophilic poly(styrene sulfonate) outer block (Figure 2). This $PMAA_x$-b-$PMMA_y$-b-PSS_z architecture provides the desired characteristics (i.e., water solubility, strong electrosteric repulsions, and an affinity for DNAPL). Using an emulsion procedure developed in the researcher's laboratory[7], TCE-water emulsions were formed using nanoiron modified with these triblock copolymers (Figure 3). Figure 3 shows that a distinct shell of aggregated iron nanoparticles surrounds the TCE droplets. The flocculated particles surrounding the emulsion droplets appear to form dendritic structures, and the emulsion droplets are held apart by these aggregates of particles. The width of the aggregated nanoiron shells around the droplets is approximately 1 μm, indicating that they are approximately 5-10 particles thick. Nanoiron was not found inside the emulsion droplets, which is consistent with the facts that the emulsion was of the oil-in-water type and that the polymer-coated nanoparticles are not dispersible in pure TCE. The ability of these particles to form a highly stable emulsion phase demonstrates the ability of amphiphilic triblock copolymer modified iron nanoparticles to preferentially localize at the TCE/water interface.[6]

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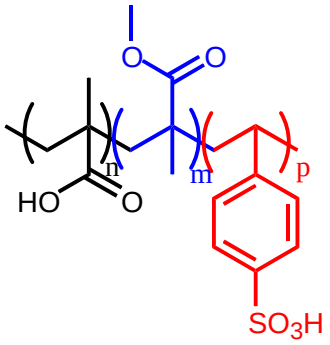

Figure 2. Hydrophobic-hydrophilic triblock copolymer containing a short anchoring group (PMAA), short hydrophobic section (PMMA), and an extended hydrophilic block (PSS).

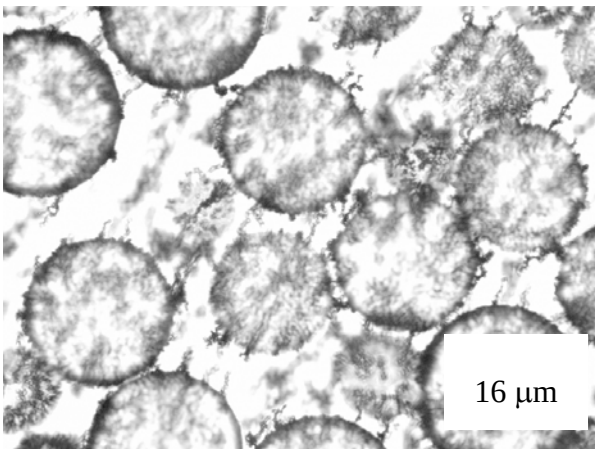

Figure 3. Micrograph of emulsified TCE droplets in water stabilized by "raw" $PMAA_{42}$-$PMMA_{26}$-triblock copolymer-modified iron nanoparticles (Saleh, et al., 2005b).

Dispersion stability and transport of modified nanoiron in water-saturated porous media. Without surface modification, RNIP particles rapidly flocculate and sediment from solution (Figure 4). Modification by each polymer increased the stability of the suspensions relative to bare RNIP. The suspension stability increases as the PSS block degree of polymerization increased from 462 to 650. Thus, the larger PSS block of $PMAA_{48}$-$PMMA_{17}$-PSS_{650} provided stronger electrosteric repulsions and better stability improvement than $PMAA_{42}$-$PMMA_{26}$-PSS_{462}, as would be expected for these polymers that are otherwise quite similar to each other. Particles modified with PSS homopolymer (PSS_{484}) were more stable than bare RNIP, but less stable than the triblock copolymers. It indicates that PSS homopolymer adsorbs to RNIP to some degree, but less effectively than the triblock copolymers containing the PMAA anchor block. Polymer-modified nanoiron is significantly more transportable than unmodified nanoiron, particularly at the high (3 g/L) concentrations needed for delivery into the subsurface (Figure 5). A systematic evaluation of the hydrogeochemical properties affecting transport and targeting, including pH, I, and flow velocity, will be conducted.

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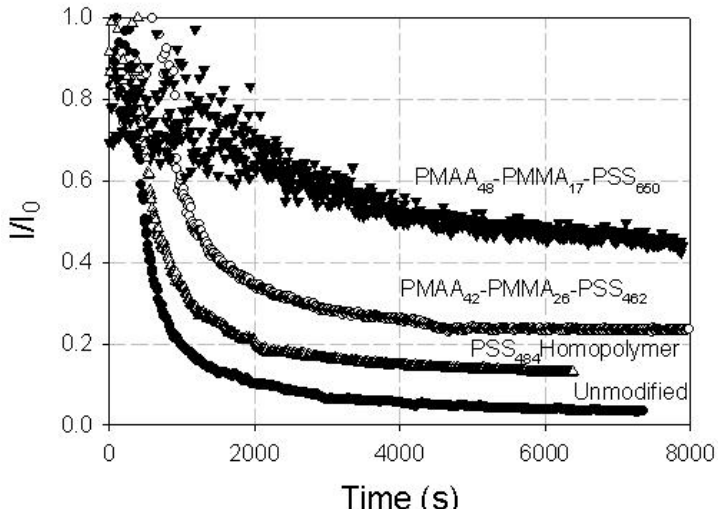

Figure 4. Sedimentation curves for bare and polymer-modified iron nanoparticle dispersions (0.08 wt%) in water.

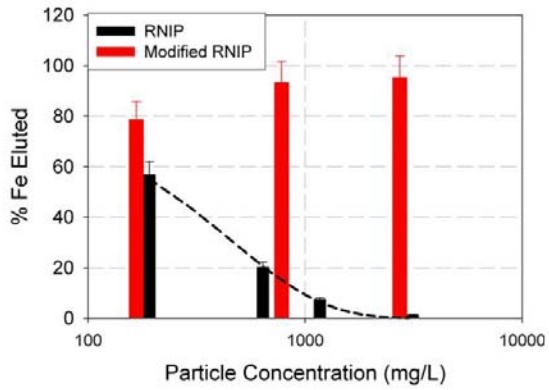

Figure 5. Effect of triblock copolymer modification on nanoiron transport in a 10 cm sand-packed column.

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Success Stories

This research has been featured in the science news sections of several newpapers and technology Web sites.

"Tiny engineered particles could one day remove common pollutant," by Byron Spice, science and technology writer for the *Pittsburgh Post Gazette*, in a feature article in the science and technology section of the *Gazette*, April 1, 2004 (http://www.post-gazette.com/pg/04092/294409.stm).

"Nanoparticles seek out solvents in groundwater," by Liz Kalaugher, editor of NanotechWeb.org, in a feature article in Nanotechweb.org on April 13, 2004 (http://nanotechweb.org/articles/news/3/4/8/1).

"Small science may clean a big problem," appeared in *The Christian Science Monitor*, Boston, Thursday, February 10, 2005.

Special Treatment: Tiny technology tackles mega messes. *Science News*, April 23, 2005;67.

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Nanostructured Catalytic Materials for NO_x Reduction Using Combinatorial Methodologies

Selim Senkan
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Abstract

New advances in combinatorial methodologies are exploited for the discovery and optimization of nanostructured catalytic materials for the reduction of NO_x under fuel lean combustion conditions. Recent developments in automotive engineering have made possible the production of more fuel efficient—up to 25 percent—lean-burning gasoline engines. The lack of appropriate catalytic technology to reduce NO_x emissions under lean burn conditions, however, impedes the commercialization of such engines. Although the existing three-way catalysts allow for the effective control of CO, hydrocarbon (HC), and NO_x emissions in current gasoline engines that operate under stoichiometric conditions, they are ineffective in the presence of excess oxygen encountered in lean-burn engine exhausts. Therefore, the development of a new generation of catalysts that will allow NO_x control in oxygen-rich environments is urgently needed.

In the current program, libraries of catalytic materials were prepared by individually impregnating five support materials of Al_2O_3, CeO_2, SiO_2, TiO_2, and Y-ZrO_2 by salt solutions of 42 elements from the periodic table into the resulting five different metal loadings. These support materials were used because of their durability in harsh engine exhaust conditions. Catalytic materials were then tested for their NO reduction activities using array channel microreactors and mass spectrometry. Overall, several thousand catalytic materials were prepared and then tested at 1 atm pressure and in the temperature range 100 to 500 ºC, and at a GSHV of 60,000 h^{-1}. The feed gas used was 500 ppmv NO, 500 ppmv C_3H_6, 1,400 ppmv CO, 8 percent O_2, 10 percent H_2O, and the balance helium. These test conditions realistically simulate the actual engine-out conditions, thereby rendering the findings immediately relevant to automobile exhaust treatment catalysis. These systematic investigations led to the discovery of Pt/TiO_2 and Pt/SiO_2 as the most significant leads, both of which exhibited superior performances, reducing the levels of NO by 25 percent and 20 percent, respectively.

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A Bioengineering Approach to Nanoparticle-Based Environmental Remediation

Daniel Strongin
Temple University, Philadelphia, PA

Abstract

Ferritin and ferritin-like protein can be used to assemble nanosized catalytic metal oxyhydroxide particles in the size range of 1 to 8 nm. Horse spleen ferritin and *Listeria innocua* ferritin-like protein were used to assemble Fe(O)OH particles ranging from 4 to 8 nm and 1 to 4 nm in diameter, respectively. Probe molecules were used to investigate the surface reactivity of the nanoparticles assembled within ferritin, with and without the surrounding protein, as a function of size. With regard to the latter circumstance, ferritin was deposited on an Si support, dried, and exposed to oxidizing conditions to remove the protein shell. The reactivity of the supported nanoparticles toward environmentally relevant reactant showed a strong dependence with the particle size and structure.

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Nanoscale Bimetallic Particle for *In Situ* Remediation

Wei-xian Zhang
Lehigh University, Bethlehem, PA

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^2/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.

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Nanostructured Catalysts for Environmental Remediation of Chlorinated Compounds

Yunfeng Lu and Vijay T. John
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Abstract

This research is directed towards the development of novel mesoporous materials that act as supports for zero-valent iron nanoparticles used in the breakdown of chlorinated compounds. Halogenated organic compounds, such as chlorinated aromatics, chlorinated aliphatics, and polychlorinated biphenyls, are typical of dense non-aqueous phase liquids (DNAPLs) that are prevalent at contaminant sites. In recent years, the use of zerovalent iron has represented a promising and innovative approach to the destruction of these compounds.[1,2] Of particular interest is the number of publications recently that describe the use of nanoparticles of Fe in remediation through hydrodechlorination.[3] The enormous surface area of nanoparticles leads to enhanced efficiencies. Additionally, the colloidal nature of Fe nanoparticles indicates that these materials may be pumped to contaminated sites. Alternatively, "funnel and gate" treatment systems may be devised where porous barriers of iron particles are constructed in the path contaminated groundwater plumes.[4]

As a result of the high surface energy of nanoparticles, the particles tend to aggregate leading to larger units that do not maintain colloidal stability. Although Fe nanoparticles may be superparamagnetic, if the particle dimensions exceed 10-15 nm, they exhibit ferromagnetism and this also leads to aggregation and dropout of solution. Finally, iron is hard to functionalize with organic compounds to attempt to maintain stability in aqueous or in organic systems.

The project's technical approach combines the simplicity and affordability of the sol-gel processing techniques for ceramic synthesis with the efficiency and spontaneity of surfactant/silica cooperative assembly to manufacture nanostructured decontamination materials using a simple aerosol processing technique.

Figure 1 schematically depicts the formation of nanostructured particles by the aerosol-assisted self-assembly process.[5] Starting with a solution of soluble silica and surfactant in ethanol/water solvent, the aerosol apparatus atomizes the solution into droplets that undergo a drying and solidification step generating nanoparticles that are collected in a filter. During this process, solvent evaporation enriches the surfactant and silicate from the air-liquid interface of the droplet towards its interior, resulting in their co-assembly and in the formation of nanostructures growing from the interface towards the interior. Subsequent condensation reactions of silica during the drying and heating steps freezes the mesophases and results in nanostructured particles that exhibit hexagonal, cubic, lamellar, or other nanostructures.

A wide variety of additives (e.g., metal ions, organic functional ligands, monomers, polymers, metal colloidal particles, and catalyst particles) can be readily introduced to the surfactant/silicate solutions and incorporated into the nanostructured particles. This method provides an extremely simple and efficient approach to synthesize various nanostructured composite particles. Figure 2 shows the representative transmission electron microscopy (TEM) images of nanostructured particles containing highly ordered hexagonal, cubic, or lamellar pore channels, suggesting that porous nanostructured silica particles can be readily prepared using this approach.

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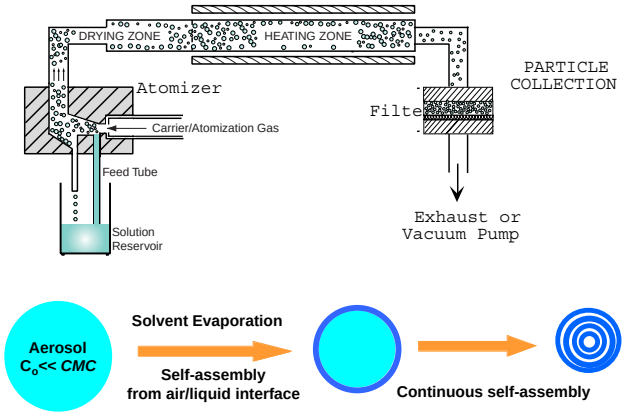

Figure 1. Schematic of the formation of nanostructured particles using the aerosol-assisted surfactant self-assembly.

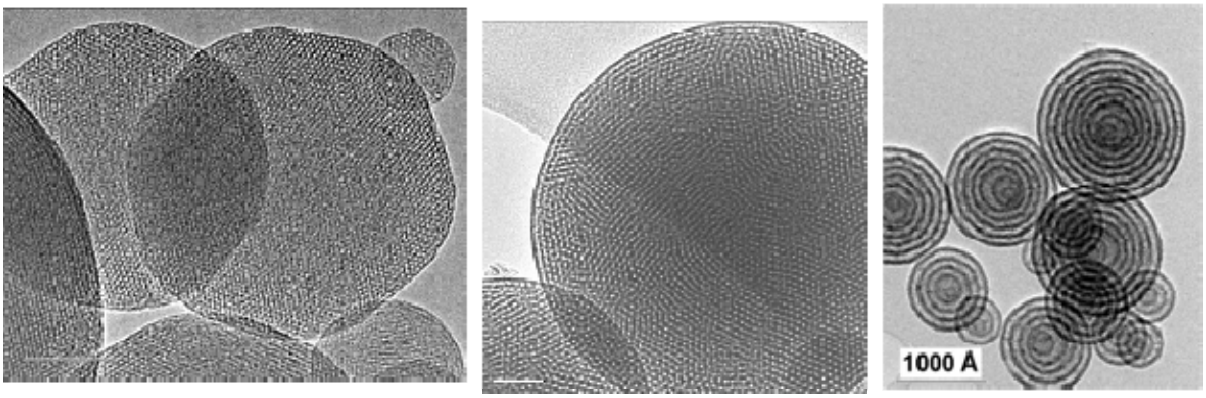

Figure 2. Representative TEM images of hexagonal (Left), cubic (Center), and lamellar (Right) nanostructured silica particles prepared using aerosol-assisted surfactant self-assembly.

