Proceedings

EPA Nanotechnology and the Environment: Applications and Implications STAR Progress Review Workshop

August 28-29, 2002
Arlington, Virginia

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Introduction

Nanoscale science, engineering, and technology, collectively referred to as nanotechnology, is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. Nanotechnology is a crosscutting area involving disciplines such as chemistry, physics, biology, and engineering, with truly revolutionary transformation potential for an entire host of products and processes, including those that enhance environmental quality and sustainability through pollution prevention, treatment, and remediation.

The U.S. Environmental Protection Agency's (EPA) 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 in 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 of our capabilities to assess and solve environmental problems. EPA is also interested in predicting and understanding both the positive and negative environmental effects of this new technological revolution and the changes it will bring to our society.

EPA's objective in the nanotechnology research area is to support innovative research that could help us define and understand significant emerging environmental problems. We seek novel approaches that can lead to significant breakthroughs providing enhanced environmental benefits.

The results from the EPA-sponsored nanotechnology research outlined within this document have the potential to be used to monitor and remediate environmental problems, curb emissions from a wide range of sources, and develop new "green" processing technologies that minimize the generation of undesirable by-product effluents. In addition, the results offer fundamentally new ways to manufacture new chemicals and pharmaceutical products; measure, control, and remediate contaminants in various media; and contribute to dematerialization resulting in less environmental impact from the extraction, transport, manufacture, use, and disposal of materials.

This Progress Review Workshop brings together EPA's extramural scientists as well as scientists and policymakers from government, academic, and non-government organizations to address both the environmental applications and implications of the emerging area of nanotechnology. The research described in this report has not been subjected to the Agency's required peer review and policy review, 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 either Barbara Karn, Ph.D.,at 202-564-6824 (karn.barbara@epa.gov); or Nora Savage, Ph.D., at 202-564-8228 (savage.nora@epa.gov).

U.S. EPA National Center for Environmental Research

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Executive Summary

Overview

The EPA Nanotechnology Grantees Workshop brought together researchers from academia, industry, and government to discuss ongoing research on nanotechnology and the environment. The 58 Workshop participants listened to presentations by EPA grantees; the Director of the Center for Biological and Environmental Nanotechnology at Rice University; the Chair of the Whitehouse Subcommittee on Nanoscale Science, Engineering and Technology; the Director of the Woodrow Wilson Foresight and Governance Project; and EPA scientists. Participants had an opportunity to interact with presenters during a poster session. In addition, the group enjoyed a dinner presentation by Dr. Debra Rolison of the Naval Research Laboratory. This report briefly summarizes the presentations.

WELCOME AND INTRODUCTION

Barbara Karn, U.S. EPA

Dr. Karn welcomed participants to the workshop. She described EPA's research mission and the role of the National Center for Environmental Research (NCER) in supporting extramural research, including the Science to Achieve Results (STAR) program. The STAR program has issued two Requests for Applications targeted toward nanotechnology—the first in FY 2001 that supported 16 grantees and the second in FY 2002 that received more than 130 applications. More information on STAR grants is available on the NCER Web Site at http://www.epa.gov/ncer.

Dr. Karn outlined the goals of the workshop. First, the meeting was designed to develop a community of scientists and engineers who maintain an understanding and appreciation for potential environmental implications and applications while doing their research in nanotechnology. Second, the meeting was intended to serve as a stimulus for increased research and knowledge of environmental aspects of nanotechnology.

PLENARY SESSIONS

Each day began with a plenary session in which experts discussed broader issues in nanotechnology research and development.

Plenary Session Day I

Environmental Implications of Nanotechnology: Progress in Developing Fundamental Science as a Basis for Assessment
Vicki Colvin, Director, Center for Biological and Environmental Nanotechnology, Rice University
Mark Wiesner, Center for Biological and Environmental Nanotechnology, Rice University

Dr. Wiesner opened with a cautionary note based on the current lack of information about the environmental and health effects of nanotechnology. The Center for Biological and Environmental Nanotechnology (the Center) risk assessment research on nanotechnology focuses on exposure because little is known about nanotechnology's health effects, impacts from nanoreagents, and impacts associated with colloidal materials. The Center also is conducting research on fate and transport, including transport in porous media, adsorption and desorption of known environmental contaminants on nanoparticles, and biodegradation of fullerenes.

Dr. Colvin discussed the potential consequences of nanomaterials on public health. She noted that concern over the effects of inorganic particles on health has existed since the industrial revolution, with a recent focus on asbestos. The two current areas of concern are the effects of ultrafine particles on lungs and wear debris from surgical implants. Research on nanoparticles includes exploring potential exposure routes: inhalation was the primary exposure route for classic particles, but nanoparticles do not aerosolize as readily so this route might be less likely. Ingestion is a possible route as is dermal exposure; however, there is little information on dermal contact as a possible route. Research is underway to explore the effects of material derived from wear damage of implants, because there is concern that it could lead to autoimmune disease. Another concern is bioaccumulation of nanoparticles.

One of the potential positive implications of nanoparticles for the medical field is the ability of these particles to pass through cell walls. Dr. Colvin closed by noting that researchers need to collaborate on a realistic public message about nanotechnology, because some of the groups that oppose genetic engineering are beginning to oppose nanotechnology research. The message should emphasize that the nanotechnology research community is responsible and proactive in exploring effects and potential risks, that nanoparticles are not altogether different from other particles, and that many of the benefits have already been established.

Environmental Technologies at the Nanoscale

Tina Masciangioli, AAAS Fellow at the U.S. EPA
Wei-Xian Zhang, Lehigh University

Dr. Masciangioli described the large environmental challenges in the 21st Century and the promising role of nanotechnology in improved detecting and sensing techniques; removal of the finest contaminants from air, water, and soil; and the discovery of new "green" industrial processes that reduce waste products. She stated that nanotechnology could contribute to pollution prevention by making manufacturing processes environmentally benign, by creating benign materials or manufactured products to replace toxic substances, or by reducing the use of raw materials. This could enable production of smaller and lighter products with fewer by-products. Nanoscale technologies can be used to detect biological pathogens, organics, heavy metals, and other contaminants in the environment. In some cases, they can both sense and treat waste. Dr. Masciangioli pointed out that this multifunctionality is one of the promising features of nanotechnology (or nanotechnology products).

Dr. Zhang discussed a few of the many questions about nanotechnology. An example includes what will be the impact of the dark color (absorptivity) of nanoparticles on water quality, photosynthesis, air quality, and global warming? Most current EPA research addresses larger particles—will there be a need for new technological research on smaller particles? What will be the applications of fast reaction rates and high contaminant sorption? Dr. Zhang listed three gaps that are important for nanotechnology research: (1) gaps in knowledge, because nanoscale science and engineering is highly interdisciplinary; (2) gaps in tools, because conventional environmental laboratories are not equipped for nanoscale work; and (3) gaps in education, because new courses, laboratories, and programs will be needed to educate the next generation. He concluded by stating that new approaches are needed that offer capabilities to prevent, treat, or remediate highly toxic or persistent pollutants and result in more effective monitoring of pollutants or their impacts in ways not currently possible. Nanoscience, engineering, and technology hold great potential for the continued improvement of technologies for environmental protection.

Plenary Session Day II

EPA Futures Program

Pasky Pascual, U.S. EPA

EPA has established a "Futures Program" to help the Agency anticipate future environmental issues rather than simply react to them. The program has three major components: (1) scanning for weak signals, consisting of literature searches for "leads," and review of these items for novelty, scope, severity, visibility, timing, and probability; (2) scoping strong signals, which involves tapping expert knowledge and discussing issues with senior Agency managers so that crises can be avoided in the future; and (3) developing better forecasting tools, such as the ecological indicators developed in collaboration with the State of Pennsylvania. Nanotechnology is included in the EPA Futures Program.

Background and Challenges of Nanotechnology for the United States
Mike Roco, National Science Foundation

Dr. Roco opened by stressing the broad societal goals of nanotechnology, and the expanding areas of relevance to energy conversion, nanobiosystems, molecular system architecture, realistic multiphenomena modeling, agriculture and food systems, and environmental issues. Dr. Roco described the National Nanotechnology Initiative (NNI), which encourages innovative, interdisciplinary research. Several areas of nanotechnology are moving from fundamental discovery into technological innovation: advanced materials, electronics, chemicals including catalysts, and pharmaceuticals. Concerning the environmental implications, it is important to present to the public a balanced view between advantages of a sustainable development using nanotechnology and the unexpected consequences. The positive outcomes of nanotechnology far outweigh the possible negatives. Nanotechnology has major implications for the environment—it is a means for attaining sustainable development; it reduces waste through "exact manufacturing"; it addresses current health and environmental issues as well as unintended consequences; it can be used to remove existing pollutants; and it can provide more detailed monitoring capabilities over larger areas. The NNI is comprised of 16 governmental agencies and departments and was responsible for $604 million in Federal research programs in FY 2002. He noted that Japan is the largest investor in nanotechnology in the world, and Asia is the fastest growing region. The NNI's priorities for FY 2003 are: (1) tools for manufacturing; (2) detection/protection for biological, chemical, radiological, and explosive hazards; and (3) instrumentation and metrology. More information and reports from the NNI are available on the Internet at http://www.nano.gov.

Getting Ahead of the Learning Curve
David Rejelski, Woodrow Wilson Center

The Woodrow Wilson Center has a cooperative agreement with EPA to identify "game changers"—things that could change the way EPA might operate. A major challenge is how institutions and organizations learn and how they will react to nanotechnology. In a conventional learning curve, as experience increases, performance is expected to increase. There are several types of environmental learning curves: (1) "learning too late"—this is how organizations learned before EPA was established, making environmental errors/problems and then cleaning up the mess; (2) "learning through mandate"—since 1970, organizations responded to mandates; (3) "learning by doing"—beginning in 1990, many companies internalized a goal of having less environmental impact, often to avoid mandates; and (4) "learning before doing"—starting in 1995, companies have been able to make virtual prototypes and to identify environmental issues before production begins. Learning about the environmental implications of nanotechnology could go from one extreme of an absence of learning with all of the unintended consequences to the other extreme of fast, anticipatory learning in which the environmental aspects are co-optimized as part of nanotechnology development. He quoted a Kodak manager, "bad news is good as long as it's early." With new technologies coming to market so quickly, EPA should begin working with research scientists in industry, not just the environmental health and safety people who are now the major contacts. There also will be a need for new types of communications and new tools.

DINNER SPEAKER

Societal Implications of Nanobiotechnology
Debra Rolison, Naval Research Laboratory

Dr. Rolison explored the broader scientific and societal context of integrating biomolecular function with nanoscale objects—nanobiotechnology. She explained that nanobiotechnology is a vision on a nearby horizon—the initial prospects of which are being imagined, designed, and created right now. Dr. Rolison emphasized that even at this early juncture, we should contemplate what societal impacts might arise from a technology based on objects, devices, and processes that blend biomolecular function with nanoscopic fabrication and manipulation. She urged scientists, governmental program managers, policymakers, educators, industrialists—and citizens—to be involved in this undertaking, because technology is rarely implemented without changing society in foreseen and disturbingly unforeseen ways.

PRESENTATIONS BY EPA STAR GRANTEES

STAR Grantees presented projects in four areas: sensors, treatment, remediation, and other areas of application. Some grantees were just beginning their projects; others had preliminary results.

Session 1: Sensors
Moderators: Nora Savage (Day 1) and Y'Vonne Jones-Brown (Day 2)

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

The goal of this project is to develop highly piezoelectric microcantilever arrays for *in situ*, rapid, simultaneous multiple pathogen quantification to replace current filtration culture and fluorescence-based methods. This new method would enhance the capability to respond to terrorist threats and ensure the safety of water supplies. The project has discovered that piezoelectric cantilevers less than 0.7 mm long are 20 times more sensitive than the Quartz Crystal Microbalance (QCM). Rapid, real-time, *in situ* detection of *Escherichia coli* via attachment and release using piezoelectric cantilevers was demonstrated. Microfabrication of piezoelectric PZT/Mo microcantilevers and development of Sr-doped lead titanate films that can be heat treated at 450 °C for better piezoelectric microcantilever fabrication also was discussed.

Chemosensors for Marine Toxins
Robert E. Gawley, University of Miami/University of Arkansas

The goal of this project is to design and prepare nanoscale biomimetic receptor/sensors for the detection of marine toxins (domoic acid, brevetoxin, ciguatoxin, cylindrospermopsin, and tetrodotoxin) based on research and proof of principle conducted on saxitoxin. The project plan is to use combinatorial chemistry and incorporate a host compound into a dendrimer. At present, mouse bioassay is the most common detection method for aquatic toxins. The nanoscale sensors would be inexpensive and more rapid than current technology. Coumarin was found to be both selective and sensitive as a fluorophore for saxitoxin. The project is proceeding to use these results to test additional toxins with similar properties, including a good model of a protein binding site.

Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for Carcinogenic Chromium(VI) and Arsenic (V)
William Trogler, University of California, San Diego

The goal of this project is to develop new selective solid-state sensors for carcinogenic and toxic chromium(VI) and arsenic(V) in water, based on redox quenching of the luminescence from nanostructured porous silicon and polysiloles. Dr. Trogler applied principles derived from the investigation of sensors for explosives (TNT). Results were presented concerning the use of polysilole nanoaggregates and aminosilole nanoaggregates as well as incorporation of the nanoaggregates in a nanotextured microcavity between two porous silicon Bragg stacks.

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

The goal of this project is to develop a high-performance, low-cost sensor for initial onsite screening of surface and groundwater to detect heavy metal ion pollution. The sensor consists of an array of nanoelectrode pairs on a silicon chip, separated by an atomic-scale gap. Electrochemical deposition of even a few metal ions can bridge the gap and form a nanocontact, triggering a quantum jump in electrical conductance. The project has successfully fabricated the nanoelectrodes, and a method for mass production is in progress. Additional research is underway to develop a higher precision measurement method for the conductance.

Real-Time Chemical Composition Measurements of Fine and Ultrafine Airborne Particles

Murray V. Johnston, University of Delaware

As concern over health effects of ultrafine particles increases, new methods are needed to determine the composition of these particles in air. The goal of this project is to develop a new technology that will determine chemical composition of airborne particles down to about 5 nm in diameter. Two problems that must be overcome are inefficient sampling of particles and inefficient analysis of those particles that have been sampled. The project has discovered that individual nanoparticles can be efficiently detected only if quantitatively converted to atomic ions.

Session 2: Treatment

Moderator: Y'Vonne Jones-Brown

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

Wilfred Chen, University of California, Riverside

The goal of this project is to develop high-affinity, nanoscale biopolymers with tunable properties for the selective removal of heavy metals such as cadmium, mercury, and arsenic. Conventional technologies often are inadequate to reduce concentrations in wastewater to acceptable regulatory levels. The project found that biopolymers with amino acid His_6 or His_{12} tags can serve as a simple metal binding domain; both T_t and metal binding capacity can be regulated easily, and biopolymers can be recycled. Metalloregulatory protein for mercury (MerR) can serve as a specific mercury-binding domain.

Transition Metal Carbides as an Environmental Nanocatalyst

S. Ismat Shah, University of Delaware

Current catalytic converters will not be able to meet future emissions reduction targets without increasing the amount of Pt-group precious metals to levels at which the converters might become prohibitively expensive. The goal of this research project is to investigate synthesis, characterization, and application of nanoparticles of transition metal carbides and oxycarbides as replacements for the Pt-group metals. The project has found that tungsten carbide (WC_{1-x}) is a possible replacement for the Pt-group metals in automobile catalytic converters. WC_{1-x} nanoparticles were produced by reactive magnetron sputtering and were characterized for their chemistry and structure.

Simultaneous Environmental Monitoring and Purification Through Smart Particles

Wolfgang M. Sigmund, University of Florida

The goal of this project is to investigate whether nano-engineered smart particles based on a modular building concept enable simultaneous monitoring and purification of water and air. The smart particles undergo visible change in color when a pollutant is present and are being developed to utilize magnetic and photocatalytic nanoparticles for treatment.

Session 3: Other Areas of Application

Moderator: Nora Savage

Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

George Chumanov, Clemson University

The goal of this project is to develop a novel hybrid photocatalyst that consists of silver or gold nanoparticles encapsulated in a titanium dioxide (TiO_2) shell. TiO_2 is environmentally friendly, relatively inexpensive, and a potentially efficient photocatalyst; however, wide technological use of this photocatalyst is largely hindered by the fact that ultraviolet light, which does not constitute a significant fraction of the solar spectrum, is required for its activation. Silver and gold are very efficient for capturing energy from the visible portion of the spectrum. In the initial research phase, a TiO_2 shell on silver nanoparticles has been synthesized.

Measuring and Modeling Nanoparticle Forces
Darrell Velegol, Pennsylvania State University

A significant limitation of nanotechnology is the ability to produce bulk quantities of dispersed particles. The goal of this project is to determine whether solvation or depletion forces can be manipulated to produce dispersed suspensions of "bare" nanoparticles (i.e., without adsorbed additives). Specifically, the research explores two questions: (1) What are the magnitudes of the van der Waals, solvation, and depletion forces for nanoparticle systems? and (2) What variables can we control to alter these forces? Comparing van der Waals and solvation forces, it has been found that solvation forces are comparable to van der Waals forces and might be used to stabilize particles.

Development of Nanocrystalline Zeolite Materials as Environmental Catalysts: From Environmentally Benign Synthesis to Emission Abatement
Sarah C. Larsen, University of Iowa

Zeolites are widely used in separations and catalysis, but the crystal size formed during conventional synthesis ranges from 1,000 to 10,000 nm. For some applications, it would be advantageous to use zeolite crystals in the range of 10 to 100 nm. The goals of this project are to: (1) synthesize and characterize nanometer-sized zeolites and nanostructures (films, fibers); and (2) determine the effectiveness of utilizing nanometer-sized zeolites as environmental catalysts for use in NO_x emission abatement, photocatalytic decomposition of organic contaminants, and environmentally benign selective oxidation reactions with cation-exchanged zeolites.

Ion-Induced Nucleation of Atmospheric Aerosols
Peter H. McMurry, University of Minnesota

The goals of this project are to: (1) determine whether or not ion-induced nucleation leads to the formation of significant numbers of particles in the atmosphere; and (2) explore the physics and chemistry of ion-induced nucleation in the atmosphere. This is important in the identification of the effects of nucleation on climate and human health. The project will involve atmospheric measurements to identify the composition of positive and negative ions during nucleation events and the determination of ion mobility distributions. Preliminary results show that daytime and night-time compositions are very different.

