SYMPOSIUM S

Nanomaterials and the Environment

November 28 - December 1, 2005

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* Invited paper

SESSION S1/G1: Joint Session: LCA Principles
Monday Morning, November 28, 2005
Room 203 (Hynes)

8:30 AM *S1.1/G1.1

Integration and application of Life Cycle Assessment within the design of products and processes - an important step towards sustainable development. Marc Binder and Harald Florin; PE Europe GmbH, Leinfelden-Echterdingen, Germany.

Sustainable development is the strategy to find the balance between the needs of present generation without compromising the ability of future generations to meet their own needs. Sustainable development integrates ecology and economic progress and is aiming for social equality between and within generations. This presentation will give a brief introduction into sustainable development focusing on Life Cycle Assessment (LCA), the most acknowledged and comprehensive method to realize and assess the environmental aspect of sustainable development on a quantitative basis. The methodology of LCA will be presented showing the audience the necessary step when performing an LCA. It will show why it is important to consider the total life cycle and include various environmental impact categories and not only consider primary energy demand and CO2 emissions. The second emphasis will be on the demonstration of a time and resource efficient way to integrate LCA into the design process using existing sources of information (companies internal documentation systems, public-/ commercial LCI databases, and tools). It will be shown how to perform an LCA in an efficient way, which information in what level of detail is necessary, who needs to be involved, what steps have to be performed, and how the study can be used and communicated within the company and to external stakeholders. Goal of this presentation is to give the audience an impression of the possibilities of LCA in general, its role within sustainable development, and show them the relation between effort and benefit of the application of the methodology of LCA within the design process.

9:00 AM *S1.2/G1.2

A Sequential Interindustry Model as an LCA Tool. Stephen H. Levine[1] and Thomas P. Gloria[2]; [1]Civil and Environmental Engineering, Tufts University, Medford, Massachusetts; [2]Five Winds International, Newton, Massachusetts.

LCA is a systems level approach to the evaluation of environmental impacts. Combining LCA with economic input-output (EIO) techniques facilitates the extension of the system boundaries to include all the economic activity indirectly as well as directly required to produce a product or a project. However, traditional EIO models, similar to LCA, provide a minimal temporal description of environmental impact. Yet such a description can be important in determining the environmental burden that the product or project may generate. This is especially true when the life span of the product or project is of long duration. Additionally, inclusion of indirect requirements for production extends the relevant time frame well before the product or project is completed. Probably the extreme example of a project whose production phase is of long duration is the proposed transition from a hydrocarbon to a hydrogen-based economy. Government estimates for this transition are on the order of forty years. The Sequential Interindustry Model (SIM) is an input-output model that by accounting for the time required by production and construction activities can provide the basis for a temporally explicit description of environmental impacts. Recent extensions of the model allow it to account for those resources required during the use and retirement phases as well as the production phase of a product or project. For many products and projects the use phase is of far greater duration than the production phase, even when indirect requirements are accounted for. Thus while all the production activities directly or indirectly required for an automobile may occur over several months the automobile may be on the road for many years. This paper will describe how SIM might be used in conjunction with LCA to strengthen the temporal component of the resulting analysis.

9:30 AM *S1.3/G1.3

The use of Life Cycle Engineering/ Life Cycle Assessment within the design process of production facilities; A business case: Different options of handling overspray. Marc Binder, Johannes Kreissig and Harald Florin; PE Europe GmbH, Leinfelden-Echterdingen, Germany.

This presentation will illustrate how to expand the view by considering the total life cycle in an efficient way into the decision making process and why it is important to do so. The business case will show, how the - ecological and - economic aspects considering the total life cycle of different design options have been considered when determining the preferable design options out of an holistic point of view. Life Cycle Engineering (LCE)/ Life Cycle Assessment (LCA) integrated in the design Process LCE methodology is evaluating ecological, technical and economic aspects considering the total life cycle of processes/products. LCA studies are the basis for the ecological evaluation within LCE. LCE studies are based on material and energy flow information needed while running the facilities or for producing products. LCE is a simulation tool show optimization potentials as well as supporting the decision making process within the design phase. As various databases hold information on ecological impacts of material- and energy production and information on the economic values is available within the involved companies, time consuming research on basic materials and energies is not necessary. Therefore first estimations on scenarios can be made within days to support the decision process not causing any time delay. LCE studies can be conducted within the design process and on existing facilities/products. If LCE is used within the design process optimization potentials can be shown in early stages of the design phase of facilities/products. Integration of LCE within early stages of the design ensures an efficient way of improving the ecological profile of processes and products and reducing the overall costs considering the total life cycle. Business case: Overspray handling of new rear axle paint shop of DaimlerChrysler The methodology of LCE has been integrated into the design process of the new rear axle paint shop of DaimlerChrysler focusing on the handling of the overspray. The design of the facilities have been modeled according to the material and energy flow. This enables the user to run scenario analysis for different design options based on the process flow model. Different design options have been analyzed and arguments were made explicit to support the decision making process. As LCE was part of the whole design process from the beginning, the effort for all participants could have been minimized. Conclusions The case study has shown that the integration of LCE into the design process provides additional information and is not causing any delay of the decision making process. LCE enables a transparent presentation of the economics and ecological impacts on a process bases. Optimization potentials, ecological and economic, can be shown at all stages of the design phase and result in reducing the overall costs and environmental burdens caused by the paint process.