Recent Results

The aerosolization technique employing surfactants as structure directing agents leads to the generation of mesoporous ceramics. The idea was to incorporate iron precursors into the solution to be aerosolized with the expectation that iron species would become entrapped in the silica particles. The hypothesis was that if zerovalent iron can be entrapped in porous silica nanoparticles, they would not aggregate. Furthermore, silica can be surface functionalized quite easily to prepare particles that are hydrophobic or hydrophilic and stay sustained in an aqueous or in an organic phase. Because silica is essentially inert, the composite would be expected to be safe.

The results are extremely interesting. Shells of silica with zerovalent nanoparticles of iron were obtained. The transmission micrographs of Figure 3 illustrate the results.

The continuing work seeks to test the efficiency of these materials in the breakdown of trichloroethylene. The researchers are tremendously interested in studying the transport of these particles in pump-and-treat technologies. Research is underway to functionalize these materials so that they partition to the organic-water interface or to the organic bulk phase for maximum efficiency.

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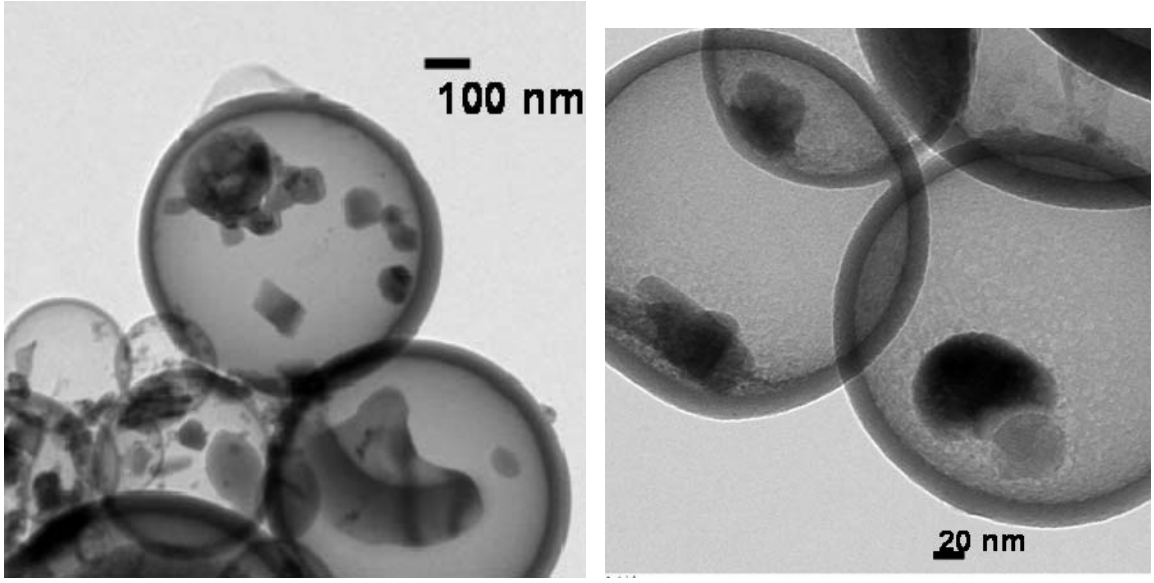

Figure 3. TEMs of aerosolized silica particles containing zerovalent iron nanoparticles.

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Nanostructured Materials for Environmental Decontamination of Chlorinated Compounds

Yunfeng Lu and Vijay T. John
Tulane University, New Orleans, LA

Environmental Implication/Application

Non-aqueous phase liquids (NAPLs) are substances such as oils, solvents, gasoline, and any organic substance that is sparingly soluble in water. NAPLs can be divided into two types: ones that are lighter than water (light non-aqueous phase liquids, or LNAPLs) and ones that are denser than water (dense non-aqueous phase liquids, or DNAPLs). DNAPLs are of particular concern because they are denser than water, have very low solubility, and can persist in groundwater sources for long periods of time, eventually making their way into drinking water sources.[1] When DNAPLs enter groundwater, they are hard to remove and may be pushed deeper into aquifers by removal attempts. The ability of treatment methods to break down the aquifer-trapped NAPL in a safe and effective manner becomes of utmost importance.

Halogenated organic compounds such as chlorinated aromatics, chlorinated aliphatics, and polychlorinated biphenyls are typical of DNAPLs that are prevalent at contaminant sites. In recent years, the use of zerovalent iron has represented a promising and innovative approach to the destruction of these compounds.[2,3] Of particular interest is the number of publications recently that describe the use of nanoparticles of Fe in remediation through hydrodechlorination.[4] The enormous surface area of nanoparticles leads to enhanced breakdown efficiencies. Additionally, the colloidal nature of Fe nanoparticles indicates that these materials may be pumped to contaminated sites. Alternatively "funnel and gate" treatment systems may be devised where porous barriers of iron particles are constructed in the path of contaminated groundwater plumes.[5]

However, there are difficulties with the use of iron nanoparticles. Due to the high surface energy of nanoparticles, the particles tend to aggregate leading to larger units that do not maintain colloidal stability. Although Fe nanoparticles may be superparamagnetic, if the particle dimensions exceed 10-15 nm, they exhibit ferromagnetism and this also leads to aggregation and dropout of solution. Finally, iron is hard to functionalize with organic compounds to attempt to maintain stability in aqueous or in organic systems.

This project directly addresses these issues through the development of a novel carrier for iron nanoparticles. Mesoporous silica nanoparticles are being developed into which zerovalent iron can be trapped. The following are specific advantages of the technology with environmental implications:

- Silica is innocuous in the environment, and the composite with zerovalent iron also is expected to be totally innocuous.

- This research should result in the design of zerovalent iron carriers that can be positioned at the organic-water interface or in the bulk organic phase. The researchers are able to prepare hollow silica nanoparticles where the low density will prevent settling out of the carriers during *in situ* soil treatments.

- The easy functionalization of these carriers should allow greater flexibility in the transport and partitioning of the zerovalent iron.

This research will result in the development of inexpensive and effective nanparticles for the *in situ* degradation of chlorinated organics.

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Synthesis and Application of a New Class of Stabilized Nanoscale Iron Particles for Rapid Destruction of Chlorinated Hydrocarbons in Soil and Groundwater

Dongye (Don) Zhao
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Abstract

The overall goal of this research project is to develop a cost-effective, *in situ* remediation technology that employs a new class of highly dispersible iron-based nanoparticles for the rapid destruction of chlorinated hydrocarbons in soil and groundwater. The specific objectives are to: (1) synthesize a new class of stabilized iron-based nanoparticles using low-cost and "green" stabilizers such as starches and celluloses; (2) test the effectiveness of the stabilized nanoparticles for dechlorination of select contaminants (tetrachloroethylenes and polychlorinated biphenyls) in soil and groundwater; and (3) test the feasibility of an *in situ* remediation process that is based on the nanoparticles.

The preliminary data showed that a water-soluble or sodium carboxymethyl cellulose can serve as the dispersant to effectively stabilize palladized iron (Fe-Pd) nanoparticles. Compared to non-stabilized Fe-Pd particles, the stabilized nanoparticles displayed markedly improved physical stability, soil dispersibility, chemical reactivity, and reactive longevity. Column tests showed that the stabilized nanoparticles can be readily dispersed in a loamy-sand soil and then be recovered completely. Batch dechlorination tests demonstrated that the starch-stabilized nanoparticles degraded TCE 37 times faster than non-stabilized counterparts based on the pseudo first-order rate constant.

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Section 5. 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.

Metal Biosensors: Development and Environmental Testing

Anne Anderson, Charles Miller, and Joan McLean
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Abstract

Cells of a soil-borne pseudomonad respond differentially to the toxic metals Cu and Cd. Increasing concentrations of Cu induce cell death, whereas Cd initially causes stasis of growth from which cells recover if the metal is present at sufficiently low concentrations. Modeling of speciation with citrate and phosphate as potential ligands show differences in complexation between Cd and Cu. Cd phosphate was demonstrated not to elicit growth cessation in cells indicating that it was not bioavailable. Thus, the environment of the ion has a major effect. Promoter fusions of a reporter gene cassette were used that encodes a luciferase and genes involved in oxidative stress to determine the threshold concentration at which cells show a response. Logarithmic cells respond between 0.01 and 0.1 mg Cu/L, whereas stationary phase cells require 10 mg Cu/L for the same decline in luciferase activity. Thus, age of cells is important in constructing a biosensor. For Cd, concentrations of 10 mg/L were needed to decrease luciferase activity in log phase cells and 100 mg/L had no effect in stationary phase. Stationary phase cells of a catalase A isozyme reporter showed increased activities in time-dependent manner at 10 mg/L. An increase in this catalase isozyme and a second catalase isozyme was confirmed in wild-type stationary phase cells at 2 h of treatment. Three proteins, shown by a proteomics approach as being upregulated in Cd-treated cells, are identified as proteins that respond to oxidative stress in the cell. Proteomics of Cu-treated cell extracts identified three cell membrane proteins among those upregulated. None of the 15 proteins identified that increased in level after metal treatment correspond to those predicted to be metal-sensitive in publications. Thus, our knowledge of how Cu or Cd interact with cells is not complete.

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Nanosensors for Detection of Aquatic Toxins

Robert E. Gawley
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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 (Kd 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.

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Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS Transistors (CνMOS)

Edwin C. Kan and Bradley A. Minch
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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. The researchers have developed a Si-based neuron MOS transistor with a novel extended floating-gate structure that permits molecular/chemical sensing. The sensor, called a chemoreceptive neuron MOS (CνMOS) 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^+ and K^+ 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 CνMOS 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 CνMOS 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 CνMOS.

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 CνMOS have been demonstrated in the proof-of-concept manner for sensitivity, selectivity, power consumption, and system integrability with CMOS technology and circuits. The developed CνMOS 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.

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Compound Specific Imprinted Nanospheres for Optical Sensing

Barry K. Lavine
Oklahoma State University, Stillwater, OK

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 1.0×10^{-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 1.0×10^{-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 mm, 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.

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Advanced Nanosensors for Continuous Monitoring of Heavy Metals

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Abstract

The overall objective of this research project is to incorporate novel, colloidal-metal nanoparticles into a bed of electrically conducting polymers, and then use these for the development of nanosensors. During the first year of the project, the feasibility of designing advanced conducting polymeric materials for sensing and remediation applications was explored. These include the synthesis of: (1) polyamic acid-silver nanoparticle composite membranes, (2) polyoxy-dianiline films, and (3) electrochemical deposition of gold nanoparticle films onto functionalized conducting polymer substrates. These were characterized using electrochemical and surface morphology techniques, including TEM, AFM, CV, and FTIR. The summary of the synthetic efforts has been published in *Langmuir* and the *Journal of Electrochemical Society*.

The highlight of second year of this project is the development of a palladium (Pd) synthetic approach that was tested as an environmental catalyst for the conversion of hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(III)]. One of the synthetic nanostructured materials developed in the first year of the project was selected and tested as an environmental catalyst for the conversion of higher valent to low valent Cr in soil and water samples. Chromium exists in the environment mainly in two different oxidation states: Cr(III) and Cr(VI). Although Cr(III) is considered a nutrition supplement for regulating normal bodily functions, Cr(VI) is a potential carcinogen with remarkable harmful effects on both plants and animals. Currently, Cr(VI) is converted to Cr(III) using chemical assay formats such as wet acid digestion, which are usually labor intensive and require the use of hazardous chemicals. Therefore, there is a need to design novel Cr(VI) remediation approaches that are safe, fast, and can efficiently convert Cr(VI) to Cr(III).

The application of nanoparticles could be used to address such needs due to their relatively large surface areas that allow for high reactivity rates. There is, however, little or no information regarding the application of palladium-nanoparticles (Pd-NPs) in the conversion of Cr(VI) to Cr(III) in soils and aqueous media. The real sample application of the Pd nanoparticles-sulfur mixture tested using soil samples produced more than 92 percent conversion in the presence of Pd-NPs/S within 1 hour. In contrast, only 33 percent of the same concentration was converted to Cr(III) in the absence of Pd-NPs/S. This represents more than a 500-fold improvement in conversion rate as compared to current microbial approaches. This work offers a new and safe application of nanotechnology for the reduction of high oxidation state heavy metal pollutants. In addition, the researchers have reported the use of Bismuth electrodes for sensing.

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

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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 $3x10^{-11}$ 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 μm thick with piezoelectric properties better than those of specially-cut single crystals. After electroplating 4-μm thick Cu, PMN-PT/Cu microcantilevers were made by wire-saw cutting. With a 600 μm 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 μm will achieve better femtogram sensitivity.

US EPA ARCHIVE DOCUMENT

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

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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 ultralow-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.

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A Nanocontact Sensor for Heavy Metal Ion Detection

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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. The researchers have been developing an integrated sensor chip to meet such demand. The sensor chip consists of an array of nanoscale 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 (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 NG0, where N is an integer and G0 is conductance quantum (=2e2/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 (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 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 Ni^{2+} onto cysteamine-Gly-Gly-Cys increases the conductance approximately 100 times, which is several times smaller than the case of 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 (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

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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.

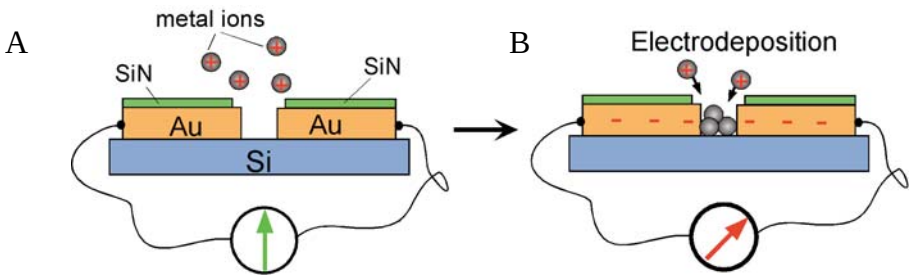

Figure 1. (A) A drop of sample solution is placed onto a pair of nanoelectrodes separated with an atomic scale gap on a silicon chip. (B) Holding the nanoelectrodes at a negative potential, electrochemical deposition of a single or a few metal atoms into the gap can form a nanocontact between the two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

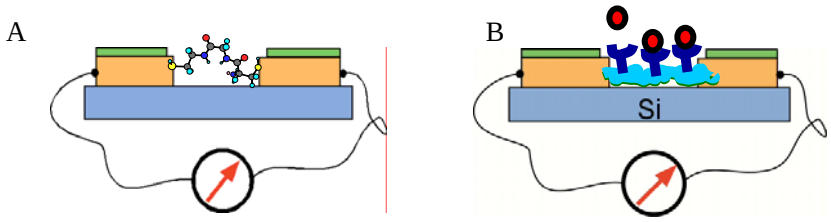

Figure 2. (A) A molecular junction is formed by bridging a pair of nanoelectrodes with molecules terminated with linker groups that can bond to the nanoelectrodes covalently. (B) Bridging the nanoelectrodes with conducting polymers results in polymer junctions. By attaching different molecular probes 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.

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Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring

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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.