Session 4: Remediation
Moderator: Nora Savage

Dendritic Nanoscale Chelating Agents—Binding of Cu(II) Ions to PANAM Dendrimers in Aqueous Solutions
Mamadou S. Diallo, Howard University

The goals of this project are to: (1) explore the fundamental science of metal ion uptake by dendrimers in aqueous solutions; (2) assess the extent to which this fundamental knowledge can be used to develop high capacity and reusable chelating agents for industrial and environmental separations; and (3) develop FeS dendrimer nanocomposites with enhanced reactivity, selectivity, and longevity for reductive detoxification of organic and inorganic pollutants in aqueous solutions and subsurface formations. To date, the study has discovered that in aqueous solutions, dendrimers such as Poly(amidoamine) (PANAM) can serve as nanoscale containers or high capacity chelating agents for transition metal ions such as Cu(II); the extent of Cu(II) binding depends on metal ion dendrimer loading, dendrimer generation and surface chemistry, and solution pH and ionic strength; and the combination of the extended x-ray absorption fine structure (EXAFS) and Cu(II) uptake. Preliminary data suggest two primary mechanisms of binding.

Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature
Dibakar Bhattacharyya, University of Kentucky

The goal of this project is the development and fundamental understanding of reductive dechlorination of selected classes of hazardous organics by immobilized nanosized metal particles in ordered membrane domains. Preliminary results of chloride formation from trichloroethylene (TCE) dechlorination showed significantly better performance results from iron nanoparticles in Poly-L-glutamic acid (PLGA) functionalized membranes as compared to using free iron microparticles.

Bioengineered Nanoparticles for Environmental Remediation: The Photocatalytic Reduction of Cr(VI)

Daniel Strongin, Temple University

The goal of this project is to develop new nano-sized materials based on ferritin that may serve as catalysts in photochemical degradation processes of common contaminants. This project has found that ferritin catalyzes Cr(VI) reduction to Cr(III) using visible light. Electron transfer appears to occur both through contact with the inorganic core and through the protein shell. Ferritin shows excellent stability as a photocatalyst as compared to protein free particles, because photocorrosion is inhibited by the protein.

SMALL BUSINESS PERSPECTIVES—SBIR GRANTEES

Carbon Nanofiber-Based Solutions

Jayesh Doshi, eSpin Technologies, Inc.

eSpin Technologies manufactures nanofibers that are 100 times smaller than human hair and miles long. The company can produce 10,000 yards of fabric material every day from any material the client wants to use. The fibers can be manufactured into mats that can filter very small particles (less than 3 microns) in water, air, oil, car exhaust, and other media. They also can be made into insulation, cosmetic, and many other products. The company is testing the use of carbon nanofiber for beverage filtration. It has found that nanofibers are fragile, so they pose unique manufacturing and shipping problems, but they offer superior filtration and adsorbancy features.

Nanotube Composites for Clean Coatings

Ted Sun, Intematix

Plastic composites are replacing steel in manufacturing, and the composites need to be coated for protective or decorative purposes. Current technologies involve spraying and applying an electrostatic coating over sprayed primer. Carbon nanotube (CNT) filled conductive composites offer a primerless electrostatic coating process, which would save more than 250 million pounds of spray-painted fascia material and corresponding volatile organic compounds (VOCs) in the automobile industry alone. This project addresses two issues in CNT composite application: cost and bonding.

Nanoparticle Anchored Plasticizers

Andrew Myers, TDA Research, Inc.

Plasticized plastics can lose plasticizers to air, water, solvents, and saliva. If the plasticizer could be immobilized in the polymer, it would benefit the environment and human health. The goal of this project is to develop a method for binding plasticizing compounds to nanoparticles. The results have shown that the nanoparticle-bound plasticizers soften polyvinyl chloride (PVC), do not escape, retain pliability over longer periods of time, lower or eliminate migration of phthalates, are easy to process, and are inexpensive.

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EPA Nanotechnology Grantees Workshop
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Hilton at Crystal City (IEEE Meeting Venue)
Arlington, VA
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AGENDA

<u>**Wednesday, August 28, 2002**</u>

1:00 – 1:30 Registration

1:30 – 2:00 Welcome and Introduction
Barbara Karn, National Center for Environmental Research, EPA
Purpose of the Workshop

2:00 – 2:45 Plenary Session

Nanotechnology: Environmental Friend or Foe
Vicki Colvin, Mark Wiesner, Rice University

2:45 – 3:00 Break

3:00 – 3:30 Environmental Technologies at the Nanoscale
Wei-Xian Zhang, Lehigh University
Tina Masciangioli, AAAS Fellow at EPA

3:30 – 4:30 Presentations by EPA/STAR Grantees
Moderator: Nora Savage

Sensors:

3:30 – 3:50 Wan Shih, Drexel University
Ultrasensitive Pathogen Quantification in Drinking Water Using Highly Piezoelectric PMN-PT Microcantilevers

3:50 – 4:10 Robert Gawley, University of Miami
Nanosensors for Detection of Aquatic Toxins

4:10 – 4:30 William Trogler, University of California, San Diego
Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for Carcinogenic Chromium(VI) and Arsenic(V)

4:30 – 4:45 **Small Business Perspective I**

eSpin Technologies, Inc. Jayesh Doshi

4:45 – 6:15 **Poster Sessions - Focus on Research Plans**

4:45 – 5:30 Posters manned by Chen, Shah, Sigmund, Diallo, McMurry, Bhattacharyya, Strongin, Zhang

5:30 – 6:15 Posters manned by Shih, Gawley, Trogler, Tao, Johnston, Chumanov, Larsen, Velegol

6:30 **Dinner**

Thursday, August 29, 2002

8:30 – 8:40 **Opening Remarks**
Pasky Pascual, Futures Program, EPA

8:40 – 9:30 **Plenary Session: Background and Challenges of Nanotech for the U.S**.
Mike Roco, NSF

EPA/Nano Collaboration
Dave Rejeski, Wilson Center

9:30 – 10:10 **Presentations by EPA/STAR Grantees**
Moderator: Y'Vonne Jones-Brown

Sensors (continued):

9:30 – 9:50 Nongjian Tao, Arizona State University
A Nanocontact Sensor for Heavy Metal Ion Detection

9:50 – 10:10 Murray Johnston, University of Delaware
Elemental Composition of Freshly Nucleated Particles

10:10 – 10:20 **Break**

10:20 – 11:20 **Presentations by EPA/STAR Grantees**

Treatment:

10:20 – 10:40 Wilfred Chen, University of California, Riverside
Nanoscale Biopolymers With Tunable Properties for Improved Decontamination and Recycling of Heavy Metals

10:40 – 11:00 Ismat Shah, University of Delaware
Synthesis, Characterization and Catalytic Studies of Transition Metal Carbide Nanoparticles as Environmental Nanocatalysts

11:00 – 11:20 Wolfgang Sigmund, University of Florida
Simultaneous Environmental Monitoring and Purification Through Smart Particles

11:20 – 12:00 **Small Business Perspective II**

Intematix Corporation	Ted Sun
TDA Research, Inc.	Andrew Myers

12:00 – 1:30 **Lunch**

1:30 – 4:00 **Presentations by EPA/STAR Grantees**
Moderator: John Barich

Other Areas of Application:

1:30 – 1:50 George Chumanov, Clemson University
Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

1:50 – 2:10 Darrell Velegol, Pennsylvania State University
Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticles Forces

2:10 – 2:30 Sarah Larsen, University of Iowa
Development of Nanocrystalline Zeolite Materials as Environmental Catalysts: From Environmentally Benign Synthesis Emission Abatement

2:30 – 2:50 Peter McMurry, University of Minnesota
Ion-Induced Nucleation of Atmospheric Aerosols

2:50 – 3:00 **Break**

3:00 – 4:00 **Remediation:**

3:00 – 3:20 Mamadou Diallo, Howard University
Dendritic Nanoscale Chelating Agents: Synthesis, Characterization, Molecular Modeling and Environmental Applications

3:20 – 3:40 Dibakar Bhattacharyya, University of Kentucky
Membrane-Based Nanostructured Metals for Reductive Degradation of Hazardous Organics at Room Temperature

3:40 – 4:00 Daniel Strongin, Temple University
A Bioengineering Approach to Nanoparticle Based Environmental Remediation

4:00 – 4:10 **Wrap Up**

4:10 **Meeting Adjourns**

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Section 1. Sensors

Sensors - *Novel sensing technologies or devices for pollutant and microbial detection.*

Protection of human health and ecosystems requires rapid, precise sensors capable of detecting pollutants at the molecular level. Major improvement in process control, compliance monitoring, and environmental decisionmaking could be achieved if more accurate, less costly, more sensitive techniques were available.

Examples of research in sensors include the development of nanosensors for efficient and rapid *in situ* biochemical detection of pollutants and specific pathogens in the environment; sensors capable of continuous measurement over large areas, including those connected to nanochips 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.

Nanosensors for Detection of Aquatic Toxins

Robert E. Gawley
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Abstract

This project will 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 used to optimize binding in libraries of peptidic host molecules immobilized on solid support (polystyrene beads). Unlike side chain arrays in the native (protein) receptors, the combinatorial synthesis techniques 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. It is anticipated that 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 used for mimicking toxin receptor sites also can be used to mimic enzyme receptor sites. Thus, by using models of enzyme active sites, it is anticipated that this methodology could be used to mimic enzyme reactions to produce solid phase catalysts.

Nanosensors for Detection of Aquatic Toxins

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

Environmental Benefits

This project addresses the STAR-K1 initiative, "Exploratory Research on Nanotechnology," by working at the molecular level to create large structures with fundamentally new molecular organization. Among the possible future applications of this technology, but beyond the scope of the present project, could be applications such as molecular synthesis of new catalysts for industrial processes, and reactive surface coatings that destroy or immobilize toxic compounds.

The specific pollutants (toxins) for which chemosensors are being developed are: tetrodotoxin, cylindro-spermopsin, domoic acid, brevetoxin, and ciguatoxin. There are alarmingly increased quantities of these toxins in parts of the environment as never seen before. As an example, recent issues (May 27, 2001) of the *Orlando Sentinel* and the *Miami Herald* include articles entitled "Poisons from algae lurk in the water we drink." In the spring of 2002, another series of stories detailed poisonings by saxitoxin that entered the human food chain via pufferfish caught near Cape Canaveral, Florida. This is the first occurrence of saxitoxin poisoning in the Atlantic south of New England.

These stories also went to other newspapers via the Associated Press (AP) wire service. They refer to the recently detected presence of toxins never seen before in Florida—even alligators have succumbed to recent algal blooms. Why are these blooms occurring? Were the algae always present but now are blooming in larger quantities because of some stimulus? This is unknown. As a result, fast, cheap ways to detect the toxins are needed.

Real-Time Chemical Composition Measurements of Fine and Ultrafine Airborne Particles

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Abstract

For more than a decade, mass spectrometry has been used to determine the chemical composition of individual airborne particles in real time. It has been coupled with various size measurement or size selection methods to provide correlated size-composition information of ambient aerosols. Most of these methods work well for particles down to approximately 500 nm in diameter; a few methods work well down to approximately 50 nm in diameter. Currently, none are acceptable for particles smaller than approximately 30 nm in diameter.

Over the last few years, our emphasis has been on the analysis of particles between approximately 30 and 500 nm in diameter. Correlated size-composition information is obtained by sampling the aerosol with a size-selective inlet and ablating individual particles on-the-fly with a pulsed laser. This approach has been used to obtain size-resolved mass spectra of several hundred thousand ambient particles at multiple urban sampling sites. Extending these measurements to particles down to approximatley 5 nm in diameter requires the development of new technology. Two specific problems must be overcome: (1) efficient sampling of particles into the mass spectrometer, and (2) efficient analysis of those particles that have been sampled.

In this presentation, the current state-of-the-art in fine particle analysis will be discussed along with ambient particle data from several urban sampling sites in the United States. New instruments that are capable of extending these measurements to ultrafine particles also will be described.

Real-Time Chemical Composition Measurements of Fine and Ultrafine Airborne Particles

Murray V. Johnston
University of Delaware, Newark, DE

Environmental Benefits

The technology developed in this research project will permit the chemical composition of airborne nanoparticles (down to about 5 nm in diameter) to be determined. Knowledge of the chemical composition will provide a better understanding of the sources of these particles and how to control their formation in a manner that reduces their impact on human health.

It is now well established that long-term exposure to fine particulate matter is a significant risk factor for cardiopulmonary and lung cancer mortality in humans.[1] In urban air, fine particulates typically exhibit a maximum in both number and mass in the 100 to 300 nm diameter range. Most of these particles are produced directly from combustion sources. However, a significant fraction of particles in this size range also may arise from growth and/or coagulation of much smaller particles. Indeed, particle formation events have been identified in a variety of locations around the world, including urban locations such as Atlanta.[2] These events are characterized by sudden bursts of ultrafine particles 10 nm diameter and smaller, usually early in the day, followed by growth to larger sizes. The mechanism of particle formation is difficult to assess without chemical composition measurements during these events.

Technology already exists for chemical analysis of fine particles.[3] Our group has characterized particles in this size range at the Atlanta, Houston, Baltimore, and Pittsburgh supersites. An example of the information that can be gained from these measurements is shown in Figure 1. The spectrum shows a signature indicative of iron. Particles containing iron at this particular site are normally observed when the wind is blowing from the south-southwest and most likely correspond to emission from a specific source. Other particle compositions correspond to other emission sources. Thus, size- and time-resolved measurements of particle composition potentially allow the ambient aerosol to be apportioned into the various sources of particle emission.

Unfortunately, these methods cannot characterize particles smaller than about 30 nm in diameter. The technology to be developed in this work addresses the two fundamental limitations associated with nanoparticle analysis. First, an improved size-selective sampling method will be developed for particles down to about 5 nm in diameter. Second, an improved particle analysis method will be developed that allows the elemental composition of these particles to be determined.

The technology developed in this project will fill an important gap in particle analysis, allowing particles within the entire range of sizes finally to be handled so that the ambient aerosol can be fully characterized.

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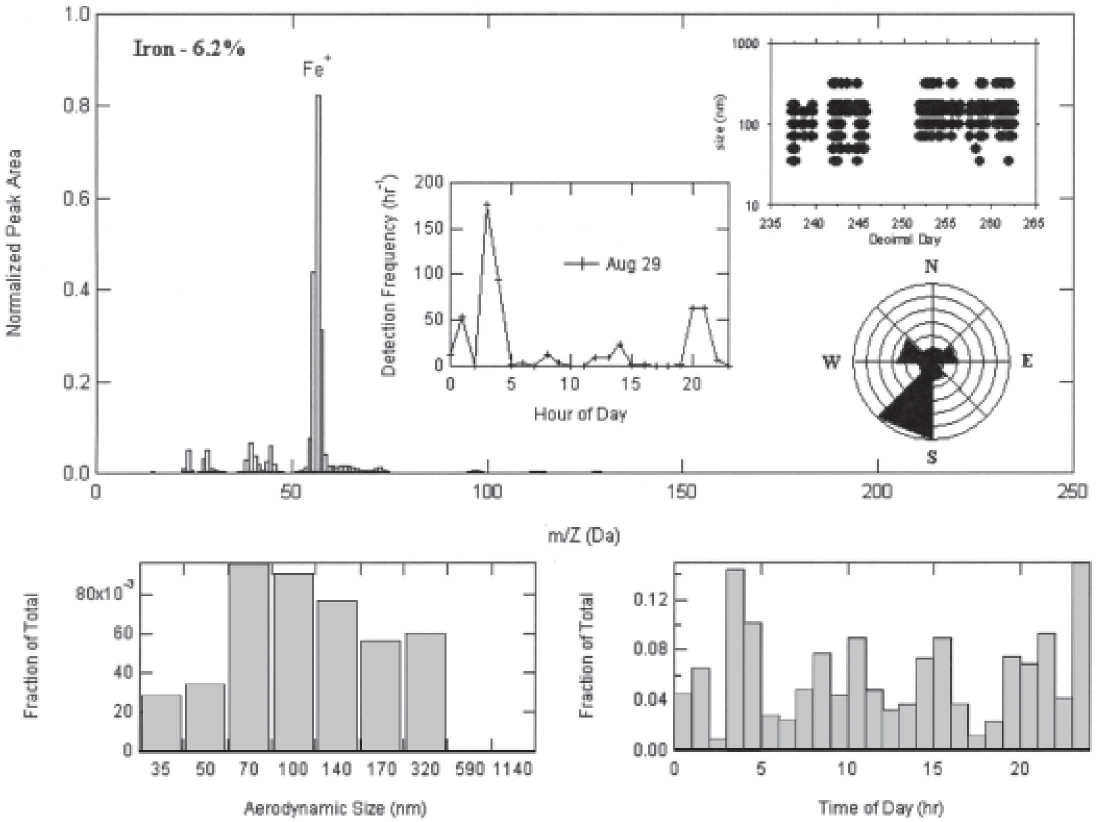

Figure 1. Characteristics of a class of ambient particles containing iron: size, date, time of day, and wind direction.

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

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Abstract

The goal of the proposed research is to develop highly piezoelectric microcantilever arrays for *in situ* rapid, simultaneous multiple pathogen quantification using electrical means in source water with unprecedented sensitivity (10^{-15} g). The proposed piezoelectric microcantilevers—smaller than 10 micrometers in length with antibodies specific to the target pathogens immobilized at the cantilever tip—will measure the presence of pathogens with femtogram (a small fraction of a cell's mass) sensitivity in source water. Binding of target pathogens is detected by monitoring the resonance frequency shift. This represents the ability to detect a single cell. The use of the highly piezoelectric microcantilever for simultaneous quantification of model pathogens, *Escherichia coli O157, Cryptosporidium parvum,* and *Helicobacter pylori* will be demonstrated.

To achieve the proposed piezoelectric microcantilever sensor arrays, parallel efforts will be conducted in the following major task areas: (1) microfabrication of miniaturized piezoelectric cantilevers for femtogram mass detection sensitivity, (2) demonstration of pathogen quantification in source water by selective antigen-antibody binding, and (3) characterization of the robustness of various cantilever designs for optimal performance.

On the selectivity front, initial results on antibody-antigen binding and antibody-gold surface binding will be presented using piezoelectric lead zirconate titanate (PZT)/stainless steel cantilevers of minimeter length with a stainless steel tip. The unique design of such cantilevers allows picogram detection capabilities, and permits the quantification of both binding of antibody with or without linkers to the gold-coated cantilever tip surface and that of *E. coli* to the immobilized antibody by directly minitoring the cantilever's resonance frequency shift. The resonance frequency shift transient of antibody-coated cantilever can be used to characterize the amount of pathogens present in the water. This will allow characterization of antibody immobilization and *E. coli* detection in low to moderate concentrations.

On the miniaturization front, the most critical step in the microfabrication of piezoelectric microcantilevers is the development of highly piezoelectric thin layers that have a low sintering temperature that are compatible with the standard silicon microfabrication processes. Development of piezoelectric thin layers will result in strontium-doped lead titanate (PST) thin layers that can be sintered at 450 ºC.