10:30 AM *S1.4/G1.4

Environmental Assessment of Micro/Nano Production in a Life Cycle Perspective. Stig Irving Olsen, Dep. Manufacturing Engineering and Management, Technical University of Denmark, Lyngby, Denmark.

The concept of life cycle assessment (LCA) is build upon the object of assessment, namely the functional unit, i.e. all impacts etc. are related to a specific service or function in the society. In a LCA context, the assessment of emerging technologies like Nanotechnology is challenging due to a number of knowledge gaps. It may not be known exactly what is the function (or functional unit) or what the technology may substitute and production may still be at an experimental level, raising questions about technology or materials choice. For prospective LCA studies methodologies like consequential LCA may be useful because future changes are taken into account. However, it still does not suffice for emerging technologies. In a recent “Green Technology Foresight” project a methodology was developed based on five elements: Life-cycle thinking, systems approach, a broad dialogue based understanding of the environment, precaution as a principle and finally, prevention as preferred strategy. When assessing emerging technologies three levels should be considered. First order effects are connected directly to production, use and disposal. Second order are effects from interaction with other parts of the economy from more intelligent design and management of processes, products, services, product chains etc. and the effect on the stocks of products. An example could be dematerialisation. Rebound effects may be considered as third order effects, like when efficiency gains stimulate new demands, which balances or overcompensates the savings. In the Micro/Nano Production area a range of new possibilities arise both within applications, production technology and materials. The Department of Manufacturing Engineering and Management at The Technical University of Denmark has staked on a joint effort in manufacturing engineering and environmental assessment for eco efficiency improvement. A review of knowledge and studies on environmental assessments in the micro/nano technology area is performed and will be used to further detail the general framework for assessment outlined above to be more specific for micro/nano production.

11:00 AM *S1.5/G1.5

Energy and the Environment: Perpetual Dilemma or Nanotechnology-Enabled Opportunity? Debra R. Rolison and Jeffrey W. Long; Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia.

The global demand for the energy that sustains human-based activity drives extraction, production, and in-use processes that can compromise environmental quality. Yet the global and local environment can only be sustained, cleaned, and preserved through the expenditure of energy. A perpetual irony it may be, but thermodynamics demands that truism. Are there environmentally green opportunities that can be realized by re-thinking and re-designing energy production and power generation from a nanoscopic perspective? Multifunctional materials are prerequisite to deliver high performance in electrochemical power devices, but independent control of the elementary processes that give rise to energy-relevant functionalities is difficult-to-impossible with bulk materials. For example, even with decades of work, fuel cells still require the design of improved structures to maximize the effective area of the three-phase boundary as well as the transport of all species to and from it. These challenges are opportunities awaiting creative nanoarchitectural design. We describe the genesis of a carbon- and ionomer-free fuel-cell electrode in which an ultraporous nanoarchitecture that affects efficient transport of fuel is self-wired with a Pt-catalyzed, three-dimensional electron/proton nanowire.

11:30 AM S1.6/G1.6
Input/Output−But What Does It Really Mean? Mark Goedkoop[2] and Lise Laurin[1,3]; [1]EarthShift, Eliot, Maine; [2]PRe Consultants, bv, Amersfoort, Netherlands; [3]Sylvatica, North Berwick, Maine.

Input/Output databases and LCAs that rely on them exclusively (Input/Output LCA) or partially (hybrid LCA) are relatively new concepts in LCA. Unlike traditional LCA data that is collected for each material or process by painstakingly accounting for the kilograms and joules of everything going into them and the emissions caused by their extraction or manufacture, Input/Output LCA data is collected from national datasets for large sectors. Since the one thing we can easily track from one sector to another is money, the unit of measure is the dollar (or euro, or yen). The advantage of Input/Output databases is that they encompass all products produced in a particular region, and that they take into account impacts that are often ignored in traditional LCA, such as the impacts of marketing and legal activities. The disadvantage is that they provide very coarse data, making it impossible to see the difference between two different types of plastics, for example. The way around this disadvantage is to use a hybrid LCA−use specific data for the plastics and Input/Output data for the rest of the system. There is good input/output data available for the USA, Australia, Denmark and the Netherlands, and an EU database is in the works. In this paper we will explore the uses of Input/Output databases, the limitations and special considerations to take into account while using them, and interesting information we can gain from them.

11:45 AM S1.7/G1.7
Addressing Environmetal Issues for the Automotive Industry. Stella Papasavva, [1]Chemical & Environmetal Sciences Lab, General Motors, Warren, Michigan; [2]General Motors, Warren, Michigan.