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Conducting-Polymer Nanowire Immunosensors Array for Microbial Pathogens

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Abstract

A promising approach for the direct (label-free) electrical detection of biological macromolecules uses one-dimensional (1-D) nanostructures such as nanowires and nanotubes, configured as field-effect transistors that change conductance upon binding of charged macromolecules to receptors linked to the device surfaces. Combined with simple, rapid, and label-free detection, potentially to a single molecule, these nanosensors are also attractive due to the small size, low power requirement and, most of all, the possibility of developing high-density arrays for simultaneous analyses of multiple species. Although current nanosensors based on carbon nanotubes and silicon nanowires have elucidated the power of 1-D nanostructures as biosensors, they have low throughput and limited controllability and are unattractive for fabrication of high-density sensor arrays. More importantly, surface modifications, typically required to incorporate specific antibodies, have to be performed postsynthesis and postassembly, limiting the ability to individually address each nanostructured sensing element with the desired specificity.

The overall objective of this research project is to develop a novel technique for the facile fabrication of bioreceptor (antibody)-functionalized nanowires that are individually addressable and scalable to high-density biosensor arrays and to demonstrate its application for label-free, real-time, rapid, sensitive and cost-effective detection of multiple pathogens in water. Electropolymerization of conducting polymers between two contact electrodes is a versatile method for fabricating nanowire biosensor arrays with the required controllability. The benign conditions of electropolymerization enable the sequential deposition of conducting-polymer nanowires with embedded antibodies onto a patterned electrode platform, providing a revolutionary route to create "truly" high-density and individually addressable nanowire biosensor arrays. The nanowire immunosensor array's utility will be used to simultaneously quantify three important model pathogens: poliovirus, hepatitis A virus (HAV) and rotarvirus.

The researchers recently reported (Ramanathan et al., 2004) simple, yet powerful, facile technique of electrochemical polymerization of biomolecule-friendly conducting polymers, such as polypyrrole, will be conducted in prefabricated channels of tailor-made aspect ratio between two contact electrodes at a site-specific position to synthesize nanowires of tailor-made properties for fabricating individually addressable high-density nanowire biosensor arrays. Detection of pathogens will be achieved by the extremely sensitive modulation of the electrical conductance of the nanowires brought about by the change in the electrostatic charges from binding of the pathogens to the antibodies.

The effects of monomer concentration, dopant type and concentration, aspect ratio, and electrochemical polymerization mode on the sensitivity, selectivity, and durability of poliovirus, HAV, and rotavirus antibodies-functionalized polypyrrole nanowires as label-free bioaffinity sensors of these important model viral pathogens in water will be investigated to establish optimum synthesis conditions of biomolecules-functionalized nanowires to successfully realize this innovation to practice.

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Exploring the Impact of a Nanostructure's Size and Shape on Cellular Uptake, Clearance, and Metabolism

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Abstract

Novel discoveries on molecular differences between diseased and healthy cells and tissues, and the developments of nanotechnology probes and tools are transforming the way we treat and diagnose disease. Biological molecules provide a means to direct nanostructures to a diseased site where the nanostructure can be optically, electrically, or magnetically lit up or treat the diseased site. A key to this hybrid research field is the ability to engineer nanostructures with defined properties. Essentially, a nanostructure provides a system that has custom-tunable function based on its size and shape. Recently, these researchers and others have demonstrated the use of such nanostructures for cell, tissue, and animal imaging and therapeutic applications for the early detection and treatment of cancer. The interface of these two fields has prompted the need to address several important questions. These questions include: Are the nanostructures toxic? How does a cell process these nanostructures? What is the fate and clearance of these nanostructures? Are these processes related to the dimensional or surface chemical characteristics of the nanostructures? These fundamental questions must be answered before nanostructures become useful for clinical applications. The results from this research project provide guidance for the design of nanostructures for biomedical applications.

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Section 6. 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.

Applications of Nanoscale Tunable Biopolymers for Heavy Metal Remediation

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Abstract

Soil contamination by heavy metals is prevalent at hazardous waste sites in the United States. To remediate these sites, there is a strong interest in developing novel polymeric materials that have superior affinity and selectivity because of their unique physical, chemical, and biological properties. Genetic and protein engineering have emerged as the latest tools for the construction of novel materials that can be controlled precisely at the molecular level. Previously, an elastin-like polypeptide (ELP) composed of a polyhistidine tail (ELPH12) has been shown to have promising cadmium removal capability. ELP undergoes a reversible thermal precipitation within a wide range of temperatures, enabling easy recovery of the sequestered cadmium. The goal of this research project is to further investigate the feasibility of utilizing ELP biopolymers for both *ex situ* and *in situ* soil cadmium remediation application. Different metal-binding domains will be incorporated to investigate the efficiency of cadmium removal from contaminated soil.

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Synthesis, Characterization, and Catalytic Studies of Transition Metal Carbide Nanoparticles as Environmental Nanocatalysts

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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_x. 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, the researchers have 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_2 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_2 and N_2O. Furthermore, all three surfaces preferentially produce N_2 over N_2O 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_x Decomposition With WC_x Nanoparticles. Preliminary experiments to study NO_x decomposition with WC_x 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

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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 NO_x occurs according to the reaction: $NO_x \rightarrow N_2 + O_2$.

The N_2 signal is detected by GC. Figure 2 shows the increase in the 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.

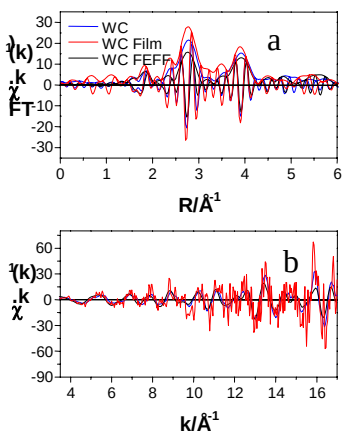

Figure 1. EXAF results comparing the nanoparticles, bulk and theoretical spectra.

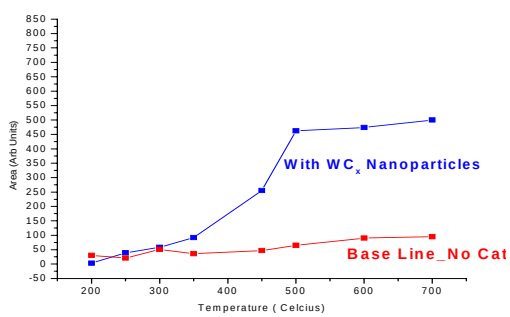

Figure 2. NO_x decomposition with and without the catalyst.

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A Novel Approach To Prevent Biocide Leaching

Patricia Heiden[1], Laurent Matuana[2], and Ben Dawson-Andoh[3]
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Abstract

Newer wood preservatives are formulated without chromium and arsenic so that negative environmental impact is reduced. However, the removal of chromium from biocide formulations also leaves them more susceptible to leach, which can negatively affect ecosystems, particularly wetlands. Loss of biocide also can reduce the useful lifetime of preserved wood products. Therefore, from both an economic and environmental standpoint, it is highly desirable to prevent biocide leach. The objective of this research project is to use nanotechnology as a means to deliver and "fix" copper and organic biocides into wood to eliminate or reduce biocide leaching. Nanotechnology, which is routinely applied to deliver and control the release of pharmaceuticals, has been too costly to use in many other areas, but new technologies and new commercial uses for nanotechnology are making this technology more efficient and less expensive. Given that the awareness of ecological and economic consequences of biocide leach has increased and nanotechnology is becoming more economical to use, this project is investigating the ability of nanotechnology to reduce biocide loss. Specifically, the researchers are seeking to develop a practical approach to incorporate wood preservatives into polymeric nanoparticles that can be introduced into wood with the effect of controlling the biocide release rate to reduce or eliminate loss to leach.

The U.S. Environmental Protection Agency determined that in 2000, the U.S. wood preservatives market was 809,000,000 pounds.[1] In 2003, the wood preservatives industry stopped using chromated copper arsenate (CCA), which has resulted in significant changes in the U.S. wood preservatives market. Although in 2005 this market was $500 to $600 million[2], the nature of these wood preservatives is changing. Although use of some types of wood products is declining, the total demand and market value for treated wood products is increasing. Discontinuing the use of CCA may have removed one ecological issue associated with wood preservative use, but at the same time it may have aggravated another, biocide leach. Newer wood preservative formulations do not "fix" to wood. Although low solubility biocides are often favored because of leaching, this is an inadequate response. Even low solubility biocides will leach, resulting in negative economic and environmental consequences.

Loss of wood preservatives to leaching not only leaves the wood product vulnerable to biological attack, which reduces its useful lifetime, but also the leached biocide has negative consequences to sensitive environments, especially wetlands and other moist environments where leaching is more rapid. If leaching can be reduced or eliminated, wetlands will be less at risk and demands need not be made on forest ecosystems to replace wood products that degraded prematurely because biocide was lost to leach.

This research project will prepare biocide-containing core-shell nanoparticles using a hydrophilic shell to allow the particle to be stable in water, and a hydrophobic core containing the biocides, as shown in Figure 1.

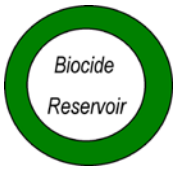

Figure 1. Core-shell nanoparticle having a biocide reservoir surrounded by a polymer shell to facilitate conventional pressure-treatment of wood.

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The key synthetic targets of the project are identifying the best methods to prepare core-shell nanoparticles with high biocide loading, good particle stability in water, and high delivery efficiency into wood. The major hypotheses to be tested are: (1) a core-shell nanoparticle structure can be used to produce a stable aqueous suspension of biocide-containing nanoparticles; (2) a suitable release rate of organic and inorganic biocides can be attained using a core-shell nanoparticle structure that can control the biocide release rate to increase the biological efficacy of the biocide and therefore increase the protected lifetime of treated wood; (3) wood preservation can be achieved using less biocide than currently required using today's technology; and (4) encapsulation of biocides within diffusion-controlled nanoparticles can reduce or eliminate biocide leaching.

Incorporating biocides into polymeric nanoparticles allows the bulk of the biocide to be safely stored within the nanoparticle's interior, where it is protected from leach and random degradative processes. The polymeric nanoparticle therefore functions initially as a biocide delivery medium, then as a protective reservoir, and finally as a controlled release device. The release mechanism is predominantly diffusion controlled, with the rate of diffusion depending on the moisture around the nanoparticle and the hydrophobicity of the polymer.[3,4]

By using a solid polymer as a biocide carrier, even water-insoluble biocides can be delivered into wood without a surfactant, which by itself reduces leaching. By controlling the hydrophobicity of the polymer, the release rate of the biocide can be kept low, ideally sufficiently low so that only the minimum amount of biocide needed to preserve the wood is ever outside the nanoparticle at a given time. By avoiding the use of surfactants and maintaining a diffusion rate of biocide out of the nanoparticle that is sufficient only to maintain biological efficacy, the risk of biocide leach is significantly reduced, thereby gives the effect of biocide fixation.

The expected benefits to be gained by incorporating biocides within a polymeric nanoparticle reservoir include all of the beneficial effects of preventing contamination of ecosystems through leaching, extending the service life of wood and wood products, and effective protection of wood products using lower levels of biocide.

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A Novel Approach To Prevent Biocide Leaching

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Environmental Applications/Implications

The EPA has determined that in 2000 the U.S. wood preservatives market was 809,000,000 pounds.[1] Although use of some types of wood products is declining, the total demand and market value for treated wood products is increasing. In 2003, the wood preservatives industry stopped using chromated copper arsenate (CCA), which has resulted in significant changes in the U.S. wood preservatives market. Although in 2005 this market was $500-600 million, Kline and Company, Inc. (Little Falls, New Jersey) observed that the nature of these wood preservatives is changing.[2] Discontinuing use of CCA may have removed one ecological issue associated with wood preservative use, but it may have aggravated another, biocide leach. Newer wood preservative formulations do not "fix" to wood, which can facilitate leach. Although low solubility biocides are often favored for the purpose of reducing leach, this is an inadequate response. Even low solubility biocides will leach, especially in moist environments, resulting in negative economic and environmental consequences.

Loss of wood preservatives to leaching has detrimental consequences to the preserved wood and to the environment in which the wood is used. Loss of biocide leaves the wood product vulnerable to biological attack, reducing its useful lifetime, and requiring premature replacement of wood products. This places additional demands on forests and is costly. The leached biocide has negative consequences to the local environments, especially wetlands and other moist environments, where leaching is more rapid. If leaching can be reduced or eliminated, wetlands will be less at risk, and the extended longevity of wood products will benefit forest ecosystems. Economic benefits are expected to include a longer useful lifetime for wood products even though less biocide might be required. Incorporating biocides into polymeric nanoparticles allows the bulk of the biocide to be safely stored within the nanoparticle's interior, where it is protected from loss to leach and random degradative processes. The polymeric nanoparticle functions first as a protective reservoir but also serves as a controlled release device, where the biocide is released by a predominantly diffusion controlled process. The rate of diffusion is controlled by controlling the hydrophobicity of the polymer carrier.[3,4]

Using a solid polymer as a biocide carrier allows even water-insoluble biocides to be delivered into wood without a surfactant, which by itself reduces leaching. By controlling the hydrophobicity of the polymer, the release rate of the biocide can be kept low, and ideally reduced to the rate needed so that the biocide concentration outside the nanoparticle is maintained at the minimum level needed to preserve the wood, while the unreleased biocide is maintained within the nanoparticle reservoir. By avoiding the use of surfactants and maintaining a low diffusion rate of biocide to a level to maintain biological efficacy, the loss of biocide to leach can be minimized, and the effect of fixation can be mimicked.

The expected benefits to be gained by incorporating biocides within a polymeric nanoparticle reservoir include all the beneficial effects of preventing contamination of ecosystems through leaching, extending the service life of wood and wood products, and the ability to effectively protect wood products at lower levels of biocide use.

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Section 7. Fate/Transport

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.

Chemical and Biological Behavior of Carbon Nanotubes in Estuarine Sedimentary Systems

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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}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.

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A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol

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Abstract

The goal of the current research is to determine the potential effects of manufactured nanoparticles on human health if they were to become entrained in the atmosphere. Because a number of physical and chemical properties are size-dependent on nanometer length scales, it is important to fully characterize nanomaterials in any studies related to the environmental and health impacts of these materials. The approach to this study is to characterize a variety of manufactured nanomaterials using a wide range of techniques and methods, including surface spectroscopy and surface reactivity so that both bulk and surfaces properties are well understood on a molecular level. These well-characterized particles are then used in inhalation exposure studies. Additional characterization of the particles are done 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 exposed to these well-characterized nanoparticulate aerosols include murine acute pulmonary inflammation assay, murine sub-acute pulmonary toxicology evaluation, and murine microbial challenge host resistance evaluation to screen for acute and sub-chronic pulmonary effects. The studies thus far have focused on some of the smallest available commercial nanoparticles, 5 nm TiO_2. A series of acute and sub-chronic exposures have been completed.

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

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Abstract

Regarding CdSe quantum dots (QDs) in soil and water, where bacterial interactions will occur, this project is addressing the following questions:

- What are the biotic fates of CdSe QDs?
- What are the effects of QDs on bacteria?
- How do fates and effects depend on: QD conjugation? QD size? Environmental factors (e.g., light, pH, reduction potential, oxygenation)? Bacterial strain? Growth habit (biofilm or planktonic)?

Thus far, the results have facilitated a working conceptual model of strain-dependent QD interactions with bacteria:

- External nonspecific labeling where unconjugated QDs cannot passively diffuse into cells.[1,2]
- Specific binding and nonspecific uptake[2] where conjugates are recognized by receptors on the cell envelope, and light-mediated membrane damage from oxygen free radicals facilitates transmembrane transport; thus allowing conjugated QDs less than 5 nm diameter to enter cells.
- External breakdown and transmembrane diffusion of constituent metals, where Cd^{2+} may be expelled; Se^{2-} may be expelled or oxidized to Se^{0} and then retained or expelled; or Cd^{2+} and Se^{2-} may combine into nanoparticles and be expelled or retained.