As a result of the proposed study, it is anticipated that ultrasensitive, rapid, specific, multiple pathogen quantification of drinking water will be achieved using arrays of highly piezoelectric PST unimorph microcantilevers of less than 10 micrometer in length with better than 10^{-15} g/Hz sensitivity, coupled with antibodies specific to the target pathogens immobilized at the cantilever tip. Because the proposed piezoelectric cantilever sensors use electrical signal for actuation and detection, the sensor and all necessary electronics can be organized in a compact form that is easily usable in such broad ranging applications as environmental monitoring and genomics-inspired proteomics.

Ulrasensitive Pathogen Quantification in Drinking Water Using Highly Piezoelectric PMN-PT Microcantilevers

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Environmental Benefits

Current development of pathogen detection in water relies on filtration culture methods, and fluorescence-based methods (e.g., fluorescence probes methods and DNA microarray methods). These techniques, however, are not effective for *in situ*, rapid, quantitative measurements. With filtration culture methods, sample water is passed through a filter that is pretreated for visualization of the target pathogen. Growth of colonies on the filter indicates the presence of the target pathogen in the test water. Both the fluorescently labeled probe methods and the DNA microarray methods rely on detection using fluorescence spectroscopy, which is not quantitative.

There is a need for rapid, quantitative, and specific pathogen detection to ensure the safety of natural and manmade water supplies, including source, treated, distributed, and recreational waters. The proposed technology uses arrays of a highly piezoelectric (e.g., strontium-doped lead titanate) microcantilever smaller than 10 micrometers in length coupled to antibody proteins immobilized at the cantilever tip for *in situ* rapid, simultaneous multiple pathogen quantification in source water, with the ability to detect pathogens using electrical means with femtogram sensitivity (10^{-15} g).

Binding of target pathogens is detected by monitoring the resonance frequency shift. The cantilever allows an unprecedented sensitivity, better than 10^{-15} g/Hz. This represents the ability to detect a single cell. The current proposed work will demonstrate the use of the highly piezoelectric microcantilever for simultaneous detection of model pathogens, *Cryptosporidium parvum*, *Helicobacter pylori*, and *Escherichia coli O157*.

Because the proposed piezoelectric cantilever sensors use an electrical signal for actuation and detection, the sensor and all necessary electronics can be organized in a compact form and easily usable in such broad ranging applications as environmental monitoring.

In addition to the proposed pathogen quantification in water, the proposed array piezoelectric microcantilever sensor technology also offers the potential for a wide spectrum of toxin monitoring, ranging from small molecular-weight gaseous species to bacteria in low concentrations both in air and in liquid because of the ultra high detection sensitivity.

A Nanocontact Sensor for Heavy Metal Ion Detection

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Abstract

As materials and devices shrink to the nanometer scale, various quantum phenomena become important. This may lead to novel applications, including those that are important to environmental analysis and protection. This project exploits the phenomena of conductance quantization and quantum tunneling to fabricate nanoelectrodes for *in situ* detection of metal ion pollution. The goal is to develop a high-performance and low-cost sensor for initial onsite screening tests of surface and groundwater to provide early warning and prevention of heavy metal ion pollution. The existing analytical techniques usually require preconcentration of samples to detect trace metal ions, which can be time-consuming and prone to cross-contamination. Moreover, many of the sensitive techniques, such as inductively coupled plasma-mass spectrometry, are not suitable for onsite monitoring. In contrast, the nanocontact sensor has the potential for detecting even a few metal ions without preconcentration and is particularly suitable for onsite detection of ultratrace levels of heavy metal ions, including radioactive elements.

The sensor consists of an array of nanoelectrode pairs on a silicon chip. The nanoelectrodes in each pair are separated with an atomic scale gap, which is achieved with the help of quantum tunneling phenomenon. Electrochemical deposition of even a few metal ions into the gap can bridge the gap and form a nanocontact between the nanoelectrodes, thus triggering a quantum jump in the electrical conductance. The sensor can achieve high specificity by combining several different measurements, such as redox potentials, point-contact spectroscopy, and electrochemical potential-modulated conductance changes.

It is anticipated that this project will lead to a prototype nanocontact sensor for detecting heavy metal ion pollution in water. In addition to the unprecedented sensitivity, the sensor will be miniaturized and cost effective, which should be particularly suitable for an initial onsite screening test of polluted samples, thus leading to early warning and prevention of heavy metal ion pollution. The capability to measure and control electrochemical deposition/stripping of a single or a few metal ions, to be fully developed in this project, may provide opportunities for a better understanding of electroanalytical chemistry of metal ions and lead to new environmentally benign fabrication methods for nanoelectronics.

A Nanocontact Sensor for Heavy Metal Ion Detection

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Environmental Benefits

The threat of heavy metal pollution is a serious environmental concern because of the toxicity of such metals on a broad range of living organisms, including humans, and the consequence of heavy metals not being biodegradable. Due to the difficulty in the remediation of sites contaminated with heavy metals, there is an urgent demand for an *in situ* sensor capable of detecting heavy metal ions before the concentration reaches a dangerous level. To date, heavy metals in the environment are usually measured with spectroscopic techniques, including atomic absorption and inductively coupled plasma-mass spectroscopy (ICP-MS). These techniques are well established but require that samples be collected and transported to the laboratory for analysis, because the instrumentation is bulky, expensive, and requires significant maintenance and operator expertise. Sample preservations and pretreatments, generally required by these techniques, may cause sample contamination. *In situ* measurements, performed in the natural environment, are highly desirable because they provide an early detection of trace metal contaminants while minimizing errors, labor, and cost associated with collection, transport, and storage of samples for subsequent laboratory analysis.

Supported by the U.S. Environmental Protection Agency's Nanotechnology Exploratory Research Program, this project includes the development of a nanocontact sensor for *in situ* detection of heavy metal ion pollution in water. It has already revealed that the sensor can be extremely sensitive with the potential capability of detecting a few metal ions. High specificity will be based on different redox potentials of metal ions, a principle that has been successfully used in anodic stripping technique. In addition, point-contact spectroscopy and electrochemical potential-induced conductance change will be used to further improve the specificity. The sensor will be miniaturized and automated, making it conducive to onsite field applications. The sensor head used in preliminary experiments is a 0.5 in. x 0.5 in silicon chip, on which 15 pairs of nanoelectrodes are fabricated. Because the sensor is fabricated with conventional microelectronic fabrication facilities and relatively simple electrochemical techniques, it also should be cost effective. It is anticipated that the sensor will be particularly suitable for initial onsite screening tests of polluted samples, thus leading to early warning and prevention of heavy metal ion pollution.

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

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Abstract

The goal of this research project is to develop new selective solid-state sensors for carcinogenic and toxic chromium(VI) and arsenic(V) in water based on redox quenching of the luminescence from nanostructured porous silicon and polysiloles.

Nanostructured porous silicon, as well as polysilole nanowire coatings, will be chemically modified to enhance binding of the chromate and arsenate anions. Chemical modification to vary the redox potential of the polysilole excited state also will be used as a way to impart chemical selectivity. Both sensor approaches will be combined by encapsulating the polysilole in a nanotextured microcavity between two Bragg stacks constructed from porous silicon. Such optical devices have been shown to provide significant detection sensitivity enhancements. The nanoporous material will readily admit small inorganic analytes, such as chromate and arsenate, and exclude biomolecules that might confound the measurements. Sensors based on silicon wafer and polymer technologies are readily adaptable to fabrication. The fluorescence quenching detection modality also is manufacturable. The essential electronics requires a blue or UV LED as the excitation source and an inexpensive photodiode detector.

Potential applications of such real time solid-state sensors include remote sensing and industrial process control. The focus on chromium(VI) and arsenic(V) detection is dictated by the redox quenching mechanism that is being used, as well as by the importance of chromium(VI) and arsenic(V) as regulated chemicals under the Safe Drinking Water Act. The results address the needs identified in the solicitation as nanotechnology is applied to the development of solid-state sensors that can be used to monitor pollutants in water that are currently of great concern to the U.S. Environmental Protection Agency's regulatory mission.

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

William C. Trogler
University of California, San Diego, CA

Environmental Benefits

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

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

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

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

Section 2. Treatment

Treatment - Technologies to effectively treat environmental pollutants.

Cost-effective treatment poses a challenge for the EPA and others in the development of effective risk management strategies. Pollutants that are highly toxic, persistent, and difficult to treat, present particular challenges. EPA supports research that addresses new treatment approaches that are more effective in reducing contaminant levels and more cost effective than currently available techniques. For example, nanotechnology research that results in improved treatment options might include removal of the finest contaminants from water (under 300 nm) and air (under 50 nm) and "smart" materials or reactive surface coatings that destroy or immobilize toxic compounds.

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

Wilfred Chen, Ashok Mulchandani, and Mark Matsumoto
University of California, Riverside, CA

Abstract

Nanoscale materials have been gaining increasing interest in the area of environmental remediation because of their unique physical, chemical and biological properties. One emerging area of research has been the development of novel materials with increased affinity, capacity, and selectivity for heavy metals because conventional technologies are often inadequate to reduce concentrations in wastewater to acceptable regulatory standards. Genetic and protein engineering have emerged as the latest tools for the construction of nanoscale materials that can be controlled precisely at the molecular level. With the advent of recombinant DNA techniques, it is now possible to create "artificial" protein polymers with fundamentally new molecular organization. The most significant feature of these nanoscale biopolymers is that they are specifically pre-programmed within a synthetic gene template and can be controlled precisely in terms of sizes, compositions and functions at the molecular level. In this manner, it is possible to specifically design protein-based nano-biomaterials with both metal-binding and tunable properties that can be used to selectively remove heavy metals from dilute solutions in one single process. The overall objective of this research is to develop high-affinity, nanoscale biopolymers with tunable properties for the selective removal of heavy metals such as cadmium, mercury, and arsenic.

The elastin domain, which has been shown to undergo a reversible phase transition upon temperature changes, will be used to generate fusion biopolymers with various metal-binding domains. Several metal-binding domains such as Gly-His-His-Pro-His-Gly, MerR (a repressor for the mercury resistance operon), and ArsR (a repressor for the arsenic resistance operon) will be used to provide high affinity and selective removal of mercury and arsenic. Synthetic genes encoding for the tunable biopolymers will be specifically tailored for the desired properties. By tuning the process pH and temperature, reversible network formation between the individual biopolymers will enable the recovery of sequestered metals by precipitation. The use of these metal-binding domains has significant advantages over existing chemical chelators, including higher specificity and affinity. The potential lower limit for heavy metal removal could be on the order of 10^{-10}M, or approximately 8 parts per trillion, depending on the metal-binding domain employed.

The ability of these biopolymers to self assemble as aggregates and their metal binding capability will be elucidated. Experiments will be conducted to determine the selectivity and metal uptake capacity of the tunable biopolymers. The potential of the biopolymers for repeated metal removal will be investigated by subjecting to several cycles of binding and stripping. The performance of the tunable biopolymers for heavy metal removal will be compared to the commercially available ion exchange sorbents such as Duolite GT-73, Amberlite IRC-718, Dowex SBR-1, and Amberlite IRA 900X.

The proposed tunable biopolymers extend ideas from nature toward entirely new objectives. Molecular-level protein-protein recognition is tailored specifically into tunable metal-binding biopolymers. These biopolymers can be easily and continuously applied with other existing technologies for bulk heavy metal removal. This operation is environmentally friendly because no toxic chemical is required for synthesis of the biopolymers and regeneration can be achieved easily. This strategy, if successful, will provide a low-cost and environmentally benign technology for heavy metal removal.

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

Wilfred Chen
University of California, Riverside, CA

Environmental Benefits

A variety of metals requiring removal and concentration exist in many contaminated sites and in ground or process waters. Increasingly restrictive Federal regulation of allowable levels of heavy metal discharge into harbors and coastal water and the need for rapid cleanup of contaminated sites has prompted the development of novel approaches and technologies for heavy metal removal. Although existing technologies are adequate to remove the bulk of the heavy metal contamination, they fail to meet the low concentration limits required by regulatory standards. It becomes clear that a robust, polishing process is required to effectively remove and recover hazardous metals in dilute waste streams. The tunable biopolymers proposed here are extensions of ideas from nature with entirely new objectives.

Molecular-level protein-protein recognition is tailored specifically into tunable metal-binding nanoscale biopolymers. The biosynthetic approach is environmentally friendly; provides precise and independent control of the length, composition, and charge density of the interacting end blocks and metal-binding domains; and allows for the flexibility in designing tunable biopolymers that can undergo transition from water-soluble to aggregate forms under a wide-range of conditions. Such precise control satisfies the needs of different process conditions. If the metal-binding proteins associated with As and Hg resistance are used, the expected lower limit for As and Hg removal using tunable biopolymers could be on the order of 10^{-10}M, or approximately 8 parts per trillion. Because of their unique properties and selectivity, it is anticipated that the new biopolymers will result in a wide range of applications for heavy metal removal/recovery. Compared to conventional chemical chelators or chelating polymers, the proposed biopolymers are environmentally friendly because no toxic chemical is required for their synthesis, and regeneration can be achieved easily. This strategy, if successful, will provide a low-cost and environmentally benign technology for heavy metal removal.

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

S. Ismat Shah and J.G. Chen
University of Delaware, Newark, DE

Abstract

The future targets for the reductions of emission gases from automobile exhaust are very demanding. For example, the 2004 Ultra Low Emission Vehicle (ULEV) Act requires that the level of NO_x must be reduced to 0.05 g/mile (i.e., one-quarter of the currently allowed value). The current catalytic converter technology is incapable of achieving such goals without increasing the amount of Pt-group precious metals to levels at which the converters might become prohibitively expensive. This project will investigate the synthesis, characterization, and application of nanoparticles of transition metal carbides and oxycarbides as replacement for Pt-group metals (Ru, Rh, Ir, Pd, and Pt). The choice of materials is based on recent results that show strong similarities in the catalytic properties between transition metal carbides and the more expensive Pt-group metals. In addition to offering a very high surface/volume ratio, nanoparticles offer the flexibility of tailoring the structure and catalytic properties on the nanometer scale.

In the first phase of the research, nanostructured WC_x thin films were prepared by reactive sputtering of a pure tungsten target in an argon-methane discharge. A DC magnetron gun was used. Nanostructured thin films were deposited on glass, quartz, silicon and sapphire substrates at temperatures up to 400 ^{o}C. The carbon content in the film was varied by changing the partial pressure of methane. The carbon content in the films was analyzed using Energy Dispersive X-ray Analysis (EDAX). The effect of temperature on the grain size also was studied using Transmission Electron Microscope (TEM). The TEM results showed that the average grain size is approximately 1.5-2.0 nm and that the grain size is constant for temperatures up to 600 ^{o}C. In reactive sputtering, compound formation occurs above a critical concentration of the reactive gas in the sputtering gas mixture leading to, among other effects, a sharp reduction in the deposition rate. The target poisoning behavior was studied by measuring the target current. The critical methane concentration at which the metal-poison mode transition occurs was measured to be around 38 percent of CH_4 in Ar. Preliminary results on the catalytic properties of nanostructured WC_x also will be presented.

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

S. Ismat Shah and J.G. Chen
University of Delaware, Newark, DE

Environmental Benefits

One of the major environmental pollution sources is automobile exhaust, which causes smog and acid rain. Since 1975, the automobile manufacturers have taken a variety of steps to reduce the level of harmful emission gases, including NO_x, CO, and unburned hydrocarbons (HC). At present, the emission levels of these gases can be reduced by catalytic reactions in the catalytic converter via the following chemical reactions:

$CO + O_2 \rightarrow CO_2$	CO Oxidation
$HC + O_2 \rightarrow CO_2 + H_2O$	HC Oxidation
$NO_x + HC \rightarrow N_2 + H_2O + CO_2$	NO_x Reduction by HC
$NO_x + CO \rightarrow N_2 + CO_2$	NO_x Reduction by CO

In these reactions, the harmful pollutants are converted into relatively harmless molecules such as CO_2, N_2, and H_2O. These reactions occur inside the automobile catalytic converters in the presence of catalysts, which consist of mixtures of platinum-group metals such as rhodium (Rh), platinum (Pt), and palladium (Pd). Due to their limited natural abundance in the Earth's crust, the platinum-group metals are among the most expensive elements. For example, the current price for a troy ounce of Rh is approximately $2,500, which is about three times more expensive than gold. For cost-effectiveness reasons, the Pt-group metals in the catalytic converter are always kept at a minimum amount, but sufficient enough to reduce the emission levels that meet the government regulations.

Recently, the U.S. Environmental Protection Agency (EPA) and the California Air Resource Board (CARB) have defined specific future targets for the reduction of emission gases of NO_x, CO, and HC. For example, the target emission levels for the 1997-2003 Ultra Low Emission Vehicle (ULEV) are 0.04, 1.7, and 0.2 g/mile of HC, CO, and NO_x, respectively. A more stringent target, set by the 2004 ULEV2 Act, requires that the level of NO_x be further reduced to 0.05 g/mile. The current catalytic converter technology is able to reach the 1997-2003 targets. However, it is insufficient to achieve a further decrease, by a factor of four, in the level of NO_x by the year 2004. Although an obvious solution is to increase the concentrations of the Pt-group metals in the catalytic converter, the cost effectiveness eventually would become a major issue for automobile manufacturers and catalyst vendors.

Our current research attempts to explore the possibility of using alternative catalytic materials, transition metal carbides and oxycarbides (defined as oxygen-modified carbides), to replace Pt-group metals for the reduction of NO_x. The carbides and oxycarbides of Groups 4-6 early transition metals are characterized by many unique and intriguing catalytic properties. Since the landmark paper by Levy and Boudart regarding the Pt-like properties of tungsten carbides, the catalytic properties of transition metal carbides (TMC) and oxycarbides (TMOC) have been the subject of many investigations in the fields of catalysis and surface science. This catalysis literature has 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 recent years, several surface science groups have performed fundamental investigations of the catalytic properties of TMC and TMOC. For example, our research group has performed extensive studies aimed at directly comparing the chemical reactivity of carbide surfaces with that of Pt-group metals. The results provided conclusive evidence that the decomposition of a variety of hydrocarbon molecules on TMC occurs via reaction mechanisms that are characteristic of Pt, Rh, and Pd. Furthermore, comparative studies of the decomposition of NO on the bulk surfaces of Mo and W carbides and oxycarbides have been performed recently. The 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. Nanoparticles of TMC and TMOC offer means of obtaining the phase and crystal surface required for efficient NO reduction.

If successful, the replacement of Pt-group metals by TMC or TMOC nanoparticles would offer enormous economic incentives for the effective reduction of NO_x. More importantly, it might offer one of the more realistic ways to achieve the NO_x emission level, 0.05 g/mile, without the use of prohibitively high priced Pt-group metal catalysts.