The integration of environmental, social, and economic objectives into bussiness decisions and future planning is the path towards sustainable development. Industrial ecology is the integral part of the three components of sustainable developemnt. The principles of industrial ecology are founded in the way natural ecosystems behave. Industrial ecology examines ways to reduce and effectively manage resources in order to maximize economic benefits to the industry and minimize virgin material inputs. This presentation addressess the concept of industrial ecology within the automotive industry providing key areas where it can be implemented.

SESSION S2: Nanotechnology Enabled Sensors for Environmental Monitoring I

Chairs: Prashant Kamat and Vivek Subramanian
Monday Afternoon, November 28, 2005
Room 203 (Hynes)

1:30 PM *S2.1
Low-cost arrayed gas sensors for environmental monitoring. Vivek Subramanian, Josephine Lee and Vincent Liu; Electrical Engineering & Computer Sciences, University of California, Berkeley, Berkeley, California.

The ability to monitor various chemical species in large expanses of currently unmonitored land resources will enable proactive response to environmental problems and will also assist in the development of more accurate models of environmental phenomena. Unfortunately, the widespread deployment of chemical sensors is generally economically unfeasible using currently available sensor technology, primarily since individual sensors are too expensive to be deployed on such large scales. In recent years, there has been tremendous interest in both nanoparticles and engineered organic materials as building blocks for the realization of ultra-low-cost electronic systems, particularly since they may potentially be printed at extremely low cost on cheap substrates such as plastic and paper. More recently, several groups have demonstrated that organic transistor channels show tremendous environmental sensitivity, though they usually lack specificity. Specificity may be achieved using arrays of organic transistors with different channel materials, thus generating unique, highly specific signatures upon chemical exposure. Since such devices may be formed entirely by solution-based processing techniques including inkjet printing, these are an attractive means of realizing low-cost gas sensors for environmental monitoring. We report on our success in realizing such a sensor technology. We describe our development of arrayed sensors based on organic transistors, fabricated using organic materials and various nanoparticle species. We study the repeatability and robustness of the organic transistor gas sensors, and study their usability in the detection of environmetal contaminants, with our initial focus aimed at organic solvents often used in industrial applications. Initial results indicate that robust, albeit slow, cycling of organic sensors for reliable detection of several solvents is highly possible. This is promising, since most environmental monitoring applications will not require high speed of response. We also demonstrate simultaneous differential sensing of various chemicals, thus establishing the potential of these sensors in electronic noses.

2:00 PM S2.2
Bi-Modal Interactions of NAD(P)H with Cyclodextrin-Modified Au Nanoparticles in Aqueous Media. The Fluorescence Study. Jian Liu, Ganesh Arumugam, Cuihua Xue and Kumaranand Palaniappan; Department of Chemistry, Michigan Technological University, Houghton, Michigan.

A new type of water-soluble, cyclodextrin-modified gold nanoparticles has been synthesized in DMF by using a one-step approach. The specially designed, positively charged beta-cyclodextrin brings not only the regular host capability of this receptor, but also the additional electrostatic force for the additional affinity of this molecule to negatively charged substrates. Thus, gold nanoparticles modified with this type of artificial host may serve as a novel nano-probe for various chemical and biological important species in aqueous media. To this end, nicotinamine adenine dinucleotide (NADH) and nicotinamide adenine dinucleotide phosphate (NADPH) have been used as the target substrates for the molecular recognition study with these receptor modified gold nanoparticles in the physiological conditions. Interestingly, we found that there were two interaction models between these co-factors and nanoparticles in the fluorescence study. One was the complexation-induced enhancement of the fluorescence when these substrates were included inside the cyclodextrin cavities. The other was the diffusion controlled physical contact between these co-factors and the particle surfaces, which led to the quench of their fluorescence. Mediation of these two competitive models on the influence of the cofactors' fluorescence could be achieved by introduction of an optical inert substrate, such as adamantanecarboxylate in the same solution. It is expected that this type bi-modal interactions of metal nanoparticle with target substrates may serve as a new mechanism for the development of future nanosensors.

2:15 PM S2.3
Specific Gas Detection Using Piezoelectric Microcantilevers Array. Qing Zhu, Jose Bermudez, Wan Y. Shih and Wei-Heng Shih; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Piezoelectric lead magnesium niobate-lead titanate solid solution (PMN-PT)/copper (Cu) microcantilevers were made from 8-10 micron thick freestanding PMN-PT films bonded to 1-3 micron thick Cu by electroplating. Microcantilever arrays were fabricated using wire-saw machining. Different receptors e.g., alumina (Al2O3) and silica (SiO2) powders of the target gases, e.g., dimethyl methylphosphonate (DMMP), a simulant of nerve gas, are coated on the tips of different microcantilevers in the array. Detection of the target gas is achieved by monitoring the cantilever resonance frequency shift due to the absorption of the target gas to the immobilized receptors. In addition, to increase the effectiveness of receptor, self-assemble monolayer including 3-Mercaptopropyltrimethoxysilane (MPS) and 11-Mercaptoundecanoic Acid (MUA) with Cu2+ ions as well as tetraethoxyorthosilicate (TEOS) silicon oxide precursor as receptors are also studied. Using a set of receptors of different adsorption kinetics (destructive or nondestructive), a unique detection profile can be established for each target gas. Results of the detection profiles of DMMP, NH3, and H2O will be discussed using several receptors. Furthermore, the PMN-PT microcantilever's mass detection sensitivity as well as their DMMP concentration detection limit will be discussed