Specific results in support of this working model were generated from studies involving several bacterial strains. In *Bacillus subtilis*, conjugated QDs produced in the dark but incubated in visible light with bacteria results in the brightest bacterial labeling and the least amount of blue shift. This result supports the concept that CdSe QDs, when exposed to light in water, produce oxygen free radicals that impart membrane damage, allowing conjugated QDs to enter cells.[2] However, light-induced membrane damage, as shown by transmission electron microscopy (TEM), appears to be transient because after a short time most cells are indicated in epifluorescence microscopy by a stain specific for viability. In *Escherichia coli*, conjugated QDs are taken in by similar mechanisms, but are then expelled after 1 hour.

Genotoxicity apparently occurs in *B. subtilis*, as evidenced by cellular elongation or the absence of cell division. Elongated cells are observed to contain CdSe rich occlusions, and several nuclear regions.

Toxicity of constituent metals is observed in *Pseudomonas* spp. liquid culture, whereby rapid growth occurs with selenite and slower growth occurs with Cd^{2+}, whether alone or with selenite. In that growth with CdSe, QDs are somewhere between growth without Cd^{2+} and with Cd^{2+}; it is likely that some QDs are breaking down and causing toxicity, while some are intact outside the cells. Under aerobic conditions, reduction of selenite to selenide and elemental selenium is occurring, and this may occur intracellularly as well.

Toxicity of Cd^{2+} to planktonic *Pseudomonas* is exacerbated by 200 mg/L selenite, and the production of fluorescence for this condition suggests that nanoparticles might be forming intracellularly, or at least very near the

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cells. In any case, whether QDs are entering the cell whole or breaking down and then entering, the co-occurrence of Cd^{2+} and large amounts of Se^{2-}, which is facilitated by the presence of QDs, appears to be more toxic than either metal alone.

When cultivated as unsaturated biofilms, the total yield of DNA in *Pseudomonas* is not affected by equimolar amounts of metals either in the form of QDs or as constituent metals. Cadmium uptake is greater for the constituent metal than for QDs. Lastly, cadmium appears to enhance intracellular accumulation of selenium, which may imply intracellular reduction of selenite followed by Cd^{2+} binding inside the cell.

In conclusion, work to date includes: (1) a putative, conceptual model for how QDs interact with bacteria; (2) evidence to support several interaction mechanisms, including light-activated QD production of membrane-damaging free radicals, free radical-assisted transmembrane transport of conjugated QDs, and conjugated QD-mediated DNA damage, arresting cellular division; and (3) early evidence for intracellular QD assembly in biofilms (Cd-enhanced intracellular sequestration of Se) and in planktonic culture (fluorescence and exacerbation of Cd^{2+} toxicity when high amounts of selenite are present).

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Absorption and Release of Contaminants Onto Engineered Nanoparticles

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Abstract

Little is known about the environmental fate of manufactured nanomaterials. Sorption is often the most important fate mechanism for environmental contaminants. This research project will test four hypotheses: (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) 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. In the first year of this project, the sorption/desorption behavior of both organic and inorganic contaminants to nanomaterials and the fate and transport of naphthalene (an organic contaminant) and colloidal C60 particles in soil column have been successfully characterized. The researchers have attended several national conferences and published 12 peer-reviewed papers (or accepted for publication) in the last year and submitted one U.S. patent application.

Environmental Fate of Carbon Nanomaterials

Many soils or sediments contain various forms of carbonaceous materials such as coals, kerogens, and black carbons, which have been reported to have high affinity for hydrophobic organic contaminants. C60 might have similarly important environmental impact as to other forms of carbon (e.g., black carbons). Although C60 is virtually insoluble in water, nano-C60 particles (a term used to refer to underivatized C60 crystalline nanoparticles, stable in water for months, mean diameter ~100 nm in this study) can be formed in water simply by stirring, or by dissolving C60 in nonpolar solvents, mixing into water, followed by the removal of the solvents. In this study, the adsorption and desorption of naphthalene and 1,2-dichlorobenzene with aqueous nano-C60 particles prepared by both methods was investigated. To compare the adsorptive property of C60 with other carbons (e.g., naturally occurring organic carbon in soils) and activated carbon, adsorption and desorption of naphthalene with Anocostia River sediment (foc = 3.7%) and activated carbon particles (commercial, and nano-activated carbon particles prepared in the laboratory) were conducted and compared with that of C60.

Results show that adsorption to nano-C60 particles is similar to that of nano-activated carbon particles, and is stronger that that of soil organic carbon. Desorption hysteresis was observed for naphthalene desorption from all three forms of carbon tested: C60, activated carbon, and soil organic carbon. A two-compartment sorption model was used to describe naphthalene adsorption and desorption with these three forms of carbon, where there are solid-water distribution coefficients for the first and the second compartment; (*f*Ýg/g) is defined as a maximum sorption capacity for the second compartment; and the factor f (0 „T f „T 1) denotes the fraction of the second compartment that is filled at the time of exposure. Data of naphthalene adsorption and desorption with C60, activated carbon, and soil organic carbon were fitted with this two-compartment model very well, indicating that there may be a common pattern for the adsorption and desorption of naphthalene with these three forms of carbon. Therefore, it may be possible to predict the properties of nano-carbons, such as C60, from that of other carbon forms. This finding may have important environmental significance.

It has been reported that nano-C60 particles are toxic to fish cells and cultured human cells; thus, people may be more concerned about the potential exposure to C60 if it is mobile in water. One might expect that C60 would not enter groundwater in great quantities due to the insolubility of C60 in water. Water-stable nano-C60

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particles, however, can be formed in water by several simple methods, as discussed above, indicating that C60 might be mobile in groundwater. Dissolved organic matter in groundwater has been reported to significantly enhance the partition of neutral organic contaminants into water and thus enhance the transport of those contaminants. It is unknown whether the release of C60 and other nano-sized carbonaceous nanomaterials into aqueous environments will have the similar effect. Therefore, it is of central importance to investigate the C60 transport in water/sediment, and its effect on contaminant transport.

In this work, the transport of nano-C60 particles through a sandy soil column (foc = 0.0027%) was investigated for the first time. Nano-C60 particles showed limited mobility at typical groundwater Darcy velocity. At the Darcy velocity of 3 ft/d, the maximum nano-C60 particles breakthrough was only 47 percent, and an unexpectedly high deposition of nano-C60 to the soil column was observed shortly after the peak value, probably indicating an irreversible sorption of nano-C60 particles on the soil column. It might be because the accumulation of nano-C60 on the collector surface served as favorable sites for subsequent nano-C60 deposition. Nano-C60 particles were more mobile in the soil column at higher flow velocities (e.g., 30 and 90 ft/d). A model developed for the transport of colloids in porous media by K.M. Yao, et al., and C.R. O'Melia, et al., was used to describe nano-C60 particles transport in the soil column. The theoretical single collector efficiency, the particle attachment efficiency, and the maximum particle travel distance were calculated for nano-C60 particles transport at different flow velocities. Experimental results showed that at the flow velocity of 30 ft/d, nano-C60 particles could travel 68 cm through the soil column before 99.9 percent of the particles were immobilized; while at the flow velocity of 90 ft/d, nano-C60 particles could travel 1.32 m through the soil column before 99.9 percent of the particles were immobilized. Spiked release of nano-C60 particles was observed repeatedly on flow resumption following a few days of flow shut-in. Spiked release of nano-C60 particles also was observed during the change of flow velocities. This observed phenomenon may have broad environmental significance.

The transport of naphthalene through the same soil column with 0.18 percent of nano-C60 particles deposited was measured. The observed retardation factor for the naphthalene breakthrough curve with the Lula/0.18 percent-nano-C60 column was about 13, indicating that nano-C60 particles deposited in the soil column adsorbed naphthalene similarly to soil organic carbon.

Adsorption and Desorption of Heavy Metal and Arsenic to Metal Oxide Nanoparticles

The objectives of the current study were to investigate the effect of particle size on adsorption and desorption of typical environmental pollutants (i.e., arsenic and cadmium) onto metal oxide bulk crystals versus nanoparticles (anatase and magnetite), and to examine the competitive sorption between naturally occurring humic materials and heavy metals. In collaboration with Dr. Colvin's group through the support of the Center for Biological and Environmental Nanotechnology (CBEN) at Rice University, several laboratory-synthesized magnetites were studied. On a surface-area basis, cadmium adsorptions to different sized anatase nanocrystals are similar. The maximum adsorption densities for arsenic to magnetite are also similar for commercially prepared large magnetite crystals (300 nm) and magnetite nanoparticles (20 nm). Surprisingly, the adsorption capacity for arsenic to laboratory-synthesized magnetite (11.72 nm) is significantly higher than the commercially available bulk and nanocrystals. Laboratory-synthesized magnetite nanoparticles can remove approximately 100 times more arsenic than larger commercial materials. With respect to desorption, the cadmium desorption from both particle sizes appeared to be completely reversible; however, arsenic was not readily released from magnetite nanoparticles, presumably because the binding of the adsorbed arsenic results in the formation of highly stable iron-arsenic complexes. The presence of natural organic matter (NOM) decreased adsorption of both arsenic species to magnetite nanoparticles. NOM in the solution probably competes with arsenite and arsenate for surface sites on magnetite nanoparticles. With joint support from CBEN, these results are currently applied to test the efficiency of magnetite nanoparticles in removing arsenic from drinking water. A U.S. patent application has been submitted.

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Fate and Transport of C_{60} Nanoparticles in Unsaturated and Saturated Soils

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Abstract

Widespread production and application of manufactured nanomaterials is expected to increase dramatically over the next decade, which will inevitably lead to the release of carbon-based nanoparticles into the environment. Our current understanding of nanomaterial fate and transport in subsurface systems is extremely limited. For example, it is not known how nanomaterials will interact with soil matrices, whether or not nanoparticle transport can be accurately modeled using classical filtration theory, and how unsaturated soil conditions will impact nanomaterial transport and retention. The overall goal of this research project is to expand our knowledge of carbon (C-60) nanomaterial fate and transport in natural soils. The three specific objectives of this project are to: (1) investigate the fate and transport of C-60 nanomaterials in water-saturated soils as a function of soil properties and systems parameters; (2) assess the effects of C-60 nanomaterials on soil water retention, water flow, and transport in unsaturated soils; and (3) develop and evaluate a numerical simulator to describe C-60 nanomaterial transport, retention, and release in subsurface systems.

This research project will focus on two relative well-characterized, commercially available carbon nanomaterials: C-60 fullerene, which is very insoluble in water but forms nanoscale aggregates (20-150 nm diameter) that are stable in solution, and fullerol, a relatively water-soluble fullerene derivative that exists as nanoparticles (1-2 nm diameter) in solution. Detailed laboratory experiments will be conducted to explore the fate and transport of these nanomaterials in natural soils. Experimental variables to be considered include soil organic carbon content, grain size, and water content. Fate and transport experiments will be performed in one- and two-dimensional flow systems, under both water-saturated and unsaturated conditions. Experimental results will be used to evaluate conceptual models of nanomaterial retention and release in porous media, and will be directly coupled to the development and validation of a numerical simulator for prediction of nanomaterial fate and transport in subsurface systems.

The research is expected to greatly improve the fundamental knowledge of engineered nanomaterial transport, retention, and release in natural porous media. The coupling of detailed experimental research and mathematical modeling will provide for rigorous testing of conceptual models of nanomaterial behavior in subsurface systems, and will culminate in the development of a numerical simulator capable of predicting nanomaterial fate and transport over a range of conditions that might be encountered in natural systems. It is further anticipated that the experimental methods, mathematical models, and numerical simulator can be adapted or directly used to predict the fate and transport of other nanomaterials, such as ferroxane and single-wall carbon nanotubes, in subsurface systems.

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Cross-Media Transport, Transformation, and Fate of Carbonaceous Nanomaterials

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Abstract

Research that accounts for cross-media effects is needed to understand the environmental fate of manufactured nanomaterials. All known studies of manufactured nanomaterials in aquatic systems have used the pure, or "fresh," form of the compounds. However, nanoparticles that are released into the atmosphere undergo transformations (coagulation, coating, and reactions) that will change the particles' size, chemical composition, and surface properties. When these "aged" particles later deposit onto the earth's surface, they may have very different fates in the aquatic and terrestrial environments compared to the "fresh" compounds.

The overall objective of this research is to conduct a cross-media assessment of the transport, transformation, and fate of manufactured nanomaterials in atmospheric, aquatic, and terrestrial environments. A key component of the project is to examine how "fresh" versus atmospherically "aged" nanomaterials behave in aquatic and terrestrial systems. The experiments focus on carbonaceous nanomaterials (CNMs, including fullerenes and endohedral metallofullerenes).

In the first set of experiments, the rates at which airborne CNMs transform under naturally occurring conditions will be determined. In the second set of experiments, the interactions of both "fresh" and atmospherically "aged" CNMs with water and soil will be examined to evaluate their environmental transport and reactivity. Specific tasks are to: (1) quantify the rate of reaction of airborne CNMs with ozone; (2) age CNMs in a smog chamber and characterize the processed aerosol; (3) evaluate transport of "fresh" and atmospherically "aged" CNMs in porous media; (4) develop CNM-functionalized atomic force microscope tips; and (5) characterize CNM interactions with soil surfaces in aquatic systems.

The cross-media approach will lead to significant gains in the understanding of how manufactured CNMs are transported and transformed in the environment. The research will determine how CNMs transform in the atmosphere under naturally occurring conditions and to what extent such transformations affect their transport in aqueous systems. This study will be the first to utilize atomic force microscopy to quantify the adhesive and repulsive forces that exist between CNMs (both "fresh" and "aged") and relevant environmental surfaces. An improved understanding of the environmental effects of manufactured CNMs will help address barriers to adoption of nanotechnology.

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Section 8. Toxicity

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 nano-technology 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

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Abstract

The overall objective of this project was to assess the effect of photocatalytic nanoparticles on the toxicity of three organisms, including bacteria, algae, and daphniad. The target organisms studied were: bacteria (*Escherichia coli*; TK2), algae (*Selenastrum capricornutum*), and daphniad (*Ceriodaphnia dubia*). A series of TiO_2 nanoparticles in different particle size fractions were manufactured using the sol gel or CMVD technique. The TiO_2 particles were characterized for the particle size using both the SEM and the DLS methods before use. Experimentally, a 28-h *E. coli* culture or 2-day neonates or log-phase algae culture were exposed to photocatalytic nano-TiO_2 at various concentrations (e.g., 0 to 1 g/L) and particle size (e.g., 3 to 100 nm) both in darkness and the presence of a simulated solar light. The growth or survival rate was used to determine the LC_{50} value of all tested organisms. EC_{50} values of daphniad were determined from the reproduction rate. Results show that in the size range of 5 to 30 nm, there appeared to be no significant difference in toxic response to the photocatalytic TiO_2 particles. The presence of light irradiation significantly decreased the survival and the reproduction (in the case of daphniad) of tested organisms due to additional photocatalytic activity. Photocatalytic reactions generated hydroxyl radical, which is a strong oxidation agent that can cause great stress and damage to the cells. Cell damage was observed in terms of lipid peroxidation (e.g., production of malondialdehyde, MDA), cellular respiration (e.g., reduction of 2,3,5-triphenyltetrazolium chloride, TTC), and antioxidant enzyme (e.g., glutathione-S-transferase, GST). Results indicated an increase in the generation of MDA, TTC, and GST upon exposure of tested organisms to nano-TiO_2; photocatalytic activity markedly increased the production of MDA, TTC, and GST.