Simultaneous Environmental Monitoring and Purification Through Smart Particles

Wolfgang M. Sigmund, Chang-Yu Wu, and David Mazyck
University of Florida, Gainesville, FL

Abstract

This project involves a multidisciplinary synthesis of technologies to design and fabricate smart particles that can purify and monitor the environment. This multidisciplinary synthesis of technologies includes self-organized structural control and smart materials with a focus on environmental purification and monitoring to create intelligent surfaces and structures that not only sense and interact with their environment, but also can fundamentally alter their own behavior and deactivate themselves as preprogrammed or as desired. The hypothesis to be tested is: Will nano-engineered smart particles based on a modular building concept enable simultaneous monitoring and purification of the water and air environment?

The project's approach is to: (1) define and synthesize smart particles that purify and monitor by indicating through a simple visible change such as color or size; (2) make particles easily separable by auto-flocculation and/or by magnetic removal; (3) synthesize ferromagnetic particles with high specific surface area that increase the specific surface area by at least two orders of magnitude compared to current magnetic photocatalysts; and (4) strongly reduce the mass of photocatalyst required for treatment and further improve pollutants mass transfer and exposure to UV-light through magnetically agitated fluidization.

The expected results of the project include: (1) atomic and molecular control of material building blocks and required engineering tools to provide the means to assemble and utilize these tailored building blocks for assembling novel smart particles for environmental applications as purifiers and sensors, which are environmentally benign; and (2) reduction of the amount of photocatalyst and an increase in the specific surface area of magnetic photocatalyst composites by two orders of magnitude.

Simultaneous Environmental Monitoring and Purification Through Smart Particles

Wolfgang M. Sigmund, Chang-Yu Wu, and David Mazyck
University of Florida, Gainesville, FL

Environmental Benefits

In addition to providing a better understanding of atomic and molecular control of material building blocks, this research project provides numerous environmental benefits. For example, future commercialization would provide efficient water and air purification systems capable of removing pollutants to below ppm levels, and provide notification when the pollutants are removed or when the active sites are no longer available.

The smart nanomaterials developed in this study are significantly smaller as compared to the current particles of a few hundred micrometers. Their greater surface area of two orders of magnitude will provide destruction of pollutants in fractions of the time it takes the current particles. The magnetically agitated design can significantly improve the contact of the particles with pollutants, resulting in the reduction of reactor size. The small size would be ideal for purification onboard the International Space Station (ISS), in homes, or onboard airplanes or ocean vessels where space is a concern. The sensing capability will result in efficient and optimized usage of energy, with minimum extraction of natural resources, and will prove to be beneficial to systems where energy sources are limited.

The mixed smart particles (photocatalytic active particles plus sensing particles) will offer a novel way of sensing and monitoring the environment. The modular concept involving a sensing module and a photocatalytic module being united in one smart particle also will open novel opportunities for sensing and monitoring. If the modular concept (either in smart mixtures or in smart particles) is successful, there will be a huge new field of applications. The modular concept would allow an exchange of sensing units as needed. Sensing modules are exchangeable and thus can be very specific in design towards a molecule/organism (bacteria/virus/protein) or any other matter ranging in size from 5 nm to 300 nm.

In addition and perhaps most importantly, the destruction of pollutants is environmentally benign, focusing on solving the problem rather than transferring one pollution form for another. For example, in groundwater remediation, several implemented technologies transfer a water pollution problem into an air pollution problem (e.g., activated carbon adsorption and regeneration).

Section 3. Remediation

Remediation - Technologies to effectively remediate environmental pollutants.

Cost-effective remediation techniques also pose a major challenge for the EPA in the development of adequate remedial 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, both because of their cancer and non-cancer hazards, include heavy metals (e.g., mercury, lead, cadmium) and organic compounds (e.g., benzene, chlorinated solvents, creosote, toluene). Reducing releases to the air and water, providing safe drinking water, and reducing quantities and exposure to hazardous wastes also are areas of interest.

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

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Abstract

The overall objective of this project is the development and fundamental understanding of reductive dechlorination of selected classes of hazardous organics by immobilized nanosized metal particles (single and bimetallic systems) in ordered membrane domains. This integrated research will examine nanoparticle synthesis in a membrane domain, the role of metal surface area and surface sites, the potential role of ordered nanometal domains in membranes, membrane partitioning, and reaction kinetics with the main emphasis on obtaining highly enhanced dechlorination rates and selectivity from dilute aqueous solutions. The overall hypothesis to be tested is that nanosized (< 50 nm) zero-valent metal domains can be created in an ordered membrane matrix by the use of novel, polypeptide-based biomolecules with helix-coil forming ability or by di-block copolymers**.** The specific objectives are hypothesis based and will lead to greater insight into hazardous organics dechlorination by providing a highly flexible membrane platform containing nanosized metals. Some of the main hypotheses to be tested include: use of polyfunctional metal binding ligands (such as polyamino acids [PAA]) will lead to high loadings of nanosized reactive metals in ordered membrane domains; PAA's proven helix-forming ability will lead to ordered zero-valent metal entrapment for potential dechlorination selectivity; dissolved metals (a consequence of dechlorination reactions) can be recaptured in these membranes and thus reused; use of block copolymers will lead to the development of very small size and mono-disperse nanoparticles; and membrane partitioning of chlorinated organics will lead to high reaction rates and selectivity.

The approach for this project is to examine immobilized nanostructured metals for dechlorination of hazardous organics. The uniqueness of the project is that, in contrast to literature reported data, membrane partitioning and *in situ* synthesis of nanoparticles in a membrane phase will provide highly enhanced dechlorination rates (200 to 1,000-fold) and selectivity. This project will establish the role of selected nanoscale particles (Fe, Zn, Pd, selected bimetallic systems) in membrane platforms, rate of dehalogenation reactions, and selectivity for the formation of particular rate-controlling intermediates, and determine the effects of nanoparticle surface area/chemistry and membrane partitioning. Significant efforts will be placed on the degradation of TCE to its intermediates, as well as the degradation of selected chlorinated aromatics. The specific organic degradation studies in dilute solutions will include: TCE and intermediates such as cis-and trans-DCE (with Fe and Zn), mono-/dichlorophenol (bimetallic systems), and 1,2 dichloro- and 1,2,4 trichlorobenzenes (M^0 - Pd nanoparticles). Because the reductive dechlorination results (in metal particle dispersed solution phase) of some of these compounds are available, direct quantitative comparisons of these membrane-based nanometal systems would be possible.

The development of the proposed membrane-based nanostructured metals synthesis for reductive dechlorination of various hazardous organics will provide a novel technique for the rapid and selective degradation of hazardous organics at room temperature. The development of this technology will have a significant impact on the role of nanostructured materials in the environmental field for current and future needs. The fundamentally new technique for creating environmentally applicable nanoparticles in an ordered fashion by immobilization in a membrane matrix provides a versatile platform to address diverse needs in both industrial manufacturing and remediation. Kinetic modeling and correlations with molecular descriptors should establish an excellent foundation for fundamental understanding of nanotechnology-based reaction systems. The additional benefits of this work will lead to reduction of materials usage and miniaturization of dechlorination reactor systems by more efficient use of metals and selectivity.

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

Dibakar Bhattacharyya
University of Kentucky, Lexington, KY

Environmental Benefits

Many chlorinated organics are toxic, even at low concentrations, and exert a cumulative, deleterious effect on receiving streams. Chlorinated aromatics and aliphatics represent a class of commercially important, but particularly toxic, chemicals that enter the environment from manufacturing operations and user applications. Reductive dechlorination of organics by various bulk metals (particularly Fe) in aqueous phase has been well documented. This research project involving nanostructured metals immobilized in membrane phase is expected to have significant positive impact on pollution remediation through compact and flexible dechlorination technology development with high reaction rates at room temperature, significant reduction of metals usage, waste minimization through possible recovery of nonchlorinated products (i.e., ethylene from TCE), and improvement in water quality. The use of nontoxic, polypeptide-based membrane assemblies to create nano-sized metal domains has significant environmental importance.

Although nanoparticles possess several advantages (i.e., high surface area and surface energy), sustainability requires particle immobilization to avoid particle loss, agglomeration, and broad size distribution. The fundamentally new technique—creating environmentally applicable nanoparticles in an ordered fashion by immobilization in a membrane matrix—provides a versatile platform to address diverse needs in both industrial manufacturing and remediation. The benefits of this work will lead to a reduction of materials usage and miniaturization of dechlorination reactor systems through more efficient use of metals and selectivity. Selective sorption of model organics and their intermediates should minimize competing reactions with natural hydrophilic solution components (e.g., nitrate reaction with zero-valent metals). Another benefit includes simultaneous organic dechlorination and recapture of reacted metals (as a consequence of dechlorination) by polypeptide acid groups in a composite material. Thus, higher value metals providing enhanced selectivity could be incorporated, thereby making the process environmentally sustainable.

The discharge and leaching (from contaminated soil) of chlorinated organic pollutants to various surface and groundwater is an area of considerable concern in terms of degradation of water quality. Chlorinated organics and many pesticides/herbicides are toxic to aquatic life, even at low concentrations, and exert a cumulative, deleterious effect on receiving streams. Thus, research dealing with highly improved reductive dechlorination techniques should lead to substantial improvement in environmental quality.

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

Mamadou S. Diallo[1,3], Lajos Balogh[2], William A. Goddard III[3], and James H. Johnson, Jr.[1]

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Abstract

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

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

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

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

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[3]California Institute of Technology, Pasadena, CA

Environmental Benefits

Dendrimers are monodisperse and highly branched nanostructures with controlled composition and architecture. Poly(amidoamine) (PAMAM) dendrimers possess functional nitrogen and amide groups arranged in regular “branched upon branched” patterns as a function of generation level (see Figure 1).

This high density of nitrogen ligands enclosed within a nanoscale container makes PAMAM dendrimers particularly attractive as high capacity chelating agents for toxic metal ions [Cu(II)], electron transfer mediators [Fe(II)], redox active metal clusters [FeS], and metal clusters with catalytic properties [Pt (II)]. PAMAM dendrimers also can be functionalized with surface groups that make them soluble in appropriate media or bind onto appropriate surfaces. This 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) redox active Fe laden nanoparticles for environmental detoxification.

Although macrocyles and their “open chain” analogues (unidentate and polydentate ligands) have been shown to form stable complexes with a variety of metal ions, their limited binding capacity (i.e., 1:1 complexes in most cases) is a major impediment to their utilization as high capacity chelating agents for industrial and environmental separations.Their relatively low molecular weights also preclude their effective recovery from solutions by low-cost membrane-based techniques (e.g., ultrafiltration). During Phase I of this project, dendrimers are being evaluated as high capacity chelating agents for transition metal ions in aqueous solutions. Our research shows that, in aqueous solutions, PAMAM dendrimers can serve as high capacity chelating agents for a variety of transition metal ions, including Cu(II), Fe(II), and Ag(I).

A variety of organic and inorganic pollutants are not easily degraded to less toxic compounds in oxic environments. These include chlorinated alkenes (e.g., perchloroethylene [PCE]), poly(nitroaromatics) (e.g., 2, 4, 6-trinitrotoluene [TNT]), and Cr(VI). Most of these compounds may, however, undergo rapid reductive transformations to less toxic products in anoxic environments. Reactive media such as Fe(0) and FeS that promote such transformations under reducing conditions are being used increasingly as functional materials to develop *in situ* permeable reactive barriers (PRB) and packed bed reactors for remediation of groundwater and surface water. Dendritic nanoscale chelating agents provide unprecedented opportunities for synthesizing high surface area metal-laden nanoparticles by reactive encapsulation (see Figure 2).

Phase II of this project will synthesize and characterize water-soluble and solid supported FeS laden dendrimer nanocomposites (DNCs) with tunable redox activity. The ability of these nanoparticles to reduce PCE in aqueous solutions will be evaluated. The successful completion of this research is expected to result in: (1) more effective functional materials for recovering or removing precious metal ions [e.g., Ag (I)] or toxic metal ions [e.g., Cu (II)] from industrial wastewater solutions by low-cost, membrane-based processes (e.g., ultrafiltration); and (2) more effective reactive media for reductive detoxification of chlorinated compounds (e.g., PCE) in aqueous solutions and subsurface formations.

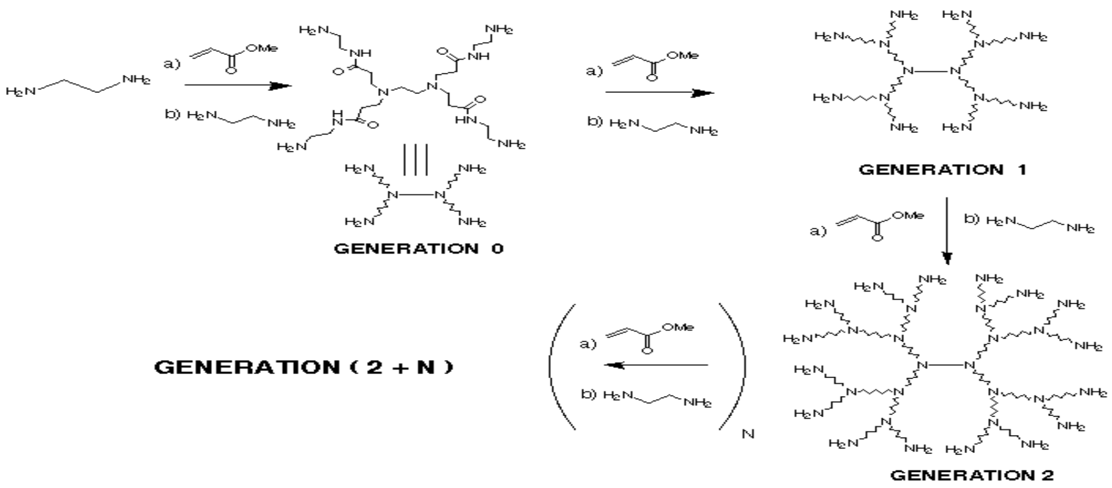

Figure 1. Structures of PAMAM dendrimers with ethylene diamine core and terminal NH_2 groups.

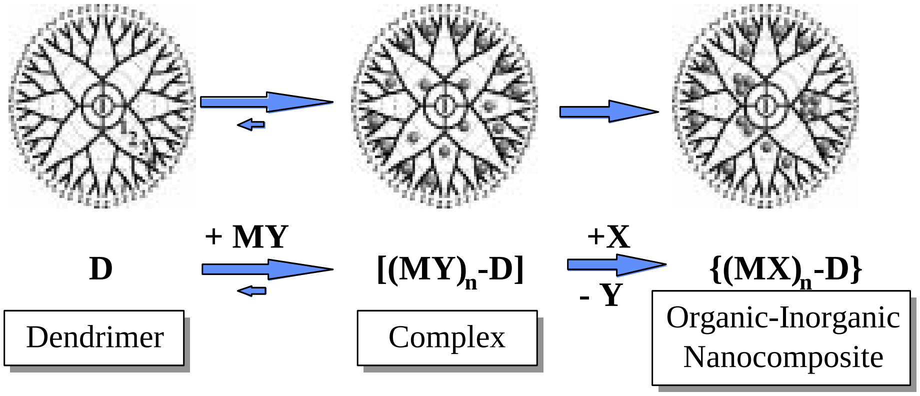

Figure 2. Synthesis of dendrimer nanocomposites by reactive encapsulation.

Photochemical Reactivity of Ferritin for Cr(VI) Reduction

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Abstract

Ferritin, which is an iron storage protein, was used to catalyze the photo-reduction of aqueous Cr(VI) species to Cr(III). Ferritin is a 24 subunit protein of roughly spherical shape with outer and inner diameters of approximately 12 and 8 nm, respectively. The native mineral core of ferritin is the ferric oxyhydroxide ferrihydrite [Fe(O)OH]. Fe(O)OH particles, which ranged from 5 to 7.5 nm in diameter, were used in the experiments. Under the experimental conditions, the ferritin protein without the Fe(O)OH core (i.e., apoferritin) was inactive toward Cr(VI) reduction, suggesting that the Fe(O)OH provided the active catalytic sites in the redox chemistry. Experiments using photon band-pass filters suggested that the reaction occurred out of a photo induced electron-hole pair and the optical band gap for the Fe(O)OH semiconductor was determined to be in the range of 2.5 to 3.5 eV. Comparison of ferritin and protein-free Fe(O)OH mineral nanoparticles indicated that ferritin provided a photocatalyst with significantly more stability to aggregation and the loss of catalytic activity.

Photochemical Reactivity of Ferritin for Cr(VI) Reduction

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Environmental Benefits

This research project is a multidisciplinary effort to develop a firm understanding of the properties of nano-sized metal oxide compounds within the protein shell (or cage) of the iron storage protein, ferritin (spherical with a 120 D diameter) (see Figure 1). These systems are unexplored in terms of their potential use in remediation processes or as a method for synthesis of nanoscale particles of metal compounds. The entire system, consisting of the inorganic core material and protein shell, provides opportunities to develop new catalysts for beneficial environmental chemistry by manipulating the composition and size of the core material, as well as chemically functionalizing the surrounding protein shell.

The proposed bioengineering approach will investigate the reactivity of a variety of metal oxides, such as Fe(O)OH, Co(O)OH, and Mn(O)OH with variable nano-dimensions that may have great potential benefits to chemical and photochemical remediation schemes (see Figure 1). Both the thermal chemistry and photochemistry of the particles toward the degradation of aromatics and chlorocarbons, as well as the particles redox chemistry, will be probed. These materials are ubiquitous components of soils, aquatic systems, and related environments, and have found uses in remediation strategies, but not at the nanoscale. Furthermore, results demonstrate the ability to reduce the metal oxide core of ferritin to yield nano-sized zero valent metal particles. Hence, our bioengineering approach yields a synthetic route to well-defined nano-metal particles for environmental chemistry. At least one prior impediment to fully investigating and ultimately testing the utility of nano-structures has been the difficulty that their preparation and stabilization presents. Our bioengineering approach addresses and helps circumvent these difficulties in an environmentally benign and biodegradable system. The low band gap energy of most Fe(III) bearing iron oxides allows them to harness a significant amount of the solar spectrum to carry out photochemical processes. Because of their attractive semiconductor properties and low cost, iron oxides have been investigated as photocatalysts for the degradation of environmental toxins (e.g., chlorocarbons and metals). Their potential use, however, is limited; they undergo photoreduction (i.e., conversion of Fe(III) to Fe(II)), resulting in the deterioration of the catalytic particle.

This research encapsulates the nano-catalyst in a protein cage that stabilizes the iron oxide against photoreduction. Because ferritin is engineered by nature to convert Fe(II) to Fe(III, it is hypothesized that any Fe(II) produced by photoreduction will be rapidly converted back to Fe(III) in the presence of O_2. This stabilization by the protein shell will be a significant advantage over, for example, a freestanding iron oxide particle photocatalyst. Although the protein cage stabilizes the core, its presence still allows the iron oxide core to drive important environmental chemistry. Our laboratory has demonstrated, for example, that photoexcited ferritin mediates the rapid reduction of toxic Cr(VI) to the immobile Cr(III) species.