3:30 PM *S2.4
Immobilization of Lead-Specific DNAzyme on a Microfluidic Device for Pb(II) Detection. Donald M. Cropek[1], Xiaofeng

Wang[1,2], Carla B. Swearingen[1,2], Daryl P. Wernette[2], Charles S. Henry[3], Yi Lu[2], Jonathan V. Sweedler[2] and Paul W. Bohn[2]; [1]USA Construction Engineering Research Laboratory (CERL), U.S. Army Corps of Engineers, Champaign, Illinois; [2]Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois; [3]Department of Chemistry, Colorado State University, Fort Collins, Colorado.

Heavy metals are a ubiquitous and troublesome class of pollutants, and lead occupies a prominent position as a contaminant requiring constant attention. In order to develop a reliable and sensitive device for in situ measurement of lead in ground water, a Pb(II)-specific DNAzyme molecular beacon is immobilized onto poly(methyl methacrylate) (PMMA) microchip that is then assembled with a microfluidic-nanofluidic hybrid multilayer device. This DNAzyme fluorescence sensor contains a fluorescein tagged DNAzyme with an amino moiety and the quencher tagged complementary substrate strand. The fluidic movement of the sample is precisely controlled by application of an electric field across distal ends of the channels. A nanoscale fluidic molecular gate consisting a thin polymeric membrane along the channels can manipulate fluid flows and perform molecular separation on tiny volume of material. In the presence of lead, a fluorescence signal can be generated by the cleavage of the substrate DNA and removal of the quencher. Hybridization of the immobilized DNAzyme with its complementary substrate strand will regenerate the sensor chemistry, allowing multiple sensing cycles. By introducing different DNAzymes at different locations in the detection channel, it is possible to identify multiple heavy metal ions with a single injection.

4:00 PM *S2.5

Semiconductor Nanostructures as Smart Materials for Simultaneous Detection and Degradation of Organics from Air and Water. Vaidyanathan Subramanian[1], Istvan Robel[1,3], Kaylie L. Young[1], Joan F. Brennecke[2] and Prashant V. Kamat[1,2]; [1]Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; [2]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana; [3]Department of Physics, University of Notre Dame, Notre Dame, Indiana.

Semiconductor nanoparticles are useful as photocatalysts for environmental remediation. The emission properties of these materials can also be used to sense the chemical environment and probe the clean up process. The photoemission of ZnO and CdS thin films cast from colloidal particles provides a direct way to monitor the presence of carboxylic acids such as CH3COOH and HCOOH. these chemicals in the gas phase can be detected by monitoring the green emission of ZnO films. Similarly aliphatic and aromatic amines can be detected using the emission from CdS quantum dots. The photocatalytic activity of ZnO films also initiates the degradation of these chemicals eventually leading to their mineralization. Continuous monitoring of ZnO emission also provides a means to monitor the course of degradation and the effectiveness of clean up process. The degradation process can be significantly enhanced by introducing TiO2 catalyst. The use of ZnO/TiO2 composite films for the remediation of gas phase contaminants is discussed.

4:30 PM S2.6

Real-time, in situ, Multiplexed Biodetection and Quantification of Pathogens Using Piezoelectric Microcantilever Arrays. John-Paul McGovern, Qing Zhu, Joseph Capobianco, Wan Y. Shih and Wei-Heng Shih; Materials Science and Eng, Drexel University, Philadelphia, Pennsylvania.

Rapid, precise, specific, and in situ detection of biological agents is of great need in today's world of bioterrorism as well as in the ever growing field of medical diagnostics. To this end, piezoelectric microcantilevers have been developed to perform direct detection and quantification of biological agents and pathogens in situ. Bacillus anthracis spores, Bacillus globigii spores (a non-viral B. anthracis simulant), and Salmonella typhimurium are detected and quantified herein. The microcantilevers are composed of a piezoelectric ceramic layer bonded to a non-piezoelectric layer, glass or metal, and are characterized by specific resonant frequencies when driven by an alternating current. These resonant frequencies can be monitored and, as has been shown in previous work, the shift of their position to lower frequencies can be interpreted as a mass attached to the sensor tip. The monitoring of these frequencies is accomplished by monitoring the impedance of the cantilever, thus providing for an all electrical means of detection and eliminating the need for laser monitoring and allowing for the construction of compact and easily monitored array systems. Furthermore, by taking advantage of the natural selectivity of antibody-analyte systems, the tips of these cantilevers can be functionalized such that specific recognition of the aforementioned cells contained within a mixture of biological agents and pathogens can be performed. When each microcantilever in an array is functionalized with a specific antibody, multiplexed detection of an unknown mixture of cells and proteins can be performed along with simultaneous determination of the concentrations of each analyte. The present lower detection limit of Bacillus spores is 5000 cfu/ml, while the sensitivity of cantilevers used for current experiments is 4 x 10^{-12} g/Hz. Preliminary data using a flow cell system shows a frequency shift increase by a factor of 5 for a given concentration of B. globigii. Current work aims to manifest this frequency shift increase in a lower detection limit for each biological systems studied.