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Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity

Robert Hurt and Agnes Kane
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Abstract

Carbon nanotubes (CNTs) and nanofibers (CNFs) are now being synthesized and processed in large quantities, but their potential health risks have yet to be fully assessed. CNTs and CNFs are long, thin, and bio-persistent and have properties in common with asbestos, a group of crystalline, iron-containing mineral fibers that are known human carcinogens. One hypothesis for asbestos-related disease is that redox catalyzed generation of reactive oxygen species causes DNA damage and cytotoxicity. The redox-active species in asbestos is iron, which can be mobilized from the crystal lattice by natural chelators, and then redox cycles to generate free radicals, such as superoxide anion and hydroxyl, in the presence of physiologic reductants such as ascorbate. Hydroxyl radical is particularly aggressive, reacting at diffusion-limited rates with DNA and most other biological molecules. Iron is the single most common element used in CNT/CNF catalyst formulations and, despite purification procedures, most CNT/CNF samples contain significant quantities of residual catalyst.

This study examines the potential cytotoxicity of iron-containing carbon nanomaterials using a variety of molecular and cellular endpoints, including iron mobilization, induction of plasmid DNA single-strand breaks, and the viability and morphology of murine macrophages. The iron in catalytically grown nanotubes varies in chemical composition (metal, oxide, carbide) and can be partially or wholly encapsulated by carbon, hindering its interaction with species in surrounding fluid media and possibly suppressing redox activity. To manage this complexity, experiments were first carried out on a model nanomaterial system in which the amount, form, and accessibility of iron were carefully controlled. The model system chosen was non-catalytic, template-fabricated carbon nanofibers in two forms: (1) high-purity as synthesized, and (2) surface doped with accessible iron nanoparticles. A second set of experiments were conducted on commercial multi-wall nanotubes in four forms: (1) raw; (2) vendor purified with reduced iron content; (3) purified, then partially oxidized; and (4) purified, then ground. The last two samples are included to test if post-synthesis handling/processing can further expose encapsulated iron and accelerate the free radical generation process.

The doped model nanofibers showed significant Fe mobilization by ferrozine in the presence of ascorbate, a higher frequency of DNA single-strand breaks, accompanied by macrophage activation and increased cell death. The raw commercial nanotubes showed similar results to the Fe-doped model nanofibers indicating that at least some of the iron is indeed redox active and not fully passivated by carbon shells. The purified nanotubes had much lower Fe mobilization and DNA single-strand break frequency. Partial oxidation of the purified sample restored some of the iron mobilization, suggesting that additional iron was made accessible by oxidative tube damage. Mechanical grinding had little effect. Overall, these results suggest practical guidelines for fabricating, purifying, and handling iron-containing carbon nanomaterials to minimize toxicity.

Success Stories

Principal Investigators (PIs) Agnes Kane and Robert Hurt gave a joint invited talk on their EPA-sponsored research at NanoDays 2005 in October 2005, which was hosted by Rice University's Center for Biological and Environmental Nanotechnology. Roger Hurt received an invitation to give a plenary lecture at the International Symposium on Eco-Materials Processing and Design in Kyushu, Japan, in January 2007. Agnes Kane gave a keynote lecture at Carbon2004 on fiber and nanofiber toxicity. Agnes Kane and Robert Hurt are serving as editors of an upcoming special edition of the scientific journal, *Carbon*, devoted to the Toxicology of Carbon Nanomaterials.

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The Fate, Transport, Transformation, and Toxicity of Manufactured Responses of Lung Cells to Metals in Manufactured Nanoparticles

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Abstract

This research project is based on the hypothesis that transition metals in particles induce pro-inflammatory signaling and cell damage through the production of reactive oxygen species. Established cell culture models and toxicology assays are being applied to the analysis of manufactured nanomaterials. Based on the literature and the researcher's data, the researchers expect that the small physical size and high surface area of nanoparticles (d < 30 nm) will increase cellular uptake and increase induction of pro-inflammatory signaling as compared to larger particles with the same elemental composition. *In vitro* studies with human and rat lung cells are being used to evaluate the effects of manufactured nanoparticles. The emphasis is on lower-cost nanomaterials that are sold in powder or liquid suspension form because these materials are expected to be produced and ultimately released in the largest amount.

Currently, this study is in its first phase, using low-cost assays to screen a wide range of samples with sufficient replicates for statistical power. This phase (Figure 1) emphasizes measurement of cytotoxicity, induction of the proinflammatory cytokine IL-6, and dissolution rate in simulated lung fluid. Materials selected in the screening phase will be used for more detailed, mechanistic studies. The second phase will test selected materials for particle uptake by the cells, for the induction of additional cytokines, and for the effect of antioxidants. Phase two physical characterization will include electron microscopy, BET surface area, zeta potential, and trace element analysis. In the third phase, the most inflammatory and most benign nanomaterials will be used in hypothesis-based toxicology experiments to evaluate plausible mechanisms by which the particles induce specific responses in cells. Cell culture toxicology studies with BEAS-2B cells, an immortalized human lung epithelial cell line, are emphasized and are consistent with the goal of refining, reducing, and replacing animal use. To establish the relevance of cell culture data to whole animals and to human health, experiments using normal macrophages and normal epithelial cells that are freshly harvested from rats will be conducted to test the ability of the cell culture assays to predict the induction of inflammation by specific nanomaterials.

The vendors' nominal size of selected powders sold as nanomaterials has been verified (Figure 2). Some supermicron size particles appear to have internal porosity. The tentative result of the *in vitro* assays used in the screening phase is that the nano-size particles of metal oxides are not highly potent as compared to micron-sized particles of the same compound or compared to positive controls that are representative of environmental particulate matter. This may be good news for those concerned about the potential health effects from nanoparticles in consumer products, but much more work is needed to confirm these results before publication.

This is the first year of a 3-year study. Verification of the relatively low potency of nano-sized particles will be added to the cell culture and physical characterization studies already planned.

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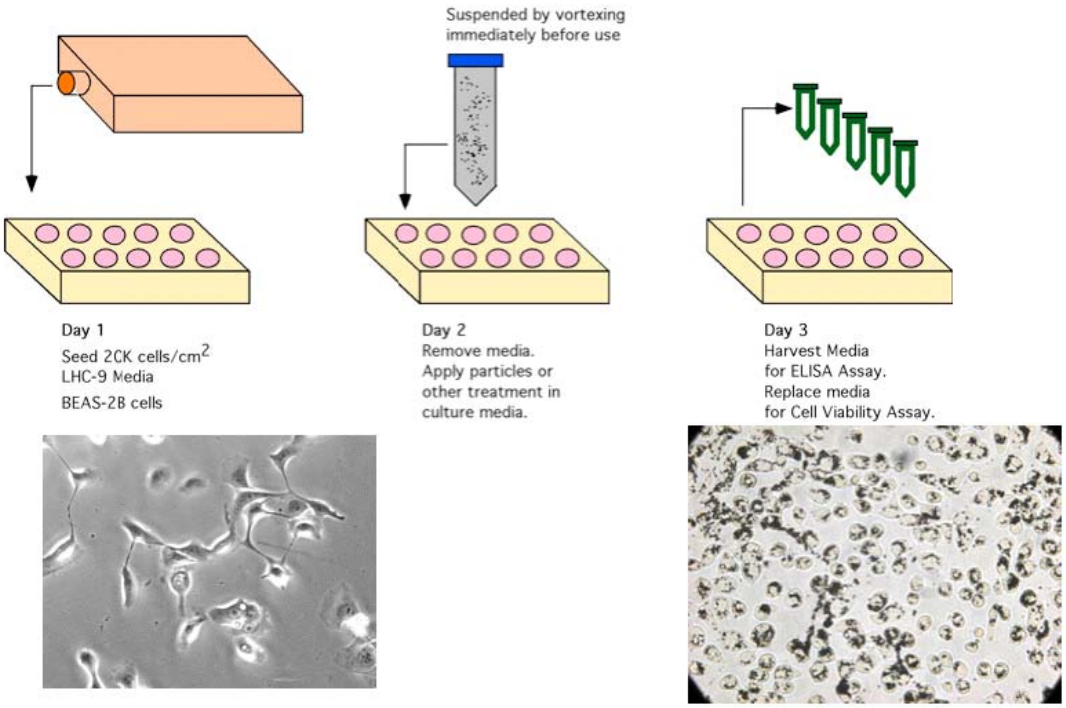

Figure 1. Using *in vitro* cell culture to measure cytotoxicity of and IL-6 induction by a range of nano- and micro-sized particles.

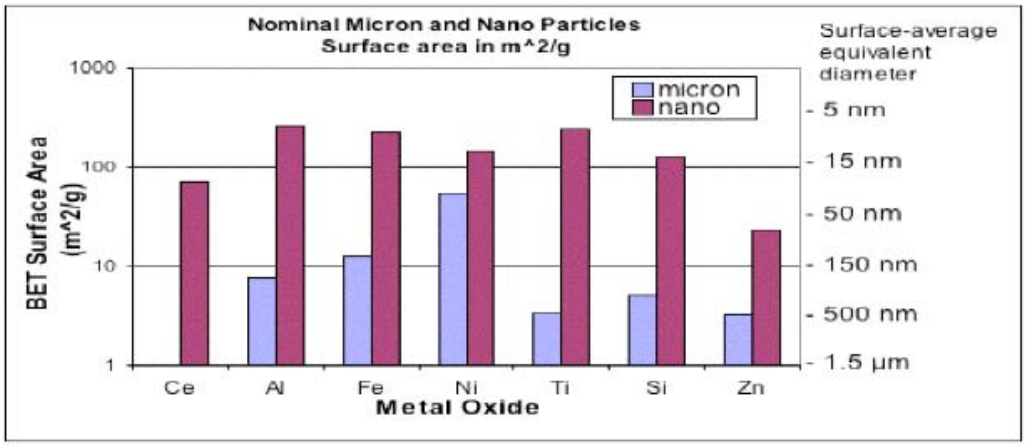

Figure 2. BET surface area for nominal micron and nanoparticles. Bars are marked with the elemental symbol of the metal, but particles were in the oxide form.

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Nanomaterials in Drinking Water

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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. Also, 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. 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.

A multidisciplinary approach is underway that includes experiments to identify the fundamental uniqueness of nine nanomaterial properties and toxicity, and applied experiments aimed directly at understanding the fate and reactions involving nanomaterials in drinking water treatment plants. Advanced nanomaterial characterization techniques will be employed to determine the size distribution, concentration, and zeta potential of nanomaterials in buffered distilled water and model waters representative of raw drinking water supplies. Adsorption of dissolve pollutants (e.g., anions, metals, range of synthetic organic chemicals) and natural organic matter are proposed to quantify the potential for nanomaterials to transport such compounds and be transformed by the compounds (e.g., aggregation, change in zeta potential). Coagulation processes will be studied by compressing the electric double layer of nanomaterials, and exposing nanomaterials to alum coagulations, using mono- and heterodisperse solutions; comparable filtration work also will be conducted. Adsorption of virus onto nanomaterials and subsequent disinfectant shielding will be studied. Toxicity screening will include toxicity of nanomaterials on several cell lines selected to mimic oral ingestion routes in drinking water.

During the first year of this project, significant advances have been made. These have been incorporated in numerous invited and unsolicited presentations at national conferences. The first year focused in part on methodological advances. This included demonstrating that commercial nanoparticles do not behave as discrete nanoparticles in aqueous systems, and aggregation of these materials results in particles less than 1 μm. This study has focused on metal oxide nanoparticles and understanding how surface change (zeta potential) affects the removal of nanoparticles during simulated drinking water treatment. Coagulation and sedimentation processes remove 30 to 80 percent of the nanoparticles, meaning that many would not be removed. Second, experiments with inorganic (arsenic) and organic (MIB) chemicals or pathogen models (MS2 bacteriaphage) have concluded that surface change will affect the extent of interaction, and nanoparticles can facilitate the transport of these substances. Third, conditions conducive to growing various epithelial cell layers that mimic intestinal cell linings have been developed. Using resistivity-based approaches, a detrimental impact of nanoparticles has been observed, and using confocal laser microscopy it has been observed that nanoparticles penetrate the cell membranes. Over the next 2 years, this study will be expanded to include quantum dots and other nanoparticles in greater detail.

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Microbial Impacts of Engineered Nanoparticles

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Abstract

Responsible usage of nanomaterials in commercial products and environmental applications, and prudent management of the associated risks, require an understanding of nanoparticle mobility, bioavailability, and ecotoxicology. This project will elucidate processes governing the transport and microbial impacts of two classes of catalytic nanomaterials in soil-water systems: fullerenes and metallic nanoparticles (e.g., TiO_2, ZnO, and Fe (0)). Specific tasks are to: (1) characterize nanomaterials size, shape, functionality, reactivity, aggregation, deposition potential, and bioavailability; (2) screen nanomaterials of varying sizes and properties for bactericidal activity; (3) discern bacterial physiologic characteristics that confer resistance (or susceptibility) to catalytic nanomaterials; (4) evaluate the potential for fullerene biotransformation by reference bacteria and fungi; and (5) assess the impact of simulated nanomaterial releases on microbial diversity and community structure.

The researchers postulate that reactivity at the nanometric scale is intimately linked to nanoparticle mobility and microbial sensitivity. Thus, first-order factors increasing nanoparticle reactivity should increase the rate of redox reactions with second-order effects on particle mobility and ecotoxicity. Sources of reactivity may include functionalization of nanoparticle surfaces, affinity for electron uptake and subsequent transfer to species in solution, and interfacial phenomena ranging from ordered water effects such as clathrate formation around nano-particle nuclei to adsorption of naturally occurring macromolecules. Regarding microbial impacts, it is hypothesized that nanomaterials that generate reactive oxygen species or related free radicals will hinder heterotrophic and photosynthetic activities and cause population shifts that reflect differential responses and diverse protective mechanisms used by dissimilar populations. Thus, aerobic bacteria with enzymes that destroy toxic oxygen species or with thicker cell walls may have a competitive advantage. Similarly, fermenting bacteria may be more resistant than respiring or photosynthetic bacteria, because the latter employ many biomolecules to transfer electrons during phosphorylation, which could interact with catalytic nanomaterials to generate harmful free radicals.

Regarding experimental approach, a risk assessment structure will be followed to examine factors that affect nanoparticle exposure and impact. Nanoparticle exposure will be quantified in terms of mobility in soil-water systems. Microbial impact will be quantified as a function of nanomaterial properties and bacterial physiological characteristics, by measuring cell growth, respiratory, photosynthetic, and enzymatic activities. Molecular tools will be used to characterize effects on microbial community structure. The interface between exposure and impact will be examined in both batch reactors and in flow-through column experiments.