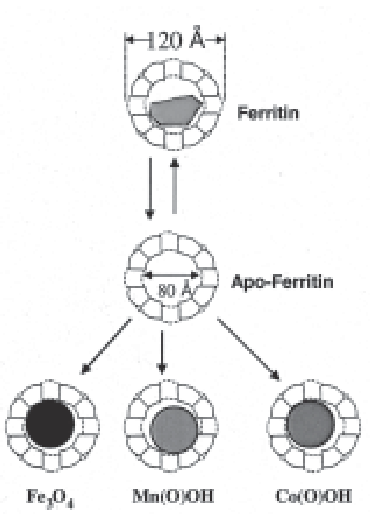

Figure 1. A schematic of the synthetic routes to different nanoparticles. A variety of other oxides can be assembled within the protein cage of ferritin (cross-sectional view shown).

Nanoscale Bimetallic Particles for *In Situ* Remediation

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Abstract

Nanoscale bimetallic (Fe/Pd, 99.9% Fe) particles are among the vanguard of a new generation of remediation technologies that could provide cost-effective remedial solutions to some of the most difficult sites. Nanoparticles feature large surface areas and extremely high surface reactivity. Equally important, they provide enormous flexibility for *in situ* remedial applications. The primary goal of this research is to continue the research and development of the nanoscale bimetallic particle technology for *in situ* remediation.

Several key technical issues of the nanoscale bimetallic particle technology will be investigated—the most important being the optimization and scaleup of the synthesis processes. A system will be built with the capacity to synthesize 500 to 1,000 grams of nanoparticles per day. The major experimental tasks include: (1) synthesis of various nanoscale particles (Fe/Pd, Fe/Ag, Fe/Ni, Fe/Co, Fe/Cu, etc.); (2) feasibility studies (batch and column) of treatment of perchlorate (ClO_4^-) and chromium (Cr(VI)) with various nanoparticles; (3) batch and column studies of treatment of mixed wastes, including organic solvents and heavy metals; and (4) modeling and column studies of injection, transport, and reactions of nanoparticles in porous media.

The complete reduction of aqueous perchlorate to chloride by nanoscale iron particles over a wide concentration range (1-200 mg/L) has been observed. The reaction is temperature sensitive as evidenced by progressively increasing rate constant values of 0.013, 0.10, and 1.52 mg perchlorate per g iron per hour, respectively, at temperatures of 25 ºC, 40 ºC, and 75 ºC. The large activation energy of 79.02 ± 7.75 kJ/mole partially explains the stability of perchlorate in water. Iron nanoparticles may represent a feasible remediation alternative for perchlorate-contaminated groundwaters, an environmental concern of growing importance. In a more general sense, the results illustrate the profound impact of particle size in surface mediated reactions.

The results of this research will provide insight and information that are essential for: (1) cost-effective production of the nanoparticles in large quantity; (2) potential applications of the nanoparticles for *in situ* remediation; and (3) education of students in environmental nanotechnologies.

Nanoscale Bimetallic Particles for *In Situ* Remediation

Wei-xian Zhang
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Environmental Benefits

Nanoscale bimetallic (Fe/Pd, 99.9% Fe) particles are among the vanguard of a new generation of remediation technologies that could provide cost-effective remedial solutions to some of the most difficult sites. Nanoparticles feature large surface areas and extremely high surface reactivity. Equally important, they provide enormous flexibility for *in situ* remedial applications. The primary goal of this research is to continue the research and development of the nanoscale bimetallic particle technology for *in situ* remediation.

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It is apparent that nanotechnology—the science and art of manipulating matter at the atomic and molecular level—has the potential to substantially enhance environmental quality and sustainability through pollution prevention, treatment, and remediation. Potential benefits include improved detection and sensing techniques, removal of the finest contaminants from air, water, and soil, and the discovery of new "green" industrial processes that reduce waste products.

This research assesses the environmental implications of nanotechnology with emphasis on research and development of new nanotechnologies for treatment and remediation. The results of this research will provide valuable information that is essential for: (1) cost-effective production of the nanoparticles in large quantity; (2) applications of the nanoparticles for *in situ* remediation; and (3) education of students in environmental nanotechnologies.

It is expected that results obtained from this research will provide insights into the potential environmental fate and transport of environmental nanoparticles. It is largely unknown how nanostructured materials and other related nanotechnologies might affect human health and interact with the environment. The eventual proliferation and use of nanotechnology could cause unintended consequences such as the creation of new classes of toxins or related environmental hazards.

Section 4. Other Areas

Other Areas - Technologies to develop new processes and better understand existing ones.

Nanotechnology has the potential to be used to develop new “green” processing technologies that 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 generation. This research could focus on the chemical, electronic, or other sectors of the economy.

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.

EPA also is interested in furthering the scientific understanding of the microphysical phenomena of aerosol particles. This 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 (CCN).

Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

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Abstract

Efficient conversion of sunlight into electrical and/or chemical energy is of great technological importance for modern society and future generations. One possibility for utilization of solar energy is based on the ability of small semiconductor particles to function as photocatalysts promoting various oxidation and reduction reactions under sunlight. Titanium dioxide (TiO_2) is the most promising material for such applications because it is an efficient, environmentally friendly, and relatively inexpensive photocatalyst. However, wide technological usage of this photocatalyst is largely hindered because ultraviolet light does not constitute a significant fraction of the solar spectrum that is required for its activation. Any improvement of photocatalytic efficiency of TiO_2 by shifting its optical response from UV to the visible spectral range will have a profoundly positive effect. The main objective of the proposed research is to synthesize and test a novel photocatalyst that consists of small silver or gold nanoparticles covered with a thin TiO_2 shell. Silver and gold nanoparticles are very efficient systems for the interaction with visible light due to the excitation of plasmon resonances. It is expected that, due to the coupling of plasmon resonances in the core with the electron-hole pair generation in the shell, these hybrid Ag/Au TiO_2 nanoparticles will exhibit photocatalytic activity in the visible spectral range, thereby more efficiently utilizing solar energy.

Coating of silver and gold nanoparticles of different sizes with TiO_2 layers of various thickness will be accomplished by sol-gel chemical reactions. High temperature calcination and hydrothermal treatment will be used to convert amorphous TiO_2 layers into the anatase form. Other hybrid nanoparticles include open TiO_2 shell around metal cores, hollow TiO_2 nanoparticles, and Ag/Au@TiO_2 particles with small RuO_2 and Pt clusters attached to their surface. All particles will be characterized by UV-Vis absorption, luminescence and Raman scattering spectroscopy, electron and scanning tunneling microscopy, and x-ray diffraction. The photocatalytic activity of hybrid nanoparticles will be assessed in model experiments using photoreduction of methylviologen and photocatalytic degradation of 4-chlorophenol.

Ag/Au@TiO_2 particles represent a new system with unknown chemical and physical properties.These nanoparticles will exhibit enhanced photocatalytic activity as compared to TiO_2 conventional catalyst. This new material will have positive impact on the development of new solar based technologies including (photo)remediation of environmental pollutants, photovoltaic cells, photochemical splitting of water, and artificial photosynthesis. The synthetic approaches developed for the preparation of Ag/Au@TiO_2 hybrid nanoparticles particles can be extended to include other metals and semiconductors. The proposed research will answer the fundamental question about the possibility of utilization of energy stored in the form of plasmon resonances in metal nanoparticles to carry different chemical reactions.

Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

George Chumanov
Clemson University, Clemson, SC

Environmental Benefits

Efficient conversion of sunlight into electrical and/or chemical energy is of great technological importance for modern society and future generations. Intensive research in this field in recent decades resulted in the fundamental understanding of principles that govern photochemical reactions. This knowledge provides a strong foundation for the development of an artificial photosynthetic system of practical significance. One attractive possibility is to use the photoinduced heterogeneous electron transfer from small semiconductor particles to drive different oxidation and reduction reactions. Titanium dioxide (TiO_2) is considered the most technologically promising material for these applications because it is an environmentally friendly, relatively inexpensive, and potentially efficient photocatalyst. However, the photocatalytic activity of TiO_2 requires the sensitization with ultraviolet radiation that comprises only a small portion of the solar spectrum; thereby limiting the solar efficiency of this material.

The main objective of this proposed research is to develop a novel hybrid photocatalyst that consists of silver or gold nanoparticles encapsulated into TiO_2 shell (Ag/Au@TiO_2). Silver and gold nanoparticles are very efficient systems for capturing energy from the visible portion of the spectrum due to the excitation of plasmon resonances. Thus, the hybrid Ag/Au@TiO_2 nanoparticles will utilize solar energy for photochemical reactions more efficiently than bare TiO_2.

It is expected that the development of this novel photocatalyst will have a positive impact on the advancement of new, solar-based, environmentally friendly technologies. For example: (1) The hybrid photocatalysts will be used for photochemical destruction of the environmental pollutants, polychlorinated phenols. Photooxidation of these pollutants using bare TiO_2 particles was successfully accomplished in the field under solar illumination. However, low solar efficiency of these photocatalysts limits its wide practical application. (2) Based on Ag/Au@TiO_2 nanoparticles, more procedures will be developed for photoremediation of a wide range of organic and inorganic pollutants such as in the removal of heavy metals in purification of water by sun-induced photoreduction processes. (3) This hybrid photocatalyst can be used for producing oxygen and hydrogen from water using solar energy. It is difficult to overemphasize the importance of hydrogen-powered technologies for the future. A vivid example is hydrogen-powered cars, an area of Research & Development, in which governments and the private sector around the world put a great deal of effort and resources. (4) Ag/Au@TiO_2 hybrid nanoparticles have a potential for the photovoltaic devices capable of direct conversion of solar energy into electricity. Devices using TiO_2 nanoparticles sensitized with organic chromophores already have proven to be very efficient for photovoltaics. However, their lifetime and durability is limited by photobleaching of organic molecules under prolonged solar irradiation. This problem is expected to be eradicated for Ag/Au@TiO_2 nanoparticles in which the inorganic metal core functions as a light-capturing chromophoric species. (5) Ag/Au@TiO_2 nanoparticles represent new systems with unknown chemical and physical properties. Further exploration of these materials may result in novel application in other areas such as photonics and microelectronics. (6) The synthetic approaches developed for the preparation of Ag/Au@TiO_2 hybrid nanoparticles can be extended to include other metals and semiconductors. Other hybrid/semiconductor nanoparticles also may find applications in various environmentally friendly, photochemical, solar technologies. The development of Ag/Au@TiO_2 nanoparticles signifies a new field in material science with wide possibilities for practical developments. (7) Finally, this proposed study addresses the fundamental question about utilization of optical energy stored in the form of plasmon resonance for carrying various chemical reactions.

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

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

Sarah C. Larsen and Vicki H. Grassian
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Abstract

This proposal describes 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. The crystal size of zeolites formed during conventional synthesis range in size from 1,000 to 10,000 nm. However, for some applications it would be advantageous to employ much smaller nanometer-sized zeolite crystals, in the range of 10 to 100 nm. Specific advantages to be gained by using zeolite nanostructures include facile adsorption and desorption, the ability to form dense films to facilitate separations applications, and optical transparency. The proposed project has two hypotheses: (1) the properties of zeolites with respect to reactant and product diffusion and light scattering can be significantly improved by using nanometer-sized zeolites and nanostructures (fibers or thin films); (2) these zeolite nanostructures will be superior materials for applications in heterogeneous environmental catalysis.

To test the hypotheses, a two-pronged approach based on the synthesis and application of nanozeolites as environmental catalysts, is envisioned. The objectives of the proposed project are to: (1) synthesize and characterize nanometer-sized zeolites (X, Y, ZSM-5, Beta) and nanostructures (films, fibers); (2) determine the effectiveness of nanometer-sized zeolites for applications in environmental catalysis, such as environmentally benign selective oxidation reactions in cation-exchanged zeolites, NO_x emission abatement, and photocatalytic decomposition of organic contaminants; and (3) investigate intrazeolite reactions using *in situ* spectroscopic methods, such as FTIR and solid state NMR spectroscopy.

The development of nanozeolites for applications in heterogeneous catalysis potentially can lead to solutions of several important environmental problems. These problems span from new methodologies in environmentally benign synthesis to new methodologies in environmental remediation. The results of these studies (e.g., the relationship between the properties of the nanozeolites and catalytic activity) are not limited to the reactions studied here. The results should extend to other types of catalytic reactions and should be important in other applications of environmental catalysis and environmentally benign synthesis.

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

Sarah C. Larsen and Vicki H. Grassian
University of Iowa, Iowa City, IA

Environmental Benefits

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 from 1,000 to 10,000 nm. However, for some applications it would be advantageous to employ much smaller nanometer-sized zeolite crystals ranging from 10 to 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 in the paragraphs that follow.

The partial oxidation of hydrocarbons is significant to the chemical industry because the products are used to convert petroleum hydrocarbon feedstocks into chemicals important in the polymer and petrochemical industries. Liquid phase air oxidations generally are preferred by the chemical industry because of the mild reaction conditions. The conversions of the oxidation processes are typically very low to maintain high selectivity. This is necessary for the desired partial oxidation products to be further oxidized easily under typical reaction conditions. A major motivation for the development of new oxidation routes is the desire to achieve high selectivities at high conversions. These factors, combined with the emphasis on cleaner and safer processes, provide the context for the proposed studies.

This approach of this project to the partial oxidation of hydrocarbons is to eliminate the use of organic solvents through the use of gas phase reactants and products. A clean, inexpensive oxidant, molecular oxygen is used in these reactions. Thus, these reactions have the potential to be green processes that use no solvents and minimal energy with catalysts (i.e., zeolites) that have been used in industry for many years.

Light scattering by the zeolite is a major obstacle to its use as environmentally benign photooxidation catalysts. In previous photooxidation work, it was found that the yield of photooxidation reactions in zeolites strongly depends on the thickness of the zeolite layer. The efficient use of light energy in zeolites requires that light is able to propagate through a long path of zeolite material. However, zeolite crystallites strongly scatter visible light due to their small dimension. Thus, only a thin photoreactive zone is obtained regardless of the zeolite bed thickness. This project uses coated optical fibers, zeolite fibers, and hollow fibers to increase the photoactive region of the zeolite sample.

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 show 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. Another aspect of these transition metal-exchanged zeolites that has been reported in the literature is the photocatalytic activity for the direct decomposition of NO_x and N_2O and the SCR-HC of NO_x. The use of zeolite nanostructures would provide some advantages similar to those discussed for the oxidation reactions such as more efficient light absorption, reactant diffusion, and increased surface area. Coating transparent objects, such as windows, with transparent zeolite thin films may be an important application for these materials. The zeolite thin film would then be activated for NO_x decomposition by sunlight.

The last system to be investigated involves the photocatalytic oxidation (PCO) of volatile organic compounds (VOCs). Photocatalysts, such as TiO_2, can be used to degrade a wide range of organic compounds found in polluted water and air. Much of the research in the last decade has focused on aqueous solution photocatalysis for the decontamination and purification of water. However, gas phase heterogeneous photocatalysis can be an effective way to remove undesirable organic contaminants from air. TiO_2 photocatalysts are active at ambient temperatures and pressures in the presence of UV irradiation and oxygen. Potential applications include purifying enclosed atmospheres such as those found in spacecrafts, offices, industrial plants, and homes. The major pollutants in these applications are oxygenates and aromatics. TiO_2 photo-catalysts have been shown to oxidize toluene, trichloroethylene (TCE), methanol/ethanol, and a number of other organic compounds. The use of nanometer-sized zeolite TiO_2 composites and nanometer-sized TiO_2 will be evaluated for applications in environmental remediation.

Ion-Induced Nucleation of Atmospheric Aerosols

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Abstract

This project will study the role of ion-induced nucleation as a mechanism for producing new nano-sized particles in the atmosphere. The hypotheses are 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 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 previously been done. A microphysical model to interpret the data will be developed. 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 our laboratories that is focused on the homogeneous nucleation by 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, etc.

Ion-Induced Nucleation of Atmospheric Aerosols

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Environmental Benefits

It is necessary to understand nucleation to establish the relationship between anthropogenic and biogenic emissions and atmospheric aerosol effects, including their effects on human health and global climate. Nucleation, for example, can produce high concentrations of very small particles, and recent toxicology research has shown that at a given mass concentration, particles in the 20 nm diameter range have a much greater impact on the lung function of laboratory test animals than approximately 200 nm particles. Nucleated particles also can grow into cloud condensation nuclei (CCN), and can thereby affect precipitation patterns and albedo. Understanding such microphysical phenomena is essential to develop valid models for predicting atmospheric aerosol size distributions and the effects of aerosols on the environment.

This research project focuses on measurements pertinent to ion-induced nucleation. Whether or not ion-induced nucleation actually occurs will be determined, and if so, what species participate. Measurements of ion composition by mass spectrometry will provide the required information on participating species, and measurements of ion mobility spectra in the 0.5 to 5 nm diameter range will provide quantitative information on rates at which particles are formed by ion-induced nucleation.

With separate funding, the formation of new particles by homogeneous nucleation (i.e., by the spontaneous nucleation of low-vapor pressure neutral molecules) is being studied. Such homogeneous nucleation processes do not involve the participation of ions. The work from these studies will be combined to determine the relative roles of homogeneous and ion-induced nucleation in different environments.

Green Engineering of Dispersed Nanoparticles: Measuring and Modeling Nanoparticle Forces

Darrell Velegol and Kristen Fichthorn
Pennsylvania State University, University Park, PA

Abstract

Nanotechnology will be critical to advances in electronics, materials, medicine, and the environment. This is due to their remarkable electronic, optical, magnetic, and mechanical properties. However, a significant limitation of nanotechnology is the ability to produce bulk quantities of dispersed particles. One possibility for dispersing nanoparticles, which have a high area/mass ratio, is to use adsorbed polymer, oligomer, or surfactant molecules; however, disposal of the enormous quantity of additives would involve huge environmental and financial stresses. The expected engineering breakthrough of the proposed research is to identify whether solvation or depletion forces can be manipulated to produce dispersed suspensions of "bare" nanoparticles (i.e., without adsorbed additives).

This research project will address two central questions: (1) What are the magnitudes of the van der Waals, solvation, and depletion forces for nanoparticle systems?, and (2) What variables can we control to alter these forces? To obtain measurements that can answer these questions, the experimental technique of "particle force light scattering" is being developed. This is an experimental method for measuring sub-piconewton nanoparticle forces. This development requires solutions to the electrokinetic equations and the development of a Rayleigh scattering device to measure aggregate breakup. The oral presentation will emphasize: (1) how the electrokinetic theory has been extended to account for triplets, which will be used in the forthcoming scattering experiments; and (2) the results from the force measurements.