4:45 PM S2.7

Electrochemical Sensor for Pyrene Assay: Based on Molecularly Imprinted Poly(2-mercaptobenzoimidazole) on Gold Electrode. Ning Luo and Kim R. Rogers; U.S. EPA, National Exposrue Research Laboratory, Las Vegas, Nevada.

Molecularly imprinted materials mimic antibody-based behaviors on sensors and provide the capacity for molecular recognition of polycyclic aromatic hydrocarbons (PAHs) and their biomarkers. The ultimate goal of the present research is to develop inexpensive, field-portable, electrochemical sensors for the detection of PAHs. In order to increase the sensitivity for PAHs, ferricyanide was used as a redox indicator. In the present contribution, the investigation is focused on the feasibility of using molecularly imprinted polymer (MIP) as the sensing layer for pyrene. To fabricate a sensor, a disk gold electrode was cleaned carefully and then submerged into an ethanol solution containing 2-mercaptobenzimidazole (2-MBI, 5 mM), KCl (25 mM), pyrene (5 mM), and water (25 %, v/v). After the self-assembled monolayer (SAM) of 2-MBI formed, the defects of the SAM were filled with n-dodecanethiol. The 2-MBI was polymerized using cyclic voltammetry with 16 scans at a scan rate of 1 V/s. Template molecules were removed with toluene and ethanol. A standard three-electrode Pyrex glass cell was used for all electrochemical measurements at ambient temperature. Pt wire and Ag/AgCl (saturated KCl) electrodes were employed as the counter and reference electrode, respectively. The bare gold or poly(2-MBI)-coated gold electrode was used as working electrode. Voltammetric measurements were performed with a CHI 620 Electrochemical Analyzer in 100 mM $NaClO_4$ aqueous solution containing 10 mM potassium ferricyanide and 50 % ethanol at a potential range of 500 to -200 mV, a scan rate 50 mV/s, initial voltage 500 mV, and sensitivity at 10 μA/V. Voltammetric measurements showed that the formation of the poly(2-MBI) caused a decrease in the peak current from 30 to 16 μA, indicating the insulation property of the polymer. When the layer formed in the absence of pyrene, the current almost completed blocked. To detect pyrene using the pyrene imprinted polymer, square wave voltammetry was conducted in ferricyanide aqueous solution at a potential range of 500 to -200 mV, frequency 15 Hz, amplitude 25 mV, quiet time 2 s, and sensitivity 50 μA/V. A significant decrease (4.3 μA) in peak current was observed for the pyrene concentration of 2.6 μM. The pyrene calibration plot was biphasic with a steeper slope at concentrations between 0 and 0.15 μM pyrene. This analytical strategy shows feasibility for measurement of pyrene and probably for the other PAHs. The optimization of molecularly imprinted poly(2-MBI) and the selectivity with other PAHs is under investigation.

SESSION S3: Synthesis of Environmentally Benign Nanocomposites

Chairs: James Hutchison and Ajay Malshe
Tuesday Morning, November 29, 2005
Room 203 (Hynes)

8:00 AM S3.1

Abstract Withdrawn

8:15 AM S3.2

Synthesis and Processing of Biodegradable LDPE-Starch Nanocomposite. Funda Inceoglu[1], Yusuf Ziya Menceloglu[2] and Cem Mustafa Inan[3]; [1]Material Science and Engineering, Sabanci University, Istanbul, Turkey; [2]Material Science and Engineering, Sabanci University, Istanbul, Turkey; [3]Material Science and Engineering, Sabanci University, Istanbul, Turkey.

Biodegradable polyethylene (PE)-starch nanocomposite having superior mechanical and optical properties have been successfully prepared in a twin-screw extruder. The predispersion of clay particles in the starch matrix have provided high tensile strength, modulus and optical clarity in the final product. The dispersion of the clay particles have been investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) and it was observed from XRD that starch molecules intercalated between the clay galleries. Most of the starch molecules in PE films has been degraded rapidly in the presence of enzyme that digests both amylose and amylopectin chains and results in the liberation of glucose molecules.

8:30 AM S3.3

Nanomaterials to Bridge the Gap between Laboratory and Field Studies in Environmental Science. Christine F. Conrad[3] and Michael J. Kelley[1,2]; [1]Applied Science, Coll. of William & Mary, Willamsburg, Virginia; [2]Free Electron Laser Dept., Jefferson Lab, Newport News, Virginia; [3]Center for Environmental Kinetics Analsysis, Pennsylvania State University, University Park, Pennsylvania.