The relevance of the proposed work to the U.S. Environmental Protection Agency's mission is related to the fact that microorganisms are the foundation of all ecosystems and are often the basis for food chains and the main agents of biogeochemical cycles. Thus, understanding their interactions with engineered nanomaterials is important to ensure that nanotechnology improves material and social conditions without exceeding the ecological capabilities that support them. This research will provide an improved understanding of the chemical and physical factors that control nanoparticle mobility and bioavailability, and their impacts on microbial activities, diversity, and community structure. This will benefit risk assessment and management efforts, and may contribute indirectly to the development of nanotechnology-based disinfection and biofouling control strategies.

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Semiconductor Nanowires and Applications to Human Health

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Abstract

This project addresses the growth and applications of semiconductor nanowires by molecular beam epitaxy using a technique called the vapor-liquid-solid (VLS) process. The VLS process uses a catalytic seed particle that spatially confines the nucleation processes responsible for semiconductor growth. Using this approach, single wires less than 10 nanometers in diameter and as long as tens of microns have been produced. By altering the conditions of wire growth, complex heterostructures may be incorporated into the wires adding optoelectronic functionality for biological applications of interest to human health, including solution assays, fluorescent labeling, optical barcoding, separation, delivery, and biosensing. The physicochemical properties of semiconductor nanowires will be studied to develop an understanding of their potential toxicological and biological impact. The capabilities of the VLS process will allow, for the first time, a systematic study of the size-, shape- and composition-dependence of the transport properties of nanoparticles and their cellular interactions.

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Interactions Between Semiconductor Nanoparticles and Biomembranes and DNA

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Abstract

Two very different modes of access have been identified, one in bacteria and one in mammalian cells. Both are dependent on the physical chemistry of the particle.

In Bacteria. Bacteria do not endocytose; thus, they are unlikely to be able to take up particles several nanometers in size unless there is a particular mechanism permitting these particles to penetrate. The researchers have identified two features critical for uptake in bacteria. First, the quantum dots (QD) must be conjugated to a biomolecule to which the bacterium has receptors, and the conjugation must not interfere with the recognition site of that molecule. Second, the QD must be readily photooxidized, and light exposure must occur during incubation with the bacteria. Certain biomolecules, such as the purines adenine and guanine, the neurotransmitter dopamine, and the amino acids tyrosine and tryptophan, make the QDs more effective at this light-induced cell penetration. Penetration is through membrane defects in the cell surface; however, treated bacteria do not show membrane compromise or associated cell death.

In Mammalian Cells. The presence of specific receptors to the QD conjugate is required for uptake. Light exposure is not required, consistent with endocytic mechanisms of uptake. QDs can be visualized in cellular endosomes, and endosomes can be ruptured by exposure to ultraviolet (UV) light.

In All Cells. Surprisingly, even cells that endocytose show preferential uptake of certain colors (sizes) of QD. This is correlated with the ability of the different sizes to transfer electrons or holes to their conjugates.

Reactivity. With membranes, hydrophobic QDs, capped with pyridine, show integration into biomimetic lipid membranes and can be delivered (with the aid of a surfactant) to the membranes of living cells. Surprisingly, the application of large voltages (± 120 mV) and exposure to high-intensity UV light (Hg lamp, 60 min) are not sufficient to produce any measurable leakage events. Hydrophilic QDs, however, capped with mercaptoacetic or mercaptoproprionic acids, create fast leakage events suggesting penetration through lipid membranes. Exposure to large voltages appears to be necessary to begin the process; after leakage events have begun, smaller voltages (± 20 mV) are sufficient to evoke additional events. Events are nonquantal and do not require light exposure.

With DNA. DNA damage by QDs appears to be related to Cd release after photodegradation of particles. Severe effects on bacterial growth were seen whenever bare core CdSe QDs were assimilated, especially in Gram positive strains. Growth using measurements of cell density (optical density at 600 nm), by inspection under epifluorescence microscopy (to investigate cell morphology, spore formation, and QD-related fluorescence), by plating, and by quantitative analysis for hydroxyguanine were investigated. When QDs were added to Gram positive *Bacillus* cultures in early log phase (OD 600 < 0.2), optical density decreased, indicating cell loss, and endospores could be visualized (n > 10). When incubation was begun at mid-log phase, OD continued to increase, but more slowly than in controls: percent of control at 2 h, 60 ± 2 percent; at 6 h, 39 ± 3 percent (n = 3). The cells, however, were unable to form colonies (n = 5; dilutions ranged from 1:5 to 1:1 for cultures of OD 600 between 0.3 and 0.5). Extraction of genomic DNA and assays for oxidative DNA damage showed an average of 7.75 ± 0.006 abasic sites per 105 base pairs in *Bacillus subtilis* cells exposed to yellow QD-adenine (n = 6). *B. subtilis* exposed to cell-wall targeted (nonassimilated) QDs under room light showed 2.33 ± 0.005 abasic sites per 105 base pairs (n = 3).

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With CdSe/ZnS core-shell QDs, less than 1 abasic site was seen per 105 base pairs. However, much less QD assimilation was observed in this case: two-fold weaker fluorescence using particles with a fifteen-fold greater quantum yield. Hence, it is possible that Cd release assists particle uptake.

Stability. The QD conjugates used in this study have all linked a biomolecule to the QD surface cap via an amide bond. Proteases in cellular lysosomes break these bonds, liberating the QD from its conjugate. Small conjugates can thus diffuse out of the lysosomes and into the cell. Using QD-dopamine, this process may be directly observed as oxidized dopamine and shows blue fluorescence.

Prolonged exposure to light and oxidizing conditions do not appear to lead to significant release of Cd from CdSe/ZnS core-shell particles. Ion chromatography/mass spectrometry (ICP-MS) revealed less than 1 ppm Cd in aqueous solutions of core-shell dopamine conjugates after 4 hours of UV exposure. The addition of antioxidants to these solutions (beta-mercaptoethanol or ascorbic acid) reduced the Cd release to less than 20 ppb.

Conclusions and Future Work. The photophysics of QDs, particularly their size, redox potential (which depends not only on band gap, but on the presence of surface states) has a great influence on the interactions of these particles with biological cells and structures. Electron transfer processes should be sought as causes of selective uptake of specific sizes of QDs. Common biomolecules can also sensitize QDs, making them more photoreactive and able to damage cell membranes with or without Cd release. DNA damage, however, has so far only been seen when Cd is released in significant quantities.

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Interactions Between Semiconductor Nanoparticles and Biomembranes and DNA

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Environmental Implication/Application

Risk of Photosensitized Quantum Dot Particles Released Into Water/Soil

QDs conjugated to electron donors are photosensitized (i.e., they are more reactive on exposure to light than unconjugated particles or particles conjugated to molecules, which cannot donate electrons). Such conjugates cause extreme oxidative phototoxicity to cells to which they are able to bind, whether these cells are mammalian, fungal, or bacterial. Thus, an important conclusion of this project is that such QD conjugates should be treated very differently from bare QDs, as they are likely to be significantly more hazardous.

In addition, this study shows great variation in reactivity and ability to be photosensitized among the different sizes (colors) of QDs. These effects cannot yet be quantitatively predicted theoretically, as they are dependent on factors other than the particle diameter or band gap. Thus, it is expected that the risks of different sizes of semiconductor nanocrystals will have to be determined independently.

Highly reactive, photosensitized particles should be prevented from entering any potential food or water supplies, particularly because they can show reactivity to particular cell types.

Risk of Exposure to Specific Cell Types

QD-dopamine conjugates are specifically taken up by dopamine-receptor bearing cells. This could pose a significant risk in animals if these particles were able to come into contact with such cells. Experiments with mouse or other animal models are needed to assess these risks.

Usefulness as Targeted Microbicides

Photosensitized particles targeted to bacterial metabolism have potential as microbicidal agents. However, most of the toxicity observed in bacteria in this study appeared to be related to Cd release, which is undesirable. The creation of highly phototoxic, bacterially targeted particles capped with ZnS or other non-Cd containing layers remains a challenge for the future.

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Understanding the Light-Induced Cytotoxicity of Quantum Dots: A Cellular, Photophysical, and Mechanistic Approach

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Abstract

Quantum dots (QDs), nanometer-sized light emitting semiconductor (i.e., CdSe) particles, are emerging as a new class of fluorescent probes for *in vivo* and cellular imaging. Due to their size, they have unique optical properties such as size-tunable emission from green to red, resistance to photo bleaching, and high emission quantum yield. Two decades ago, QDs were confined to physicists' laboratories. In 2005, QDs are commercially available worldwide in numerous forms. They are used in bioimaging, either *per se* or conjugated to biopolymers, DNA, and proteins, thus enabling target-specific imaging. They can act as an energy donor in FRET experiments and, as demonstrated recently, they also can be used as photosensitizers. The latter property is particularly exciting because it could lead to novel forms of *in vivo* photodynamic therapy.

Not surprisingly, the potential toxic effects of semiconductor QDs have become a topic of considerable importance and discussion. Indeed, *in vivo* toxicity is likely to be a key factor in determining whether QD imaging probes would be approved by regulatory agencies for clinical human use. Recent publications by the researchers and by others indicate that QDs can be highly toxic to cells under irradiation, although under given conditions QDs are much more benign. This research project focuses on the light-induced potential toxicity of QDs, using a three-pronged mechanistic approach: solution photophysics, cell imaging, and quantitative analysis of released harmful ions (Cd^{2+}).

The outcome of this study will be to gain a better understanding of a key aspect of QD cytotoxicity, an appraisal of various means to alleviate their deleterious effects, and the delineation of predictive guidelines for QD cytotoxicity.

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Section 9. Exposure

As nanotechnology progresses from research and development to commercialization and use, it is likely that manufactured nanomaterials and nanoproducts might result in exposure to humans or other organisms. Potential sources of human exposure to nanomaterials include workers exposed during the production and use of nanomaterials, general population exposure from releases to the environment during the production, use and recycle/disposal of nanomaterials, and direct general population exposure during the use of commercially available products containing nanoscale materials. Research is needed to identify potential sources, pathways, routes of exposure, potential tools and models that may be used to estimate exposures, and potential data sources for these models. Tools and resources for assessing releases and exposures, including metrics and sensors, analysis of physical and chemical properties of nanomaterials, and population sensitivities need to be developed, along with engineering controls and pollution prevention techniques capable of minimizing releases and exposures to nanomaterials.

Nanomaterial Interactions With Skin

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Abstract

The field of nanoscience has experienced unprecedented growth during the last few years and has received a great deal of attention because of the many potential applications. Nanomaterials possess unique physico-chemical properties compared to larger microparticles that enable novel engineering applications. Their large surface area and increase in reactivity can enhance the transport of nanomaterials in the environment and in biological systems. There are many challenges, however, that must be overcome before nanotechnology can be applied to the field of nanomedicine or science-based occupational or environmental exposure risk assessments can be conducted. There is a serious lack of information about human health and environmental implications of manufactured nanomaterials. This new field of nanotoxicology will continue to grow and emerge as new products are produced. Insufficient data have been collected so far to allow for full interpretation or thorough understanding of the toxicological implications of occupational exposure or potential environmental impact of nanomaterials.

Skin is a primary route of potential exposure to toxicants and nanomaterials, and the ability to traverse the stratum corneum and viable epidermal layers is a primary determinant of the dermatotoxic potential. Currently, there is no information on whether carbon nanomaterials, or nanomaterials in general, can penetrate intact skin and cause adverse effects.

The goal of this research project was to study the effects of several different types of nanomaterial interactions with skin, including dermal absorption and cutaneous toxicity and the ability to distribute to skin after systemic exposure. To date, several types of nanomaterials have been evaluated in two different *in vitro* model systems under different conditions (concentration, surfactants, and vehicles); multi-walled carbon nanotubes (MWCNT) in human epidermal keratinocytes (HEK), the fullerenes nanoC_{60} and derivatized C_{60} ($C_{60}(OH)_{24}$) in HEK. Also, fullerene-based amino acids (BAA) and fullerene C_{60} peptide with a fluorescently tagged nuclear localization signal (NLS-FITC) for 24 h and 48 h in HEK have been evaluated. In addition, quantum dots (QD) of two different sizes (6 nm and 10 nm) and three different surface coatings (polyethylene glycol, carboxylic acid, or amine) have been evaluated. All of these studies were conducted in HEK to assess cellular uptake, cytotoxicity, and inflammatory potential. The fullerene NLS-FITC and QD also were evaluated in flowthrough diffusion cells to assess skin penetration.

HEK were exposed to 0.1, 0.2, and 0.4 mg/mL of multi-walled carbon nanotubes (MWCNT) for 1, 2, 4, 8, 12, 24, and 48 h. HEK were examined by transmission electron microscopy (TEM) for the presence of MWCNT. This study showed that chemically unmodified MWCNT were present within cytoplasmic vacuoles of the HEK at all time points. The MWCNT also induced the release of the proinflammatory cytokine interleukin 8 (IL-8), a biomarker for skin irritation, from HEK in a time-dependent manner. These data clearly show that MWCNT, neither derivatized nor optimized for biological applications, are capable of both localizing within and initiating an irritation response.

Studies with the fullerenes nanoC_{60}, and derivatized C_{60} ($C_{60}(OH)_{24}$) were conducted in HEK. HEK were exposed to nanoC_{60} ranging in concentrations (0.0000025 - 0.0005 mg/mL), derivatized C_{60} ($C_{60}(OH)_{24}$) ranging in concentrations (0.000005 - 0.001 mg/mL) (n=8/treatment) for 24 h and 48 h. MTT viability showed nano-C_{60} ranging from 0.00025 to 0.0005 mg/mL decreased HEK viability significantly ($p < 0.05$) by 24 h. The inflammatory mediators IL-8 and IL-6 were significantly ($p < 0.05$) greater than controls, but IL-10, IL-1β, and TNF-α were below detectable limits. $C_{60}(OH)_{24}$ showed no toxicity to HEK at all concentrations. At high concentrations of nano-C_{60} (0.003 mg/mL), MTT viability was reduced by 48 h and IL-8 increased from 4 h to

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48 h. Additional studies with 0.5 percent Pluronic® F127 surfactant found that nano-C_{60} (0.0005 mg/mL) caused a significant ($p < 0.05$) decrease in viability and a significant increase in IL-8 production by 48 h. In contrast, $C_{60}(OH)_{24}$ treated with the surfactant showed no statistical differences in HEK viability or cytokine production. Finally, the addition of 1 percent DMSO to nano-C_{60} (0.0005 mg/mL and 0.003 mg/mL) significantly decreased MTT viability, and the 0.003 mg/mL significantly increased the release of IL-8 by 48 h. These results show that although derivatized $C_{60}(OH)_{24}$ are nontoxic in the tested range, nano-C_{60} are toxic at concentrations as low as 0.00025 mg/mL in HEK.

The amino acid derivatized fullerene C_{60} BAA has the potential to provide greater interaction between the fullerene and the biological environment yielding potential new medical and pharmacological applications. BAA can serve as a nanoparticle platform for conjugation of targeting peptides and therapeutic biomolecules. HEK were exposed to fullerene BAA concentrations of 0.4 - 0.00004 mg/mL for 1, 4, 8, 12, 24, and 48 h. MTT cell viability after 48 h significantly decreased ($p < 0.05$) at concentrations of 0.4 and 0.04mg/mL. Proinflammatory cytokines IL-6, IL-8, TNF-α, IL-1ß, and IL-10 were assessed at concentrations ranging from 0.4 – 0.004 mg/mL. IL-8 concentrations for the 0.04 mg/mL treatment were significantly greater ($p < 0.05$) than all other concentrations at 8, 12, 24, and 48 h. IL-6 and IL-1ß activities were greater at the 24 h and 48 h for 0.4 and 0.04 mg/mL. No TNF-α or IL-10 activity existed at any time points for any of the concentrations. These results indicate that concentrations lower than 0.04 mg/mL initiate less cytokine activity and maintain cell viability at control levels. BAA concentrations of 0.4 and 0.04 mg/mL in HEK decreases cell viability and can initiate a proinflammatory response in the dominant cell type of skin.