The interpretation of the measurements is being conducted using molecular dynamics (MD) simulations. MD simulations are used to characterize the interaction between two model nanoparticles (Lennard-Jones Au solids) immersed in solvent (Lennard-Jones spheres, n-alkanes, and water). Initial results compare solvation forces to van der Waals forces, showing that solvation forces might indeed be used to stabilize particles.

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Pennsylvania State University, University Park, PA

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The central scientific questions to be answered are: What are the magnitudes of the van der Waals, solvation, and depletion forces for nanoparticle systems, and what variables can we control to alter these forces? The research will involve two primary components: (1) development and use of "particle force light scattering" (PFLS), an experimental method for measuring sub-piconewton nanoparticle forces; and (2) use of molecular dynamics (MD) simulations to predict the individual forces. Synergy is essential to this research: PFLS is the first technique capable of measuring the nanoparticle forces, and MD enables the interpretation of exactly how the forces are acting. Measured forces will be compared with bulk stability and rheology measurements.

The expected engineering outcome of this research is determining whether bare nanoparticles can be stabilized by appropriately engineered solvation or depletion force systems. A positive result will avert a huge waste stream of additives that would otherwise be necessary to stabilize nanoparticle systems. To achieve this outcome, the following scientific objectives must be met: (1) MD modeling will be done to delineate the magnitude of van der Waals, solvation, and depletion forces for nanoparticles systems; the modeling will demonstrate the pertinent variables that control these forces. (2) PFLS will be developed, and measurements of nanoparticle forces between silica, titania, and barium titanate particles in water will be performed. Results from the MD modeling will be tested.

Section 5. SBIR

SBIR - Nanomaterials and Clean Technology.

EPA is interested in research that applies the principles of nanotechnology to the areas of environmental monitoring and pollution control with commercialization possibilities. Nanotechnology is emerging as a field critical for enabling essential breakthroughs that may have tremendous potential for affecting several environmental areas. Moreover, nanotechnologies developed in the next several years may well form the foundation of significant commercial platforms.

EPA's SBIR interests include development of: nanoporous filters for removal of gaseous pollutants and particulates from contaminated air streams; nanofiltration membranes for organic solvent recovery; nanoparticulate catalysts for utilization in VOC treatment devices; microelectromechanical (MEMS) systems for use in environmental analytical and monitoring devices; nanolaminated pigments and coating free of hazardous metal contaminants; technology for solvent-free production of nanosized high performance ceramic powders; and technology for the synthesis, assembly, and processing of nanostructured materials and devices for environmental applications.

Development of High Surface Area Material and Filter Media

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Abstract

The 21st Century has begun with the promise of nanotechnology, which is expected to harness novel properties of materials and unique features of phenomena at the nanometer scale. This is likely to lead to significant breakthroughs that will have major implications for environmental protection. Nanotechnologies developed in the coming years will form the foundation of significant commercial platforms. This project focuses on providing a feasibility demonstration of producing nonwoven webs of electrospun nanofibers at a commercial scale for specific environmental applications. The applications targeted are those that require the use of webs such as high surface area material or filtration media. These applications are well suited to address the problems of adsorbing gaseous pollutants (where high surface area of nanowebs is very attractive) or filtering particles smaller than 3 microns from effluent gases or liquids economically (where superior efficiency of nanowebs in capturing submicron particles is very attractive). Alternatively, such filters will increase the particle-loading capacity of the filters, or reduce the pressure drop for a variety of filtration end uses.

Initially, the nanofibers will be electrospun from a solution of polyacrylonitrile in dimethylformamide in the form of a nonwoven mat. This mat will be further processed to convert it into activated carbon fiber NanoFilter media. The web architecture will be tailored to achieve the desired filter performance and gas adsorption by varying fiber diameter, fiber orientation, fiber-packing fraction within the nanoweb, activation level, and nanoweb thickness.

This project will be carried out by eSpin Technologies—a small, high-technology startup company based in Chattanooga, TN, that specializes in providing custom-made electrospun nanofibers—in collaboration with academic centers and major corporations. Together, this group possesses the skills and facilities needed to successfully conduct the work under this project.

At the end of the Phase I and Phase II efforts, eSpin will have successfully developed nanofiber-based high surface area NanoFilters made from activated carbon for the removal of gaseous pollutants. With the active collaboration of eSpin's partners, these products will be commercialized in the United States and in the international marketplace. Apart from providing technology leadership to U.S. companies, the proposed effort also will help fulfill the mission of the U.S. Environmental Protection Agency to improve the quality of air and water.

Development of High Surface Area Material and Filter Media

Jayesh Doshi
eSpin Technologies, Inc., Chattanooga, TN

Environmental Benefits

eSpin's nanofibers can be considered an "infrastructural" technology spawning many potential industries and applications; therefore, the total health and environmental benefit of the technology can be hard to predict. However, some estimates can be offered based on potential impacts of the technology in one example application—air filtration.

Volatile organic compound (VOC) contamination and general indoor air pollution are a growing concern due to adverse effects on health and worker productivity, resulting in a need for an effective means of VOC emission reduction and control to address phenomena such as "sick building syndrome." U.S. Environmental Protection Agency (EPA) studies of human exposure to air pollutants indicate that indoor air levels of many pollutants may be two to five times, and occasionally more than 100 times, higher than outdoor levels.[1] According to the EPA and other sources such as the National Energy Management Institute, Indoor Air Quality (IAQ) problems are on the rise and are causing billions of dollars in lost productivity and health care costs; this makes IAQ one of the most important environmental and health concerns facing Americans today. Therefore, there is a present and growing need for an effective means of VOC emission reduction and control. Government and end-user guidelines are becoming more strict as the costs for noncompliance continue to grow (e.g., health, productivity, insurance, lawsuits, etc.), and governmental emphasis on reducing people's exposure to indoor air pollution is rapidly mounting.

Fortunately, there is an opportunity for activated carbon nanofiber technology to be incorporated into air filtration equipment for enhanced VOC control. Indoor air quality concerns continue to drive the air filter and air cleaner markets. According to an EPA IAQ fact sheet, improving the quality of indoor air environments is likely to boost employee morale and worker productivity, making IAQ controls an important component of operation, maintenance, and energy conservation strategies.[2] Cost-effective technologies are particularly needed for air cleaners with improved ability to remove carbon monoxide and selected VOCs from indoor air systems, for which conventional technology is inadequate.

Beyond the immediate air filtration applications, there also are many similar application possibilities in other complementary industry sectors where pollution and VOC control are important. For example, most military bases pose a threat to the environment where fuels, cleaning solvents, and degreasers have seeped into the ground due to past disposal practices, spills, or leaking storage tanks. Municipal wastewater treatment plant effluents pose serious hazards to populated communities. Leakage from landfills is another concern. eSpin's technology can have dramatic positive environmental impacts if it is adopted and utilized effectively in solving these pressing problems.

Under EPA (SBIR) funding, eSpin has produced a very high surface area activated carbon nanofiber with many significant advantages: (1) Activated carbon nanofiber is effective in absorbing toxic organic compounds from air. (2) The technology has demonstrated its ability to capture particles in water filtration that are smaller than 3 microns. This implies a new benchmark in water filtration. Activated carbon nanofiber also has shown high affinity for chlorinated compounds in water. (3) The integration of eSpin's nanofibers into filter products creates impressive improvements in filter performance—be it particle capture levels, pressure drop, or filter longevity. (4) The cost/benefit ratio of activated carbon nanofiber versus conventional media is economically favorable. (5) An appropriately optimized integrated filtration system would offer many benefits and can be designed to occupy a smaller overall footprint when installed. The compact design and long service life of the filter modules should make them ideal for many traditional and new applications.

Activated carbon nanofiber membranes can provide a filtration system applicable for micro to ultrafine particles in the 100-angstrom range. Such systems can be used to remove carbon black, tobacco smoke, virus, bacteria, pigments, and pyrogens from air and liquid without contributing particle (broken fiber) or out-gassing contamination.

Additionally, providing a small improvement in process yields and product performance over a wide range of separation tasks will have a large financial impact. A platform technology is needed that can be routinely tailored to function under a wide range of conditions, that is robust, cost effective, reliable, and easily disseminated. eSpin Technologies has the potential of fulfilling all of these needs. The current high-value markets for such filter media are ultraclean manufacturing rooms, barriers for use in biotechnology, and medical/pharmaceutical systems. Over the long term, new demands will likely come from micro- and nano-machine markets where separations will be needed to isolate and purify these machines in bulk quantities. The lower value, high-volume markets include food, agriculture, paints, pigments, coatings, chemicals, petroleum, automotive, aerospace, environment, and water treatment. Ultimately, this will set new performance standards for the filtration process, with obvious implications for a broad range of applications—civil, industrial, and governmental.

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[1] U.S. EPA, Office of Air and Radiation. Targeting indoor air pollution. U.S. EPA's Approach and Progress. http://www.epa.gov/iaq/pubs/targetng.html.

[2] EPA Web Site, http://www.epa.gov/iaq/pubs/ventilat.html.

Nanocomposite Anchored Plasticizers

Andrew Myers
TDA Research, Inc., Wheat Ridge, CO

Abstract

Plasticizers are small, often volatile molecules that are added to hard, stiff plastics to make them softer and more flexible. Because they are not directly bound to the polymer chain, they can migrate to the surface and escape from the plasticized material. Many plasticizers are toxic and they create a health risk when they leach out. This is a particular problem for polyvinyl chloride (PVC), which often is used in toys for infants. Plasticizer loss also leads to brittle and unusable materials. A system that immobilized the plasticizing agent within a polymer without compromising other necessary physical properties would find a ready market.

Permanence characterizes the tendency of a plasticizer to remain in a polymer. The proposed research effort will develop a new plasticizer system that is characterized by high permanence and longer product lifetimes, and eliminates the potential for hazardous dermal and/or ingestive exposure from plasticized polymers. The initial effort will target PVC, the highest-volume plasticized commodity plastic, but methods developed by TDA Research, Inc. (TDA) will be easily transferable to other commodity plastics.

TDA proposes to increase the permanence of plasticizers by attaching the plasticizer to the surface of a nanoparticle. The anchored plasticizer still affects the glassy-to-rubbery transition of the host material, yet the permanence of the plasticizer is substantially increased. An added benefit is that the plasticizer-functionalized nanoparticle also improves the barrier properties of the host material and may improve other mechanical and physical properties as well. Phase I research will prepare, incorporate, and test a new plasticizer system for PVC. Phase II efforts will optimize the modified PVC and prepare the material for commercialization through collaborations with TDA's industrial partners.

Plasticizers increase the flexibility and softness of a material, are incorporated into many modern high-volume plastics, and are one of the largest segments of the plastics additives market. Plastic modifiers, including plasticizers and impact modifiers, were a $9 billion business in 1997. If successful, the nanoparticle-anchored plasticizers could have an extremely large commercial impact and enable the production of safer, longer lived plastic materials.

Nanoparticle Anchored Plasticizers

Andrew Myers
TDA Research, Inc., Wheat Ridge, CO

Environmental Benefits

Plasticizers are small, often volatile molecules added to hard, stiff plastics to make them softer and more flexible. Plasticizers are not directly bound to the polymer chain and can be lost by volatilization to air, migration to a solid, or extraction into water or organic solvents. This leaves a brittle, cracked polymer and shortens the useful performance lifetimes of plasticized materials. From an environmental, health, and safety standpoint, the loss of plasticizers to the surrounding medium—whether it is air, water, or soil in the environment or saliva in the mouth of an infant —is an undesired event.

To protect children's health, the U.S. Environmental Protection Agency has proposed a plan to systematically test the toxicity of a number of high-production-volume (HPV) chemicals. The initial focus is on 50 chemicals that pose risks of exposure to children. Included in this list are phthalate esters, which are used to plasticize PVC. Loss of plasticizers is particularly a problem for PVC, as it is the most highly plasticized commodity polymer. Plastic modifiers, including plasticizers and impact modifiers, were a $9 billion business in 1997. Plasticizers represent the largest volume additive for PVC, and widespread use has distributed PVC and phthalate esters around the globe. As such, it is one of the most likely plastic additives to be extracted into the environment. PVC is used in toys for infants, geomembranes, and medical products (e.g., tubing and solution bags).

The efforts of environmental groups have made the public very aware of the presence and potential threat of phthalate esters. The evidence of the carcinogenic nature of phthalates in rodents and the lack of an understanding of the long-term effects of phthalates in the human body have focused attention on products made from plasticized PVC. Although recent studies have indicated the safe nature of several common plasticizers—the International Agency for Research on Cancer (IARC), part of the World Health Organization (WHO), has reclassified di(2-ethylhexyl) phthalate (DEHP) as "not classifiable as to carcinogenicity to humans"—public concern remains high. Some pacifiers and chewable toys are now being marketed with the phrase "PVC Free" to allay parental concerns over the possible ingestion of plasticizers.

A system that immobilized the plasticizing agent within a polymer without compromising other necessary physical properties would reduce environmental and health contamination, improve consumer acceptance of PVC, and create longer lived plasticized materials. One solution is to anchor the plasticizing moiety to the surface of a nanoparticle. If properly designed, the plasticizing nanoparticles would show good compatibility with the host polymer without the loss in physical properties observed with larger particle fillers. The "anchored" plasticizers also would display high permanence—they would remain in the polymer for longer time periods, perhaps indefinitely. In a successful Phase I project (Phase II awarded June 2002), TDA Research demonstrated that plasticizing groups could be anchored to the surface of a nanoparticle, that these nanoparticles were compatible with PVC, and that they had a plasticizing affect on the bulk polymer. TDA's nanoparticles are based on a safe, nontoxic mineral-based core. These inorganic nanoparticles are then surface modified to contain plasticizing and possibly compatibilizing groups. All of these materials can be selected from nontoxic products.

Combinatorial Screening of High-Efficiency Catalysts for Large-Scale Production of Pyrolytic Carbon Nanotubes

Xiao-Dong Xiang

Intematix Corporation, Moraga, CA

Abstract

Plastic composite materials are increasingly used in manufacturing industries (e.g., in automobile components). They need to be coated for protective and decorative purposes. It has been found that electrostatic painting offers approximately four times higher paint transfer efficiency than regular spray painting. This will result in significant reduction of paint usage and volatile organic compound (VOC) emission in the automobile manufacturing process. For this process to work, a conductive plastic with appropriate fillers is required. Of the conductive fillers available, carbon nanotube has proven to be the only viable filler to make strong and conductive plastic parts; however, its prohibitively high cost has deterred broad commercial applications. In this project, Intematix Corporation will address this critical issue using the pyrolytic production of nanotubes. The key to reaching the target cost of $100/kg using the pyrolytic method is the highly efficient catalyst. Existing catalysts are not efficient in reaching the target cost.

Intematix Corporation will leverage its unique expertise in high-throughput screening technologies to develop efficient catalyst compositions that will deliver high-quality nanotubes at the lowest possible cost in Phase I. This will pave the way for broad applications of carbon nanotubes as fillers in conductive plastic parts manufacturing. Preliminary results indicate that the high-throughput screening technologies are dramatically faster and more effective in large-scale screening and identification of promising catalyst leads than the conventional research and development approach.

Combinatorial Screening of High-Efficiency Catalysts for Large-Scale Production of Pyrolytic Carbon Nanotubes

Xiao-Dong Xiang
Intematix Corporation, Moraga, CA

Environmental Benefits

Plastic composite materials are increasingly used in manufacturing industries. Compared to steel, they have the advantages of lighter weight, easier to mold or process, better corrosion resistance, and potentially low cost. Recently, there is tremendous interest in applying plastic composites to automobile body panels, mirror shells, door handles, bumper fascias, and other auto parts. The projected demands for the plastic composite GTX (a nylon and PPO mixture) from the automobile manufacturer alone will exceed 30 million pounds in the year 2004.

The surface of plastic composite parts for automobiles needs to be finished with either a hard coating for scratch and ultraviolet (UV) resistance, and /or color paints for decorative purposes. Currently, 100 percent of the plastic parts are either painted with a sprayer, or electrostatically coated over a spray-painted conductive primer.[1] Electrostatic painting offers about four times the paint transfer efficiency over regular spray painting. This means a significant reduction of paint usage and volatile organic compounds (VOC) emission in the automobile manufacturing process.[1] Electrically conductive plastics will convert the current industrial spray coating process into a much cleaner and efficient primerless electrostatic coating process. Therefore, a conductive plastic composite with adequate mechanical properties is highly desirable for a primerless and environmentally friendly electrostatic coating process. It is estimated that such a primerless electrostatic coating process will save more than 250 million pounds of spray-painted fascia material and corresponding VOC emission used in automobiles alone. A study conducted by United Technologies Automotive (UTA) in Berne, Indiana, indicates that if the current process to produce mirrors for automobiles was converted to electrostatic coating on conductive plastics, the Berne plant alone would cut the VOC emission by 84 tons per year. This will drop their current EPA ceiling to 50 percent.[1]

Because the intrinsically conductive polymers currently available do not yet have adequate mechanical properties (e.g., impact resistance) and environmental stability (e.g., UV resistance), nonconductive plastics with external conductive filler materials currently are chosen to produce conductive plastics. The commonly used conductive fillers are carbon blacks, stainless steel fibers, carbon fibers, and recently, carbon nanotube. Carbon nanotubes are conductive, strong nanometer diameter graphitic tubes with an extremely large aspect ratio. Because of the large aspect ratio and tendency to become entangled into a three-dimensional network in the molten plastic, the fibrils are exceptionally efficient as a conductive additive. It takes less than about 2 percent of fibrils, by weight, to attain the level of conductivity needed for electrostatic painting, about 10^6 ohm-cm. For the same conductivity, about 15 percent carbon powder or carbon fiber, or 7-8 percent stainless steel fibers would be required.[1]

Darrin Keiser, Environmental Manager at UTA's Berne plant, stated that "It was clear that conductive plastics would eliminate the need for a conductive primer and might give us other benefits as well. The problem was that conductive compounds based on the traditional conductive fillers, typically carbon powder and stainless steel fibers, have their limitations." Keiser notes that the 15 percent loadings typical of carbon black degrade the mechanical properties of the base plastic, especially impact and processability. In addition, stainless steel fibers, though used at lower loadings (5-7%), tend to increase tool wear, affect surface quality, reduce processability, and are expensive. UTA demonstrated that for the 2 percent carbon nanotube loaded conductive plastic parts, the paint durability was equal to or better than the finish on the current mirrors. Most importantly, there was no significant difference in mechanical properties between the nanotube loaded conductive and nonconductive parts. The only problem for application of the environmentally friendly carbon nanotube loaded conductive plastic composite, or the nanocomposite, he acknowledged, is the high cost of carbon nanotubes.[1] Therefore, the critical hurdle to proliferate the wide industrial application of cleaner coating technology with carbon nanotube filled conductive plastics is to dramatically reduce the cost of carbon nanotube. The existing price of high quality and purity (>90%) CNT is between $100-1,000/gm, produced mostly for academic and research and development purposes. The industry would need tonnage quantities of CNT and about 2 to 3 orders of magnitude lowered price for commercial scale applications.[2] For example, a market study from Ferro Corporation (a Intematix's commercial partner) suggests that elimination of the priming step for automobile coating would be commercially feasible if nanotube composites are priced near $5/lb at 3 percent CNT loading, which will translate to a target CNT price in the order of $100/lb.