A recurring issue for environmental science is the connection between well-defined laboratory studies and the complexity of the field situation. In the area of processes mediated by mineral surfaces, specially-crafted nanomaterials offer a bridge. Mineral surface chemistry such as gamma alumina has been replicated on large-area (several m2) aluminum foil, followed by the deposition of oxide coatings such as iron and the uptake of contaminant metals such as lead. Detailed spectroscopic studies comparing these planar proxies to particulate alumina find close similarity in their chemical behavior. A special advantage of the planar materials is that they can be implanted in a field site and readily recovered for further study. We describe the results of these experiments.

8:45 AM S3.4

Nanoscale Magnets and Their Use in Biological And Environmental Engineering. Cafer T. Yavuz[1], J. T. Mayo[1], William W. Yu[1], Sujin Yean[2], Amy T. Kan[2], Joshua C. Falkner[1], Mason B. Tomson[2] and Vicki L. Colvin[1]; [1]Chemistry Dept., Rice University, Houston, Texas; [2]Department of Civil and Environmental Engineering, Rice University, Houston, Texas.

Uniform size and highly monodisperse (? = 5-10%) magnetite (Fe3O4) nanocrystals were synthesized utilizing two different solvothermal reactions of iron (III) species (FeOOH and Fe(acac)3). Wide range of sizes (4, 6, 8, 11, 12, 14, 20, 26, 33 nm) achieved, characterized and used for further applications. Utilization of size dependent magnetic properties, i.e. superparamagnatism, controllable magnetic operations are proposed. First ever size dependent magnetic separation was studied and applied to polydisperse samples successfully. Iron content of effluents was determined by ICP-AES. Magnetic field strength vs. percent retention of individual sizes reported. Magnetic multiplex separation method is created and proposed for bio-magnetic separations. Superparamagnetic limit for magnetite (Rc $\sim$ 16 nm) is experimentally reported for the first time. Arsenic adsorption to nanosize magnetite is shown and compared to bulk material as a proof of wide variety of applications. It's found that 11.72 nm nano magnetite had 1000 better adsorptivity of Arsenic than commercial nano magnetite. Also better was the stability and the recyclability. More biological magnetic separations are under investigation.

9:00 AM *S3.5

An Examination of the Environmentally Benign Means of Synthesizing Nanostructures Using the Responses of Bio-form Derivatives as Stimuli. Gayatri Natu[1], Ajay Malshe[2] and Murali Sastry[3]; [1]Chemistry, Indian Institute of Technology, Kanpur, Uttar Pradesh, India; [2]MEEG, University of Arkansas, Fayetteville, Arkansas; [3]Materials Chemistry, National Chemical Laboratory, Pune, Maharashtra, India.

The research in health and safety issues related to nanomaterials synthesis is vitally important for leading the rapid growth of nanotechnology towards an eco-friendly way. The syntheses of nanoparticles or nanostructures via the mechanical top-down approaches or the chemical bottom-up approaches are contemplated to lead to serious environmental safety concerns due to the possible particulate matter (PM) diffusion or the usage of environmentally hazardous synthetic chemicals. The novel field of biological synthesis of nanoparticles by using the responses of biomolecules and organic structures obtained from/contained within various life forms as stimuli may promise to provide environmentally benign means of synthesizing nanometer-scale particles and structures. The records of plants and microorganisms used for the synthesis till date show the procedures to have a biological safety level BL1. The procedures are simple, easily reproducible, cost-effective, putatively easy to scale-up, and have the potential to be environmentally benevolent by providing a safe way of bioremediation.

10:00 AM S3.6

Plasma assisted-MOCVD synthesis of N-doped TiO_2 for visible-light photocatalysis. Scott Edward Buzby[1], Chaoying Ni[1] and S. Ismat Shah[1,2]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Department of Physics and Astronomy, University of Delaware, Newark, Delaware.

Most organic pollutants consist of harmful constituent chemicals. Semiconductor photocatalysis uses light to activate semiconductor catalysts to break down these chemicals. Among the most promising compounds for photocatalysis applications is titanium dioxide. TiO_2 is stable in aqueous media and is tolerant of both acidic and alkaline solutions. It is inexpensive, recyclable, reusable and relatively simple to produce. It also forms nanostructures more readily than many other catalysts. Furthermore, its redox potential is appropriate to initiate a variety of organic reactions. The large bandgap of TiO_2 lies in the UV range, so that only 5-8% of sunlight photons have the requisite energy to activate the catalyst. Therefore, a visible-light activated catalyst would be much more effective. There are several known ways to increase the efficiency of a photocatalyst. Doping the catalyst with Nitrogen was used in order to increase its effectiveness by introducing trapping sites. The trapping of electrons at these sites effectively increases hole lifetime and, therefore, the probability that they will reach the surface without suffering recombination to participate in the desired photocatalysis reaction. N-doped TiO_2 nanoparticles were synthesized by plasma assisted-metalorganic chemical vapor deposition (PA-MOCVD) in gaseous ammonia. Titanium tetra-isopropoxide was used as a Ti-precursor, while a RF-Plasma was used to decompose the ammonia gas. The N-doped TiO_2 nanoparticles were deposited on stainless steel mesh under a flow of Ar and O_2 gases at 600^{O}C in a tube furnace. Several analytical tools, such as XRD, TEM, XPS and UV-VIS Spectroscopy were used to investigate the nanoparticles structure, composition, and optical properties. The photocatalytic activity of the prepared N-doped TiO_2 samples was tested by degradation of 2-chlorophenol in aqueous solution using a 100W visible lamp. The efficiency of photocatalytic oxidation of 2-CP was measured using HPLC. Results obtained revealed the formation of N-doped TiO_2 samples as $TiO_{2-x}N_x$, and a corresponding shift in the band gap. Result of the visible light photocatalytic oxidation of the 2-CP will be presented.