HEK also were exposed to concentrations from 0.4 - .001 mg/mL (n = 8/treatment) of C_{60} BAA conjugated to a peptide with a fluorescently tagged nuclear localization signal (NLS-FITC) for 24 h and 48 h. MTT viability and the proinflammatory mediator's interleukin IL-8, IL-6, IL-1β, IL-10, and TNF-α were assessed. In addition, 4.4 $\mu g/cm^2$ and 1.1 $\mu g/cm^2$ of C_{60}-NLS-FITC with and without 1 percent Pluronic® surfactant or NLS-FITC alone was topically applied to porcine flow through diffusion cells for 24 h. MTT viability decreased and was statistically significant ($p < 0.05$) in HEK at 0.4 mg/mL at both 24 h and 48 h. IL-8 and IL-6 statistically increased at 0.2 mg/mL and 0.4 mg/mL. IL-1β (0.4 mg/mL) was low but was significantly different from controls, while IL-10 and TNF-α were below detectable limits. Confocal microscopy of the flow through skin at both concentrations for C_{60}-NLS-FITC and NLS-FITC depicted penetration through all epidermal layers. Surfactant greatly enhanced the permeability for all treatments. These results showed that the substituted fullerenes can penetrate through intact skin and can elicit an inflammatory response.

QDs of two different sizes (6 nm and 10 nm) and three different surface coatings (polyethylene glycol, carboxylic acid, or amine) were topically applied to porcine skin in flow through diffusion cells at a concentration of 62.5 $pmoles/cm^2$. Confocal microscopy showed QDs were localized within the epidermis and dermis by 24 h for all QD preparations. Additional studies utilized HEK to investigate the cellular uptake, cytotoxicity, and inflammatory potential of these nanomaterials. Live cell confocal imaging showed that all types of QDs were localized within the cell by 24 h. MTT viability and multiplex ELISA for the inflammatory cytokines IL-1β, IL-6, IL-8, IL-10, and TNF-α revealed that carboxylic acid-coated QDs at a concentration of 20 nM exhibited significant cytotoxicity and increased release of IL-8 by 24 h. This study showed that commercially available QDs with diverse surface chemistries can penetrate the skin and be incorporated within HEK by 24 h, and that QD surface coatings can influence cytotoxic and inflammatory effects.

These ongoing studies and the results so far indicate that skin cells and intact skin exposed to nanoscale materials of different physicochemical properties such as size and surface charge, and different vehicles may result in localized toxicity. The dermatotoxic potential of nanomaterials is based on whether they can traverse through the stratum corneum layers, penetrate through the viable epidermal layers to the dermis, and be absorbed by the capillaries in the dermal papillary layer to have a systemic effect. These data are necessary to define the doses for systemic exposure after topical administration as well as the cutaneous hazard after either topical or systemic exposure, the two essential components of any risk assessment. If nanomaterials are inadvertently modified or if exposure occurs before cleansing, they could have untoward consequences if they gain entry through the skin. A single study will not definitively answer all of the pertinent questions relative to

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dermal risk assessment of nanomaterials, but they provide a foundation for future work. Ultimately, they should be able to provide an insight into the nature of the potential hazard of nanomaterials at certain concentrations and under various conditions and should provide an initial estimate of the dermal exposure parameters that can be used to design more definitive studies.

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

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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 cellubiase; and (4) respirating and trapping CO_2 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 ^{13}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 ^{13}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.

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Iron Oxide Nanoparticle-Induced Oxidative Stress and Inflammation

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Abstract

Although much research has been devoted to nanomaterials synthesis and manufacture, very little is known about cellular or organ responses following exposure. In this research project, it is hypothesized that the small size of nanoparticles (NP) contributes to their evasion of normal particle clearance mechanisms, increases the likelihood of contact with cells of many types, particularly epithelial cells, and allows their translocation to sites distant from the original exposure, potentially leading to inflammation and oxidant stress. This study will address these hypotheses by determining if NP: (1) induces oxidative stress and toxicity in cultured epithelial and endothelial cells; (2) causes lung inflammation or extrapulmonary effects after *in vivo* exposure; and (3) translocates to extrapulmonary sites. The first year of this project has been focused on: creating NP systems that can be used to test the study's hypotheses, investigating the *in vitro* responses of human alveolar epithelial and umbilical vein endothelial cells exposed to NPs, and monitoring NP uptake.

Fe_2O_3 NPs have been used as a model system for better understanding of the cellular and tissue responses following exposure to nano-sized materials. Although DPPC-coated 20 nm Fe_2O_3 NPs agglomerated within 1-2 hours of incubation in CM, presumably due to salt destabilization of the fatty acid coating, they did not induce adverse effects in cultured lung epithelial cells ($A549_{luc}$) up to 800 μg/well (38 μg/cm^2) (i.e., no changes in lactate dehydrogenase (LDH) release or luciferase reporter activity). Ultrafine TiO_2 (20 nm) was used as a comparison, and similar results were obtained for the same mass dose range. Until a coating can be devised that confers greater stability to the Fe_2O_3 NPs in cell culture systems, the researchers have decided to move to other model systems. One such system is the liquid-phase synthesis of several NP shapes made of Pt. What is unique about this system is that the end shape can be controlled through temperature and reaction time. The shapes that can be made include spheres, multipods, and flowers (see Figure 1); the spheres themselves are grown from either the multipods or the flowers. This Pt-based system allows the researchers to test the hypothesis that shape and surface area (SA) can predict response. Shape-related hypotheses with nano-gold also are being tested; an additional property of Au, particularly the colloidal NPs, is the potential for binding to proteins so that hypotheses related to surface modifications can be investigated.

One major focus over the first year of the project has been on the reactive oxygen species (ROS) generating capacity of a wide range of NPs, including the Pt shapes and Au colloids, in an acellular assay. The Pt shapes demonstrated a range of ROS-generating capacity, with the highest activity being found for the flowers and the spheres made from flowers. In addition, although the spheres made from the multipods are actually smaller by almost one-half as compared to the flower spheres, their ROS activity is lower. It is hypothesized that NP SA plays a role in the observed differences in ROS generating capacity (i.e., Pt flowers and spheres made from flowers have greater SA as compared to multipods and spheres made from multipods); the researchers are currently obtaining SA measurements for the Pt shapes. The Pt shapes have, by mass, lower ROS-generating capacity than the Au NPs. Au nanorods (50 x 15 nm) have the lowest activity; gas phase-generated (10, 18 nm) and colloidal (5 nm) Au NPs have similar activity by mass. Interestingly, coating the colloidal Au NPs with bovine serum albumin (BSA) dramatically reduced ROS activity (by ~8x). In comparison to other metal NPs such as Cu and Ir, the ROS-generating capacity of nano-Au and -Pt shapes is lower, but similar in magnitude to that for TiO_2, Ag, and Al oxide NPs (Figure 1). The ROS-generating capacity of the Cu NPs, which are insoluble, suggests that they may be effective positive controls for the *in vitro* studies and that are planned to test cellular responses to these particles in the near future.

One potential target for NP effects is the epithelium lining of the gas exchange region of the lung (alveoli). It has been shown through work with ultrafine particles (< 100 nm) that they are not efficiently cleared by macrophages, thereby promoting their interaction with the epithelium. In the studies of NP toxicity, A549 type

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II alveolar epithelial cells were used that are stably transfected with a luciferase reporter located in the promoter region for the interleukin (IL)-8 gene. Luciferase reporter activity is, thus, used as an indicator of oxidative stress in these cells. Some of the Pt shapes using this cell culture system have been tested; dose-related responses to Pt flowers and multipods were assessed. There was a small dose-dependent (0-500 μg/well; 0-24 μg/cm^2) increase in reporter activity with the flowers and not the multipods that was not related to increased LDH release (Figure 2).

In addition to contact with the epithelium, the researchers further suggest that NPs can move from the epithelial surface in the alveoli to gain access to the blood, thus interacting with endothelial cells. Studies have been initiated using cultured human umbilical vein endothelial cells (HUVECs) to investigate the effects of NP exposure on endothelial target cells. A dose-related increase in IL-6 release has been observed in response to colloidal Au (12-188 μg/well; 0.6-8.9 μg/cm^2) from passage 4 through 10 without accompanying changes in LDH (Figure 3); this increase was manifested in more than a doubling of IL-6 release from low to high-dose nano-Au (20 nm). Interestingly, these changes occurred in the presence of BSA coating and despite the fact that the coated Au NPs appeared to agglomerate within the first hour of culture at 37 °C. The responses to the Au colloids were slightly higher than those to ultrafine TiO_2, which was used at a higher dose range (and caused increases in LDH release). Exposed HUVEC were embedded in gelatin and then sectioned for EM analyses. Subsequently, Au NP singlets and agglomerates were found in these cells (Figure 4), particularly in lysosomes. The individual NPs are approximately 20 nm in diameter. The researchers plan to test the Pt shapes using this cell culture system.

The research efforts will focus over the next several months on *in vitro* analyses of NP effects and move to *in vivo* evaluations by the middle of the calendar year. The specific activities that are planned for the immediate future include the following: (1) continue work to define the conditions under which agglomeration occurs; and (2) continue studies on cellular uptake of various NPs using chemical detection and microscopic methods to determine if uptake is required to produce oxidative stress. The results of the studies will provide dose-, size-, and composition-related toxicological information about nanoparticles. The insight gained regarding mechanisms of response to nanoparticles and their disposition after exposure can be used to predict outcomes of human exposures in environmental, occupational, and therapeutic settings.

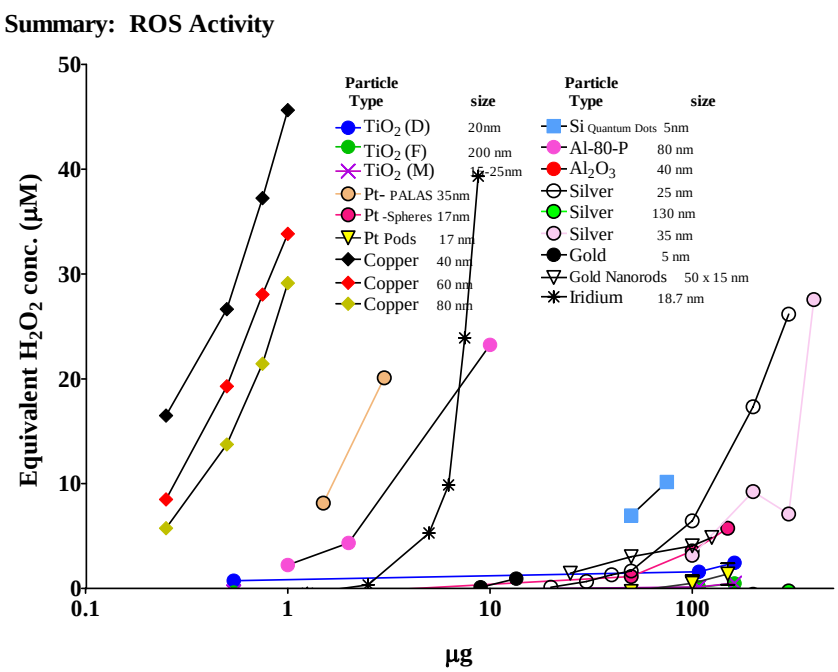

Figure 1. ROS-generating capacity of several metal nanoparticles, including colloidal gold and the platinum shapes.

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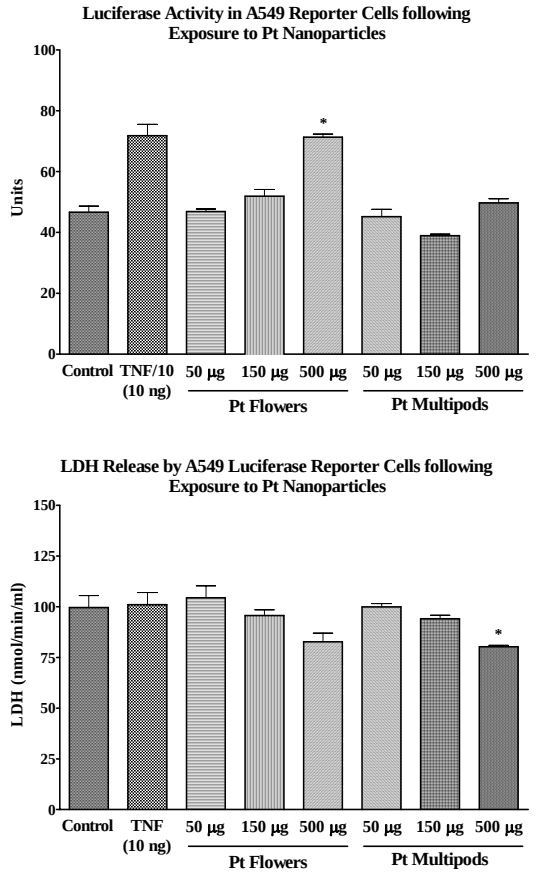

Figure 2. Activation of the IL-8 gene (luciferase reporter activity) in stably transfected A549 lung epithelial cells (top) and LDH release (bottom).

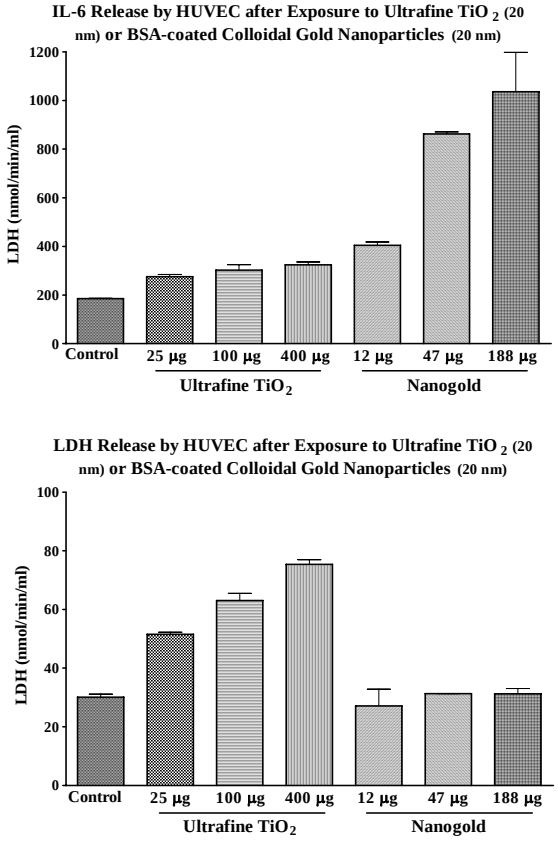

Figure 3. IL-6 (top) and LDH (bottom) release by HUVECs, example from Passage 4 cells.