After screening all of the existing methods of synthesizing CNT, we have identified the catalytic conversion of hydrocarbons with a pyrolytic chemical vapor deposition reactor as the only possible approach to reach the $100/lb target. Furthermore, the key to reach the cost target of approximately $100/lb with this catalytic synthesis approach is to develop highly efficient catalysts and a scaled up "continuous" CNT production process to dramatically increase the yield and lower the cost of CNT. In Phase I of this EPA SBIR project, Intematix has discovered the most efficient CNT catalyst ever known with our established combinatorial synthesis and high throughput screening tools. We will develop a scaled up catalytic pyrolysis reactor and process in Phase II to directly produce high-quality CNT at a target cost of $100/lb, using the advanced catalysts discovered in Phase I.

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[1] Miller B. (Consulting ed., from *Plastics World* magazine). Tiny graphite "tubes" create high-efficiency conductive plastics. From the Web site of Hyperion Catalyst International, http:www.fibrils.com/.

[2] Ajayan P, Zhou O. Application of carbon nanotubes. In: Dresselhaus M, Dresselhaus G, Avouris P (eds.). Carbon Nanotubes, Synthesis, Structure, Properties, and Applications. Springer: 2001.

EPA Nanotechnology Grantees Workshop
28 - 29 August 2002
Crystal City, VA

Societal Implications of Nanobiotechnology

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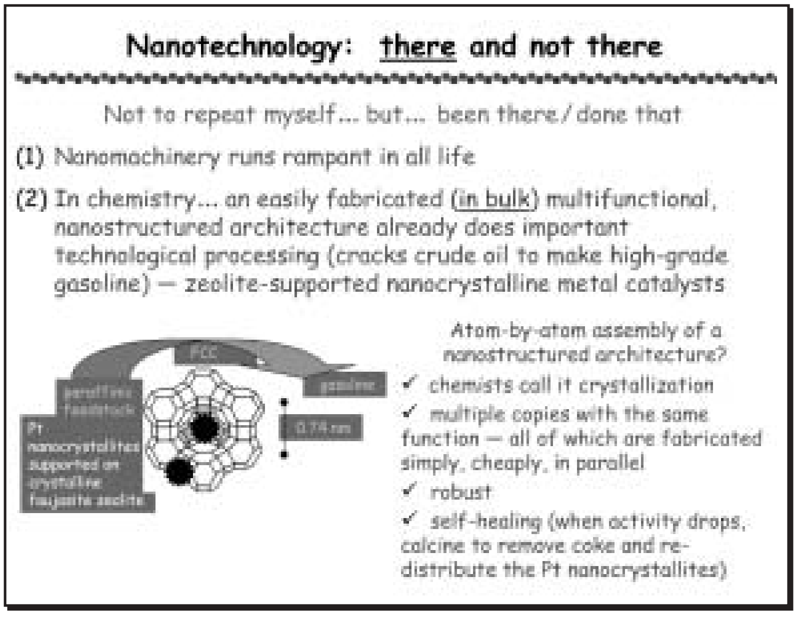
Nanobiotechnology and its societal impact
— The premise of this talk —

Nanobiotechnology is a vision on a nearby horizon — the initial prospects of which are being imagined, designed, and created right now.

Even at this early juncture, we should contemplate what societal impact might arise from a technology based on objects, devices, and processes that blend biomolecular function with *nanoscopic* fabrication and manipulation.

Scientists, governmental program managers and policy makers, educators, industrialists—and citizens—all need to be involved in this undertaking, because technology is rarely implemented without changing society in foreseen and disturbingly unforeseen ways.



Nanotechnology: <u>there</u> and not there

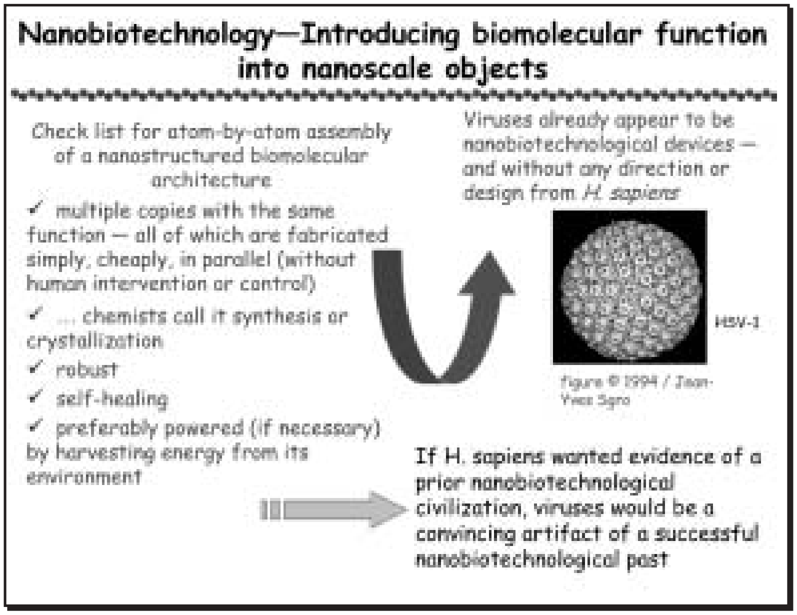
Not to repeat myself... but... been there / done that

(1) Nanomachinery runs rampant in all life

(2) In chemistry... an easily fabricated (<u>in bulk</u>) multifunctional, nanostructured architecture already does important technological processing (cracks crude oil to make high-grade gasoline) — zeolite-supported nanocrystalline metal catalysts

Atom-by-atom assembly of a nanostructured architecture?

- ✓ chemists call it crystallization
- ✓ multiple copies with the same function — all of which are fabricated simply, cheaply, in parallel
- ✓ robust
- ✓ self-healing (when activity drops, calcine to remove coke and re-distribute the Pt nanocrystallites)



Nanobiotechnology—Introducing biomolecular function into nanoscale objects

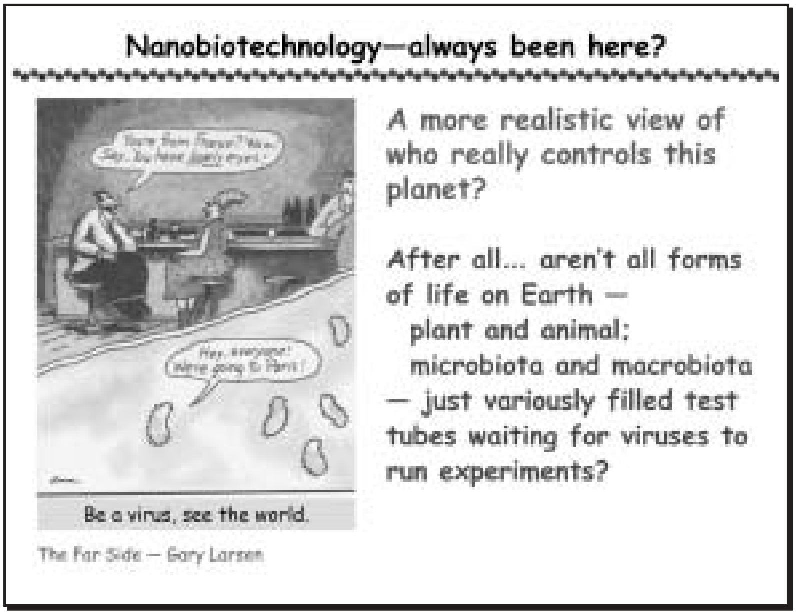
Check list for atom-by-atom assembly of a nanostructured biomolecular architecture

- ✓ multiple copies with the same function — all of which are fabricated simply, cheaply, in parallel (without human intervention or control)
- ✓ ... chemists call it synthesis or crystallization
- ✓ robust
- ✓ self-healing
- ✓ preferably powered (if necessary) by harvesting energy from its environment

Viruses already appear to be nanobiotechnological devices — and without any direction or design from *H. sapiens*

figure © 1994 / Jean-Yves Sgro

If H. sapiens wanted evidence of a prior nanobiotechnological civilization, viruses would be a convincing artifact of a successful nanobiotechnological past



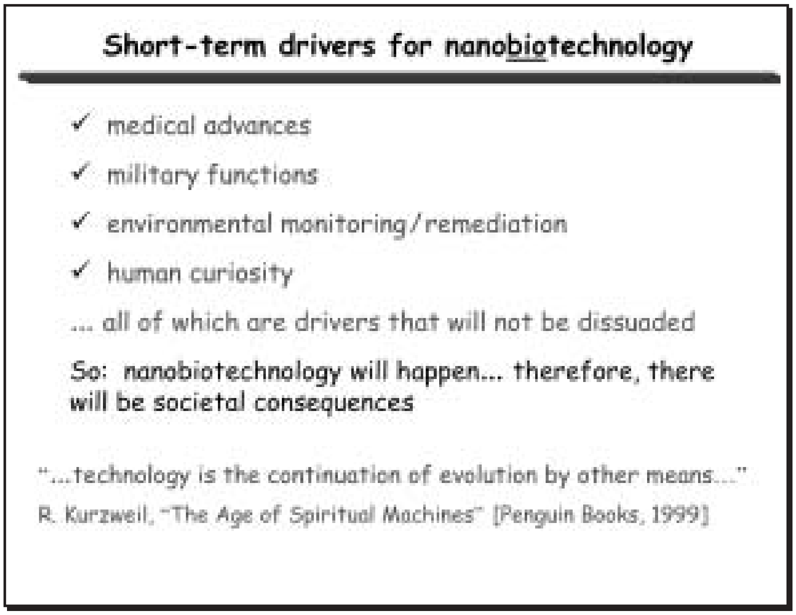
Nanobiotechnology—always been here?

Be a virus, see the world.

The Far Side — Gary Larsen

A more realistic view of who really controls this planet?

After all... aren't all forms of life on Earth —
plant and animal;
microbiota and macrobiota
— just variously filled test tubes waiting for viruses to run experiments?



Short-term drivers for nano<u>bio</u>technology

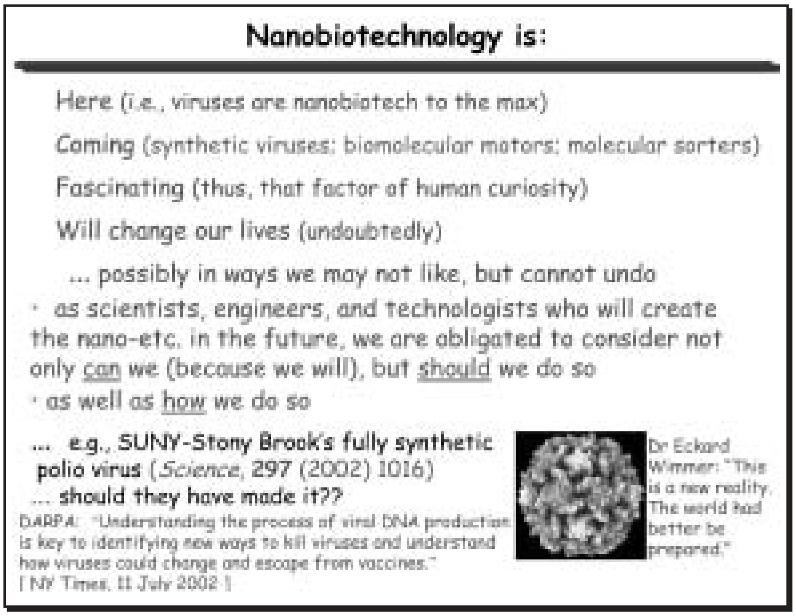
- ✓ medical advances
- ✓ military functions
- ✓ environmental monitoring/remediation
- ✓ human curiosity

... all of which are drivers that will not be dissuaded

So: nanobiotechnology will happen... therefore, there will be societal consequences

"...technology is the continuation of evolution by other means..."

R. Kurzweil, "The *Age of Spiritual Machines*" [Penguin Books, 1999]



Nanobiotechnology is:

Here (i.e., viruses are nanobiotech to the max)

Coming (synthetic viruses; biomolecular motors; molecular sorters)

Fascinating (thus, that factor of human curiosity)

Will change our lives (undoubtedly)

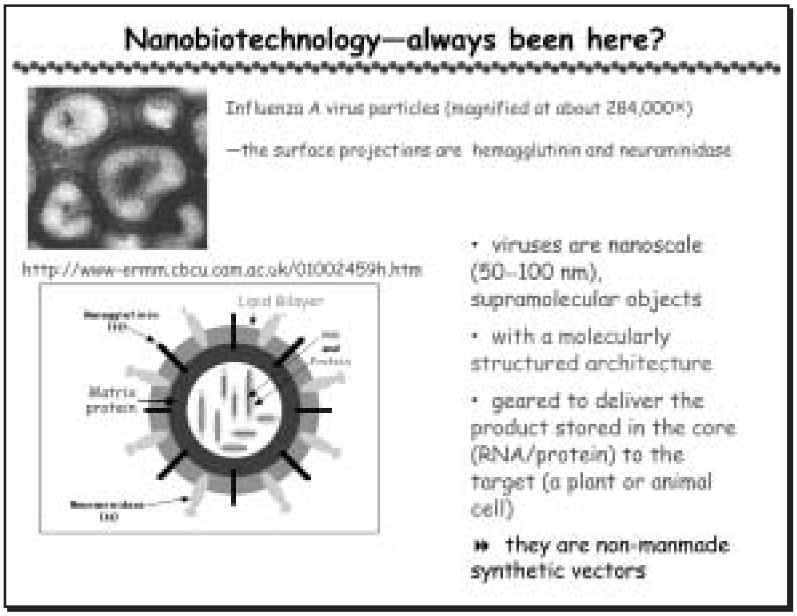
... possibly in ways we may not like, but cannot undo

- as scientists, engineers, and technologists who will create the nano-etc. in the future, we are obligated to consider not only can we (because we will), but should we do so
- as well as how we do so

... e.g., SUNY-Stony Brook's fully synthetic polio virus (*Science*, 297 (2002) 1016)
... should they have made it??

DARPA: "Understanding the process of viral DNA production is key to identifying new ways to kill viruses and understand how viruses could change and escape from vaccines."
[NY Times, 11 July 2002]

Dr Eckard Wimmer: "This is a new reality. The world had better be prepared."



Nanobiotechnology—always been here?

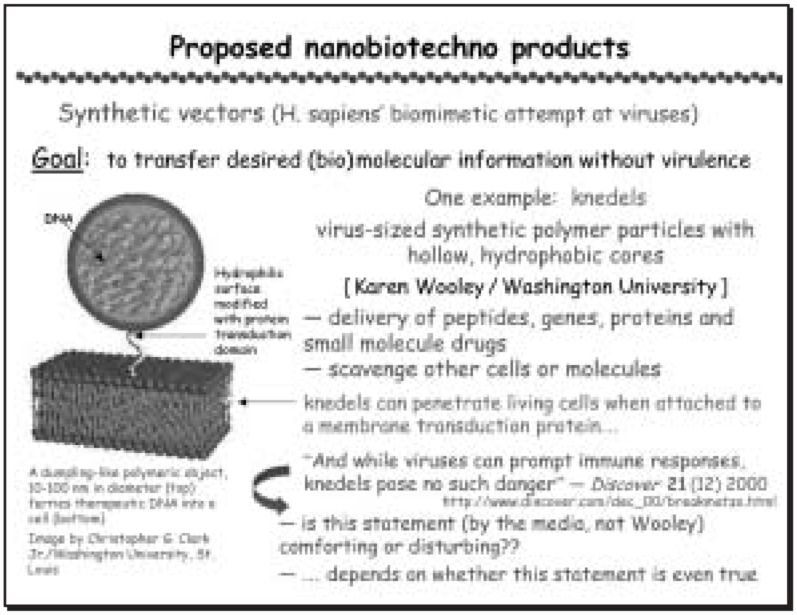
Influenza A virus particles (magnified at about 284,000×)

—the surface projections are hemagglutinin and neuraminidase

http://www-ermm.cbcu.cam.ac.uk/01002459h.htm

- viruses are nanoscale (50–100 nm), supramolecular objects
- with a molecularly structured architecture
- geared to deliver the product stored in the core (RNA/protein) to the target (a plant or animal cell)

➠ **they are non-manmade synthetic vectors**



Proposed nanobiotechno products

Synthetic vectors (H. sapiens' biomimetic attempt at viruses)

Goal: to transfer desired (bio)molecular information without virulence

One example: knedels

virus-sized synthetic polymer particles with hollow, hydrophobic cores

[Karen Wooley / Washington University]

— delivery of peptides, genes, proteins and small molecule drugs
— scavenge other cells or molecules

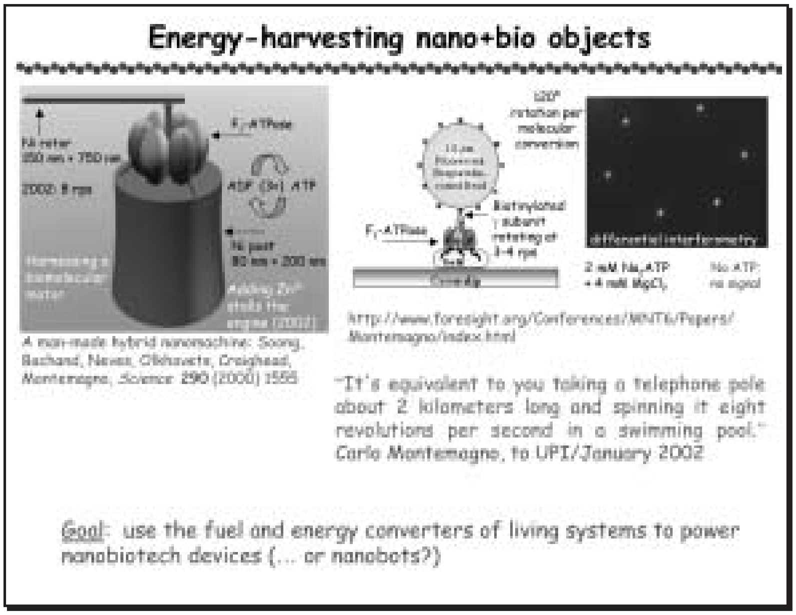
knedels can penetrate living cells when attached to a membrane transduction protein...