10:15 AM S3.7

Molecular Engineering and Design of Environmentally Benign Nanocomposites. Mary Jo Biddy[1], Michael J. Tupy[2] and Juan J. de Pablo[1]; [1]Department of Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; [2]Process Solutions Technology Development Center, Cargill Inc., Wayzata, Minnesota.

Rising concerns over the stability, cost, and environmental impact of petroleum-based lubricants are generating significant interest in finding environmentally benign alternatives. Naturally-occurring vegetable oil products are derived from renewable resources and have shown promise for industrial applications ranging from biodegradable vegetable oil-derived polymers to vegetable oil-based transformer oils and lubricants. The possibilities for developing vegetable oil-based products that will replace traditional petroleum-based products are far reaching. Our research has primarily focused on the development of molecular models capable of describing and predicting the thermodynamic and transport properties of vegetable oil-based lubricants. Methods and models have been developed to predict viscosities and densities that agree with experimentally observed values for pure triglycerides (the main components of vegetable oils) and their mixtures. The low-temperature properties of vegetable oils, which are a major limitation for their use as lubricants, have also been characterized using molecular modeling methods. The molecular-level insights obtained from this work are currently being applied to aid in the design of vegetable oils suitable for the most demanding of applications. These models and methods have been extended to the study and development of novel vegetable oil-based products that include composites formulated using nanoparticles. We will present both simulation and experimental results on these systems. It has been found that the viscoelastic properties, as well as the moduli and softening temperatures of these composites can be manipulated based on the size, composition, and type of nanoparticle incorporated. The effect of the vegetable oil chemical composition, as well as molecular architecture, has also been explored.

10:30 AM *S3.8

Toward Environmentally-benign Nanomanufacturing: Patterning Organized Metal Nanoparticle Arrays Using Biopolymer Scaffolds. James E. Hutchison, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon.

Nanotechnology promises considerable benefit to society and the environment. However, the products of nanotechnology and the manufacturing processes used to produce these products may pose threats to human health, the environment, worker safety, and security. The challenge will be to develop nanotechnology to provide maximum benefit, while minimizing the hazards. Green chemistry and engineering principles can be adopted to guide the early stages of product and process development to meet this challenge. Discoveries in nanoscience will provide new opportunities for the development of sustainable technologies. In this presentation, I will discuss how green chemistry and engineering principles can guide the responsible development of nanotechnology and how nanoscience can enable the discovery of greener products and processes. To illustrate the application of these principles in nanoscience, I'll describe an approach to patterning nanometer-scale structures through a convenient, high-precision process. Our approach is based upon functional group-directed assembly of well-defined nanoparticle building blocks. I will focus primarily on our efforts to organize ligand-stabilized gold nanoparticles onto DNA templates to form extended 1- and 2-dimensional assemblies. One of the key features of scaffolding approaches that rely on DNA templates is the precision with which the 2- and 3-D structures can be controlled. In addition to particle size and interparticle spacing, the pattern and size of the assembly can also be controlled. The spacing between neighboring nanoparticles can be tuned at the molecular level by utilizing nanoparticles possessing ligand shells of varying thickness to achieve Angstrom-level resolution at spacings of 1.5, 2.1, and 2.8 nm. This "bottom-up" approach will be compared to more traditional "top-down" lithographies to assess the performance and waste production of the methods.

11:00 AM S3.9

Inorganic Fullerene-like Nanospheres: New Superior Materials for Enhanced Lubrication. Alla Zak[1], Yekimov Sergei[1], Niles Fleischer[1], Menachem Genut[1], Lev Rapoport[3] and Reshef Tenne[2]; [1]NanoMaterials, Ltd., Rehovot, Israel; [2]Weizmann Institute of Science, Rehovot, Israel; [3]Holon Academic Institute of Technology, Holon, Israel.