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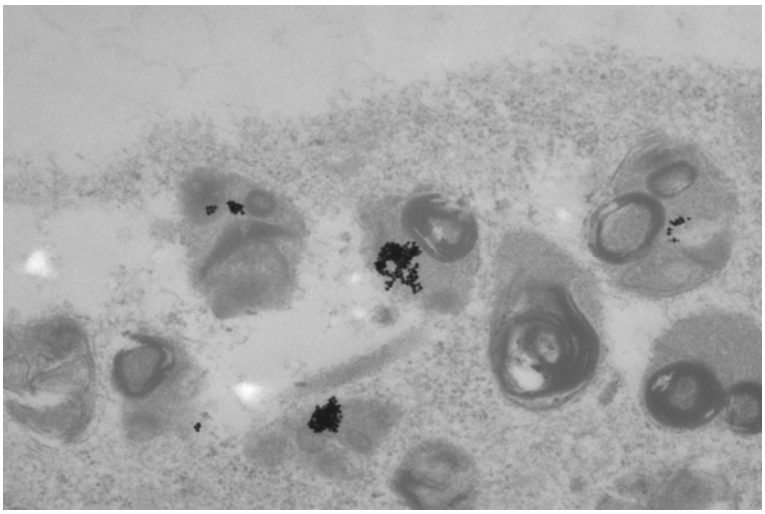

Figure 4. EM image of a section from a gelatin-embedded HUVEC exposed to 20 nm colloidal Au. Individual particles are 19-20 nm in diameter.

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Effects of Nanomaterials on Human Blood Coagulation

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Abstract

Common and serious human diseases such as myocardial infarction and stroke are caused by abnormalities of blood coagulation that predispose to thrombosis (clots). These diseases are clearly influenced by environmental factors. Because of their large surface area and reactivity, nanomaterials that enter the workplace or home have the potential to adversely affect blood coagulation, which could result in abnormal clotting and/or bleeding.

Thus, a comprehensive approach will be used to study how a wide-range of commercially prepared nanomaterials affect human blood coagulation. Techniques will focus on the two major components of the clotting system, namely, blood coagulation proteins and platelets. First, the effects of nanomaterials on blood clotting proteins will be studied using coagulation-specific laboratory assays. This project will focus on the ability of nanomaterials to promote and/or retard the catalytic activity of coagulation enzymes. This is because adsorption of enzymes on the extensive available surface of nanomaterials may alter the functional groups of the enzymes and hence, their enzymatic activity. Next, classes of nanomaterials will be identified that "activate" human platelets because platelet activation plays a role in many thrombotic diseases. Finally, the complex interactions between blood coagulation elements and nanomaterials will be characterized at the molecular level.

Research findings will be used to: (1) identify nanomaterials that can harm human coagulation; (2) determine nanomaterial thresholds of toxicity and dose-response effects on clotting proteins; and (3) classify engineered nanomaterials based on their physiologic effects on blood coagulation.

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Assessment Methods for Nanoparticles in the Workplace

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Abstract

The primary objectives of this study are to: (1) provide the scientific community and practicing industrial hygienists with verified instruments and methods for accurately accessing airborne levels of nanoparticles; and (2) assess the efficacy of respirator use for controlling nanoparticle exposures. These objectives will be reached through a combination of laboratory and field-based studies centered on the following specific aims: (1) identify and evaluate methods to measure airborne nanoparticle concentrations; (2) characterize nanoparticles using a complementary suite of techniques to assess their surface and bulk physical and chemical properties; and (3) determine the collection efficiency of commonly used respirator filters when challenged with nanoparticles.

The research approach will involve both laboratory and field work. Manufactured nanomaterials covering a range of the types available will be obtained from several sources. Measurements obtained from a variety of sampling instruments, including a novel passive aerosol monitor, will be systematically compared relative to measurements made by transmission electron microscopy (TEM) under controlled laboratory conditions. Field tests will involve the use of the instruments analyzed in the laboratory to quantify and characterize nanoparticle concentrations in workplaces that manufacture and/or use nanoparticles. This study also will provide the opportunity to refine an aerosol mapping technique that the researchers have developed to visualize the temporal and spatial variability of aerosol concentrations in a workplace. Laboratory testing will be conducted to determine the collection efficiency of respirator filters when challenged with a variety of nanoparticle types. The surface properties and chemical composition of a number of nanoparticle types will be analyzed to determine whether these qualities can aid in establishing the cause of differences in instrument performance and filtration efficiency when challenged with different nanoparticles, as well as to aid in the recognition of unknown nanoparticles encountered in a workplace or in the ambient environment.

This work is an essential first step needed to accurately identify the hazards associated with a new workplace health threat. The expected results from these studies will include a greater understanding of the strengths and limitations of instruments capable of evaluating nanoparticle exposure levels. The assessment of physical and chemical features of nanoparticles will aid in identifying nanoparticle qualities that affect instrument performance and filtration efficiency. Moreover, this work will result in guidance on the use of respirators to protect against nanoparticle inhalation in the workplace.

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Appendix

Nanotechnology and the Environment: Applications and Implications Progress Review Workshop III

October 26 - 28, 2005

Holiday Inn Rosslyn at Key Bridge
1900 N. Fort Myer Drive
Arlington, VA 22209

AGENDA

DAY I: Wednesday, October 26, 2005

Plenary Session – Rosslyn Ballroom

10:00 a.m. Registration

10:30 a.m. Welcome
William Farland, Acting Deputy Assistant Administrator for Science, Office of Research and Development (ORD), USEPA

10:50 a.m. Overview of Canadian Nanotechnology
Paul Dufour, Senior Advisor International Affairs, Office of the National Science Advisor, Privy Council Office, Government of Canada

11:10 a.m. Overview on the National Nanotechnology Initiative
Mihail Roco, Co-Chair, National Science and Technology Council

12:00 p.m. Overview on Canadian Institute of Health Research
Eric Marcotte, Canadian Institute of Health Research

12:20 p.m. Lunch

1:45 p.m. Overview on EPA and Nanotechnology
Barbara Karn, USEPA, Detailed to Project on Emerging Nanotechnologies, Woodrow Wilson International Center for Scholars at The Smithsonian Institution

2:15 p.m. Overview on Applications of Nanotechnology
David Rejeski, Director, Foresight and Governance Project, Woodrow Wilson Center

2:45 p.m. Break

3:10 p.m. Grant Presentations

Track A – Rossyln Ballroom

Nanostructured Microemulsions as Alternative Solvents to VOCs in Cleaning Technologies and Vegetable Oil Extraction
Anuradee Witthayapanyanon and Linh Do, University of Oklahoma

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Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic for Automotive Applications
Manjusri Misra, Michigan State University
James Kilduff, Rensselaer Polytechnic Institute

Ecocomposites Reinforced with Cellulose Nanoparticles: An Alternative To Existing Petroleum-Based Polymer Composites
William Winter, Syracuse University

Evaluating the Impacts of Nanotechnology via Thermodynamic and Life Cycle Analysis
Bhavik Bakshi, Ohio State University

Cross-Media Transport, Transformation, and Fate of Carbonaceous Nanomaterials
Linsey Marr, Virginia Polytechnic Institute and State University

Fate and Transport of C_{60} Nanoparticles in Unsaturated and Saturated Soils
Kurt Pennell, Georgia Institute of Technology

Grant Presentations Track B – Georgetown Room

Applications of Nanoscale Tunable Biopolymers for Heavy Metal Remediation
Ashok Mulchandani, University of California, Riverside

A Bioengineering Approach to Nanoparticle-Based Environmental Remediation
Daniel Strongin, Temple University

Interactions Between Semiconductor Nanoparticles and Biomembranes and DNA
Jay Nadeau, McGill University

Uptake and Toxicity of Metallic Nanoparticles in Freshwater Fish
Nancy Denslow, University of Florida

Assessment of the Environmental Impacts of Nanotechnology on Organisms and Ecosystems
Jean-Claude Bonzongo, University of Florida, Gainesville

Advanced Nanosensors for Continuous Monitoring of Heavy Metals
Omowunmi Sadik, State University of New York, Binghamton

5:00 p.m. Adjourn

6:30 p.m. Dinner

DAY 2: Thursday, October 27, 2005

Plenary Session – Rosslyn Ballroom

8:20 a.m. Perspective
Andrew Maynard, Science Advisor, Project on Emerging Nanotechnologies, Woodrow Wilson International Center for Scholars at The Smithsonian Institution

8:45 a.m. European Commission
Pilar Aguar, European Commission

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9:00 p.m. Grant Presentations

Track A – Rossyln Ballroom

Compound Specific Imprinted Nanosphers for Optical Sensing
Barry Lavine, Oklahoma State University

Low-Cost Organic Gas Sensors on Plastic for Distributed Environmental Sensing
Vivek Subramanian, University of California, Berkeley

Nanosensors for Detection of Aquatic Toxins
Robert Gawley, University of Arkansas

Ultrasensitive Pathogen Quantification in Drinking Water Using High Piezoelectric PMN-PT Microcantilevers
Wan Shih, Drexel University

Grant Presentations Track B – Georgetown Room

Nanostructured Catalytic Materials for NO_x Reduction Using Combinatorial Methodologies
Selim Senkan, University of California, Los Angeles

Nanoscale Bimetallic Particle for *In Situ* Remediation
Wei-xan Zhang, Lehigh University

Functional Fe(0)-Based Nanoparticles for *In Situ* Degradation of DNAPL Chlorinated Organic Solvents
Gregory Lowry, Carnegie Mellon University

Elemental Composition of Freshly Nucleated Particles
Murray Johnston, University of Delaware

10:20 a.m. Break

10:40 a.m. Grant Presentations (Continued)

Track A – Rossyln Ballroom

Nanomaterial-Based Microchip Assays for Continuous Environmental Monitoring
Joseph Wang, Arizona State University

Metal Biosensors: Development and Environmental Testing
Anne Anderson, Utah State University

Conducting-Polymer Nanowire Immunosensors Array for Microbial Pathogens
Ashok Mulchandani, University of California, Riverside

The Bioavailability, Toxicity, and Trophic Transfer of Manufactured ZnO Nanoparticles: A View From the Bottom
Paul Bertsch, University of Georgia

Hysteretic Accumulation and Release of Nanomaterials in the Vadose Zone
Tohren Kibbey, University of Oklahoma

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Fate and Transformation of C_{60} Nanoparticles in Water Treatment Processes
Jaehong Kim, Georgia Institute of Technology

Grant Presentations Track B – Georgetown Room

Iron Oxide Nanoparticle-Induced Oxidative Stress and Inflammation
Hong Yang, University of Rochester

Health Effects of Inhaled Nanomaterials
Ting Guo, University of California, Davis

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

A Novel Approach to Prevent Biocide Leaching
Patricia Heiden, Michigan Technological University

Nanostructured Membranes for Filtration, Disinfection, and Remediation of Aqueous and Gaseous Systems
Svetlana Zivanoic, University of Tennessee

Nanostructured Catalysts for Environmental Remediation of Chlorinated Compounds
Yunfeng Lu, Tulane University

Synthesis and Application of a New Class of Stabilized Nanoscale Iron Particles for Rapid Destruction of Chlorinated Hydrocarbons in Soil and Groundwater
Dongye Zhao, Auburn University

12:08 p.m. Lunch

1:40 p.m. Grant Presentations (Continued)

Track A – Rossyln Ballroom

Dendritic Nanoscale Chelating Agents: Synthesis, Characterization. Modeling and Environmental Applications
Mamadou Diallo, California Institute of Technology

Nanomaterial Interactions With Skin
Nancy Monteiro-Riviere, North Carolina State University

Physical and Chemical Determinants of Nanofiber/Nanotube Toxicity
Robert Hurt and Agnes Kane, Brown University

Natural Sciences and Engineering Research Council of Canada (NSERC) Nano Innovation Platform
Peter Grutter, National SERC Nano Innovation Platform

Track B – Georgetown Room

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

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A Focus on Nanoparticulate Aerosol and Atmospherically Processed Nanoparticulate Aerosol
Vicki Grassian, University of Iowa

Assessing the Effect of Nanoparticle Size
Warren Chan, University of Toronto

3:00 p.m. Break

3:19 p.m. Grant Presentations (Continued)

Track A – Rossyln Ballroom

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

Acute and Developmental Toxicity of Metal Oxide Nanoparticles in Fish and Frogs
Chris Theodorakis, Southern Illinois University

Role of Particle Agglomeration in Nanoparticle Toxicity
Lung-Chi Chen, New York University

Health Canada Overview: Foresight Activities
David Blakey, Health Canada

Responses of Lung Cells to Metals in Manufactured Nanoparticles
John Veranth, University of Utah

Understanding the Light-Induced Cytotoxicity of Quantum Dots: A Cellular, Photophysical, and Mechanistic Approach
Francoise Winnik, Universite de Montreal

Track B – Georgetown Room

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

Structure-Function Relationships in Engineered Nanomaterial Toxicity
Vicki Colvin, William Marsh Rice University

Chemical Fate, Biopersistence, and Toxicology of Inhaled Metal Oxide Nanoscale Materials
Jacob McDonald, Lovelace Biomedical & Environmental Research Institute

Assessment Methods for Nanoparticles in the Workplace
Patrick O'Shaughnessy, University of Iowa

Mechanistic Dosimetry Models of Nanomaterial Deposition in the Respiratory Tract
Bahman Asgharian, CIIT Centers for Health Research

Monitoring and Characterizing Airborne Carbon Nanotube Particles
Judy Xiong, New York University School of Medicine

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Gene Expression Profiling of Single-Walled Carbon Nanotubes: A Unique Safety Assessment Approach
Mary Jane Cunningham, Houston Advanced Research Center

5:00 p.m. Adjourn

DAY 3: Friday, October 28, 2005

Plenary Session – Shenandoah A and B

8:30 a.m. Remarks

8:40 a.m. International Aspects of Nanotechnology
Celia Merzbacher, Office of Science and Technology Policy, Executive Office of the President

9:10 a.m. NIOSH/CDC Perspective
Vladmir Murashov, Nanotechnology Research Program, National Institute for Occupational Safety and Health/CDC

9:25 a.m. NSF Perspective
Cynthia Ekstein, Program Director, Environmental Engineering, Bioengineering & Environment Systems Division, National Science Foundation

9:40 a.m. Grant Presentations (Continued)

Track A – Shenandoah A and B

Neuromorphic Approach to Molecular Sensing With Chemoreceptive Neuron MOS (CυMOS) Transistors
Edwin Kan, Cornell University

A Nanocontact Sensor for Heavy Metal Ion Detection
Nongjian Tao, Arizona State University

Carbon Nanotube Self-Assembly in a VOCs Monitoring Platform
Somnath Mitra, New Jersey Institute of Technology

Development of Nanocrystalline Zeolite Materials as Environmental Catalysts
Sarah Larsen, University of Iowa

Track B – Georgetown Room

The Fate, Transport, Transformation and Toxicity of Manufactured Nanomaterials in Drinking Water
Paul Westerhoff, Arizona State University

Microbial Impacts of Engineered Nanoparticles
Pedro Alvarez, William Marsh Rice University

Absorption and Release of Contaminants onto Engineered Nanoparticles
Mason Tomson, Rice University

10:50 a.m. Break

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11:10 a.m. Closing Remarks

11:45 a.m. Adjourn

1:30 – 4:00 p.m. Nanoscience Building Tour at the Naval Research Laboratory in Washington, DC

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U.S. Environmental Protection Agency
Nanotechnology and the Environment: Applications and Implications Progress Review Workshop III

Holiday Inn Rosslyn at Key Bridge
1900 N Fort Myer Drive
Arlington, VA 22209

October 26 - 28, 2005

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