"And while viruses can prompt immune responses, knedels pose no such danger" — *Discover* 21 (12) 2000
http://www.discover.com/dec_00/breaknetss.html

— is this statement (by the media, not Wooley) comforting or disturbing??
— ... depends on whether this statement is even true

A dumpling-like polymeric object, 10-100 nm in diameter (top) ferries therapeutic DNA into a cell (bottom)

Image by Christopher G. Clark Jr./Washington University, St. Louis



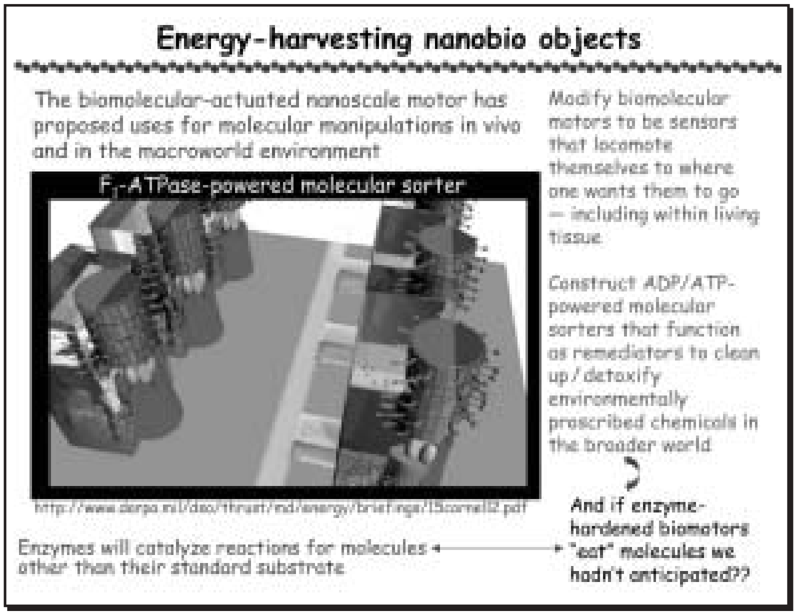
Energy-harvesting nano+bio objects

A man-made hybrid nanomachine: Soong, Bachand, Neves, Olkhovets, Craighead, Montemagno, *Science* 290 (2000) 1555

http://www.foresight.org/Conferences/MNT6/Papers/Montemagno/index.html

"It's equivalent to you taking a telephone pole about 2 kilometers long and spinning it eight revolutions per second in a swimming pool." Carlo Montemagno, to UPI/January 2002

Goal: use the fuel and energy converters of living systems to power nanobiotech devices (… or nanobots?)



Energy-harvesting nanobio objects

The biomolecular-actuated nanoscale motor has proposed uses for molecular manipulations in vivo and in the macroworld environment

F_1-ATPase-powered molecular sorter

http://www.darpa.mil/dso/thrust/md/energy/briefings/15cornell2.pdf

Modify biomolecular motors to be sensors that locomote themselves to where one wants them to go — including within living tissue

Construct ADP/ATP-powered molecular sorters that function as remediators to clean up / detoxify environmentally proscribed chemicals in the broader world

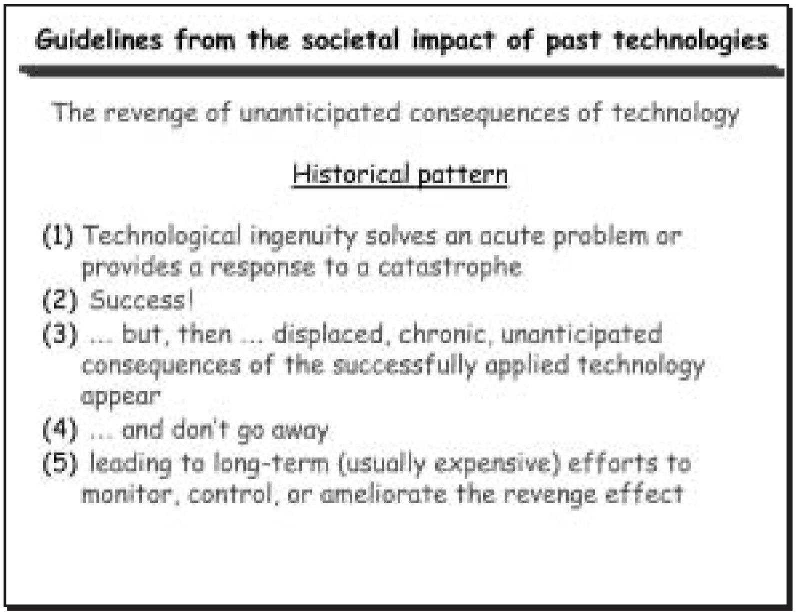
And if enzyme-hardened biomotors "eat" molecules we hadn't anticipated??

Enzymes will catalyze reactions for molecules other than their standard substrate

Guidelines from the societal impact of past technologies

- unanticipated consequences
  —originally proposed by R. Merton, "The Unintended Consequences of Purposive Social Activism" [*Amer. Sociol. Rev.* 1 (1936) 894]
- revenge effects
  —see E. Tenner, "Why Things Bite Back—The Revenge Effects of Technology" [Knopf, 1996]
  "The safety of one technology has a way of creating danger in another.… Like other revenge effect technologies, DDT **defused** one problem by **diffusing** another."
- normal accidents
  —see C. Perrow, "Normal Accidents: Living with High-Risk Technologies" [Princeton University Press, 1999; 1st edition, 1984]
  "… interactive complexity and tight coupling — system characteristics — inevitably will produce an accident… for most of the systems… neither better organization nor technological innovations appear to make them any less prone to system accidents."

… technological improvements — which are undeniable — are accompanied by changes and events, both desired and undesired

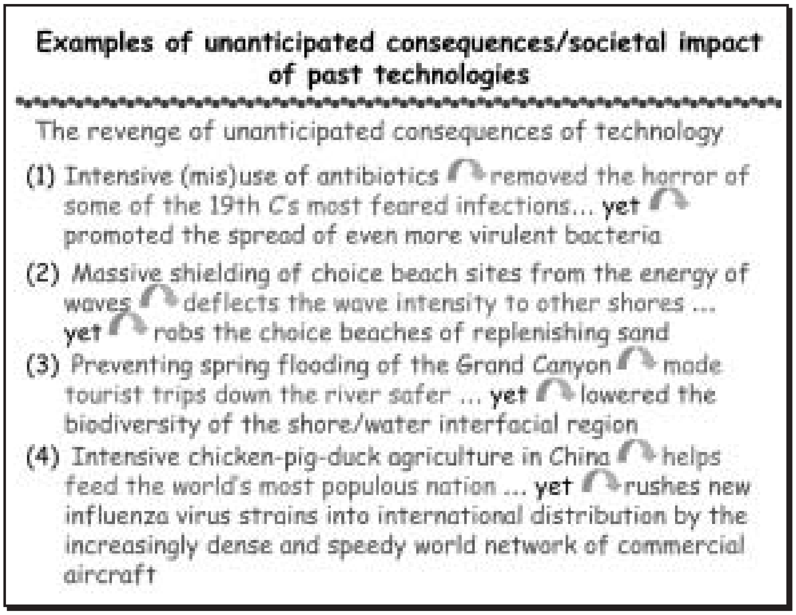


Guidelines from the societal impact of past technologies

The revenge of unanticipated consequences of technology

Historical pattern

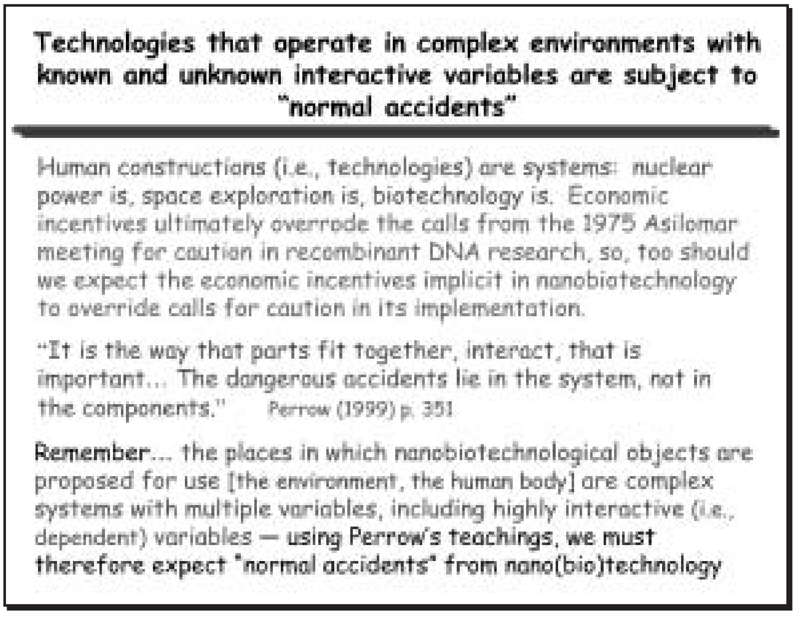
(1) Technological ingenuity solves an acute problem or provides a response to a catastrophe
(2) Success!
(3) ... but, then ... displaced, chronic, unanticipated consequences of the successfully applied technology appear
(4) ... and don't go away
(5) leading to long-term (usually expensive) efforts to monitor, control, or ameliorate the revenge effect



Examples of unanticipated consequences/societal impact of past technologies

The revenge of unanticipated consequences of technology

(1) Intensive (mis)use of antibiotics ↷ removed the horror of some of the 19th C's most feared infections... **yet** ↷ promoted the spread of even more virulent bacteria
(2) *Massive* shielding of choice beach sites from the energy of waves ↷ deflects the wave intensity to other shores ... **yet** ↷ robs the choice beaches of replenishing sand
(3) Preventing spring flooding of the Grand Canyon ↷ made tourist trips down the river safer ... **yet** ↷ lowered the biodiversity of the shore/water interfacial region
(4) Intensive chicken-pig-duck agriculture in China ↷ helps feed the world's most populous nation ... **yet** ↷ rushes new influenza virus strains into international distribution by the increasingly dense and speedy world network of commercial aircraft

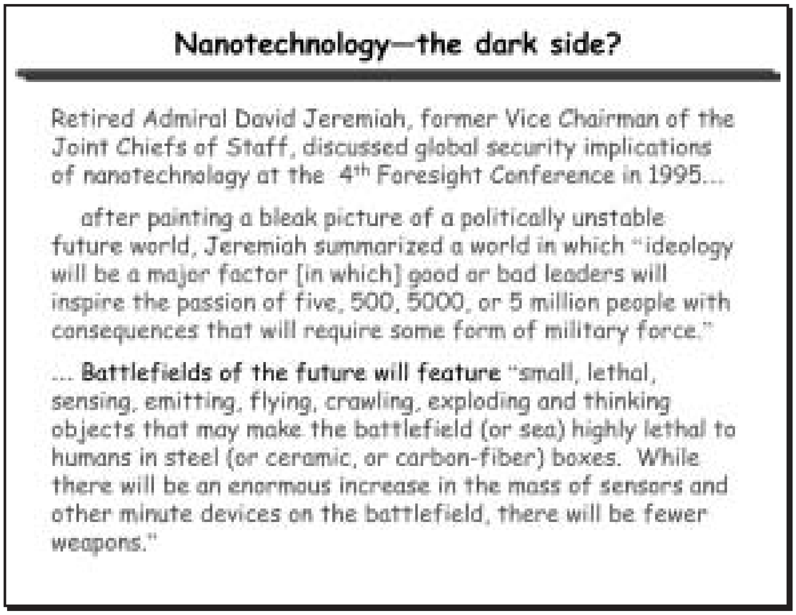


Technologies that operate in complex environments with known and unknown interactive variables are subject to "normal accidents"

Human constructions (i.e., technologies) are systems: nuclear power is, space exploration is, biotechnology is. Economic incentives ultimately overrode the calls from the 1975 Asilomar meeting for caution in recombinant DNA research, so, too should we expect the economic incentives implicit in nanobiotechnology to override calls for caution in its implementation.

"It is the way that parts fit together, interact, that is important... The dangerous accidents lie in the system, not in the components." Perrow (1999) p. 351

Remember... the places in which nanobiotechnological objects are proposed for use [the environment, the human body] are complex systems with multiple variables, including highly interactive (i.e., dependent) variables — **using Perrow's teachings, we must therefore expect "normal accidents" from nano(bio)technology**



Nanotechnology—the dark side?

Retired Admiral David Jeremiah, former Vice Chairman of the Joint Chiefs of Staff, discussed global security implications of nanotechnology at the 4th Foresight Conference in 1995...

after painting a bleak picture of a politically unstable future world, Jeremiah summarized a world in which "ideology will be a major factor [in which] good or bad leaders will inspire the passion of five, 500, 5000, or 5 million people with consequences that will require some form of military force."

... **Battlefields of the future will feature** "small, lethal, sensing, emitting, flying, crawling, exploding and thinking objects that may make the battlefield (or sea) highly lethal to humans in steel (or ceramic, or carbon-fiber) boxes. While there will be an enormous increase in the mass of sensors and other minute devices on the battlefield, there will be fewer weapons."

Lessons from the societal impact of past technologies

An 1883 cartoon urging vigilance in the face of infectious diseases in New York City
[*Time*, 21 January 2002, p. 92]

—It's not a new story—

"Technological optimism means in practice the ability to recognize bad surprises early enough to do something about them." Tenner / p. 353

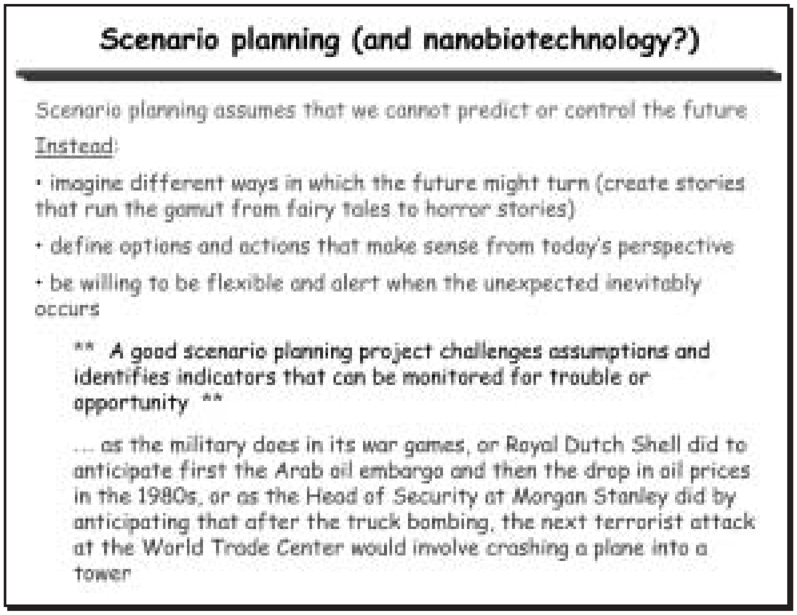
- vigilance
  - **compliance / monitoring / regulations**
- scrutiny
  - **questioning the party line**
- ritual
  - **back-up of computers, e.g.**
- screening
  - **been in an airport lately?**
- finesse
  - **e.g., domesticate a problem organism**
- resilience
  - **technology has consequences, so be ready to roll with unanticipated punches** (A. Wildavsky in "Searching for Safety" [Transaction Books (New Brunswick, NJ) 1988).

Nanobiotechnology and its creators

As the scientists, engineers, and technologists who will be creating the nano-etc. of the future, what can we do?

1) Learn the historical societal impact of prior technologies
2) Make the time to be trained in ethics within the context of science & society
   - rather than assume that our students reach such knowledge via osmosis from over-busy, often-absent, professors and mentors, who may not have been trained either
3) Encourage "uppity" behavior: willingness to challenge the thinking and dictates of those in charge
4) Incorporate scenario planning / war gaming as part of our research production experience
   - So that the individual takes responsibility for her / his contribution to new S&E&T developments
5) Communicate—engage our fellow citizens in a dialogue about the promise / potential problems of new concepts / breakthroughs

All of the above are part of our obligations as citizens



Scenario planning (and nanobiotechnology?)

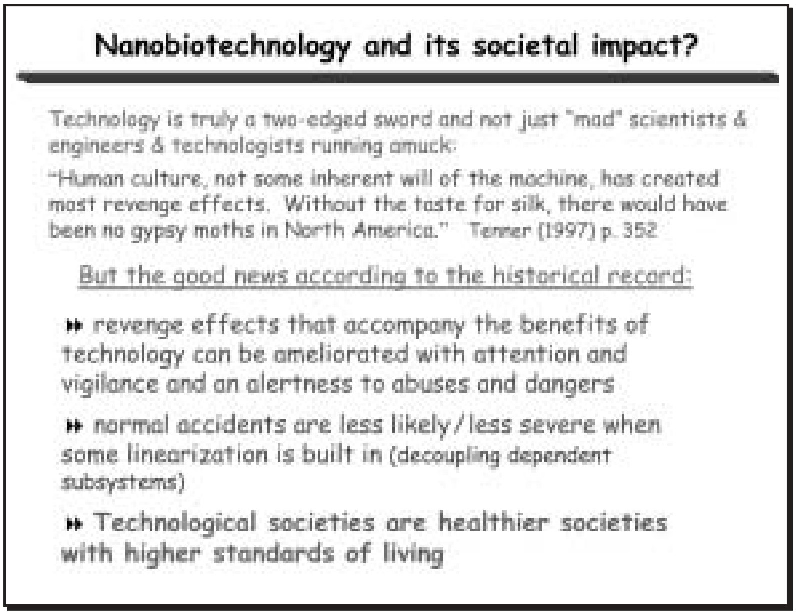
Scenario planning assumes that we cannot predict or control the future

Instead:

- imagine different ways in which the future might turn (create stories that run the gamut from fairy tales to horror stories)
- define options and actions that make sense from today's perspective
- be willing to be flexible and alert when the unexpected inevitably occurs

**** A good scenario planning project challenges assumptions and identifies indicators that can be monitored for trouble or opportunity ****

... as the military does in its war games, or Royal Dutch Shell did to anticipate first the Arab oil embargo and then the drop in oil prices in the 1980s, or as the Head of Security at Morgan Stanley did by anticipating that after the truck bombing, the next terrorist attack at the World Trade Center would involve crashing a plane into a tower



Nanobiotechnology and its societal impact?

Technology is truly a two-edged sword and not just "mad" scientists & engineers & technologists running amuck:

"Human culture, not some inherent will of the machine, has created most revenge effects. Without the taste for silk, there would have been no gypsy moths in North America." Tenner (1997) p. 352

But the good news according to the historical record:

- ⏩ revenge effects that accompany the benefits of technology can be ameliorated with attention and vigilance and an alertness to abuses and dangers
- ⏩ normal accidents are less likely/less severe when some linearization is built in (decoupling dependent subsystems)
- ⏩ **Technological societies are healthier societies with higher standards of living**

Index of Authors, Plenary and Dinner Speakers

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