Inorganic fullerene-like (IF) nano-spheres IF-MS2 (M=Mo,W) are related to the conventional layered 2H-MS2 compounds. Our special synthesis method causes the layers of such lamellar compounds to curve into concentric nested nano-sized spheres. The fortunate combination of a multi-walled onion-like structure, small size and chemically inert surface of nano-spheres provides these materials with a unique set of chemical and physical properties. Work done to obtain a better understanding of the growth mechanism of IF-MS2 nanoparticles has now resulted in our successful scale up of the IF synthesis to commercial quantities. Starting from 0.4g/batch, our new reactor design now enables us to produce up to 1000 g/batch. These new materials can be used as solid lubricants to significantly reduce friction and wear under a variety of extreme conditions of load, humidity, and ultra-high vacuum. Tribological tests show that IF appreciably outperforms the conventional 2H phase of the same compounds in friction, wear and longevity under different contact conditions. By using of IF instead of 2H phase the friction coefficient was decreased by up to 50 to 75% and wear by over an order of magnitude, depending on the application. Comparison tests of IF and 2H were done by 1) mixing the powders with oil or grease, 2) impregnating them into porous sintered materials such as bronze-graphite and Fe-Ni-Graphite, and 3) applying them as an anti-friction coating. In the case of greases and oils, the nano-sized IF particles provided appreciably better lubricating properties compared to the conventional 2H phase of the same MS2 compounds, even when the 2H powders were sub-micron in size. This can be at least partially explained by the higher strength and greater chemical stability of the IF nano-spheres. In contrast to the spherical IF, the 2H phase has a lamellar structure with reactive dangling bonds on their crystalline edges. In addition, during use the 2H particles may not always be aligned parallel to the friction surface while the symmetrical nature of the IF nano-spheres allows them to always be suitably oriented with regards to the contact surfaces. In the case of impregnation, the above mentioned properties of nano-size spherical solid lubricant IF-nanoparticles enable them to be gradually furnished to the rubbed surfaces from within the pores by unique self-lubricating mechanism. The synthesis of WO3 powder deserves particular attention since it serves as a precursor for IF production. One of the most important conditions needed in order to synthesize spherical, nano-sized IF is that the precursor WO3 powder should also be nano-sized and of spherical shape. A unique process for synthesis of WO3 particles 30-300nm in diameter of spherical shape with 100% product yield was developed in our labs.

11:15 AM S3.10

Characterization of Carbon Nanotube Purity Using a Quartz Sensor Platform. Stephanie Anne Hooker[1], Ryan Schilt[1], Natalia Varaksa[1], John Lehman[1] and Paul Rice[1,2]; [1]Materials Reliability, NIST, Boulder, Colorado; [2]Department of Mechanical Engineering, University of Colorado, Boulder, Colorado.

Carbon nanotubes are revolutionary materials, with properties that are vastly different than any other bulk form of carbon. Their unique combination of electrical, mechanical, and thermal properties makes them attractive for applications in advanced structures, biomedical devices, and next-generation electronics, among many others. However, properties can differ considerably depending on certain material characteristics (e.g., diameter and chirality). The situation is further complicated by the fact that most routes for nanotube growth do not produce just one species, but instead generate a mixture along with chemical impurities. As a result, nanotube characterization remains a critical issue for manufacturers, product developers, regulatory agencies, and biologists investigating health and safety risks. Currently, multiple separate analytical instruments are needed to measure purity, including a combination of thermogravimetric analysis (TGA), near-IR adsorption spectroscopy, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and electron microscopy. These techniques provide complementary data on chemistry and structure. However, separate specimens are typically required for each, raising concerns as to whether these individual data points adequately represent the characteristics of an entire batch. This paper describes a new platform for rapidly assessing tube quality that interrogates a single specimen. The approach utilizes an acoustic wave sensor based on a thin quartz crystal as the primary measurement apparatus on which electrical, thermal, optical, and thermo-chemical properties can be simultaneously measured. For concept demonstration, we observed the thermal purification of multi-walled nanotubes by removing the non-nanotube carbons by heating in an oxygen-containing atmosphere. We first dispersed the tubes in various liquids, including toluene, dimethyl formamide (DMF), and de-ionized water, and then applied thin coatings to the crystals by drop casting, spin coating, spray deposition, and dip coating. The crystals were externally heated from ambient to 500 C during which time the resonant frequency (4 MHz for the bare crystal) was monitored as a function of temperature using an impedance analyzer. Appreciable shifts in frequency, impedance, and phase were observed during heating, all directly attributed to mass loss. AC conductivity was also monitored during heating by means of a second electrode placed over the nanotube coating. These measurements revealed relatively high resistance for the as-received nanotubes, with conductivity increasing during purification. Results confirm that the acoustic resonances of quartz crystals can be used to characterize nanotubes. However, many measurement issues remain, including the effects of film thickness, deposition variability, crystal stability, and heat generation due to low-temperature catalyst oxidation. These challenges will be specifically discussed.

11:30 AM S3.11

In-Flight Length Classification of Carbon Nanotubes by Gas-Phase Electrophoresis. S. Kim and Michael R. Zachariah; University of Maryland and NIST, College Pak, Maryland.

We demonstrate the use of gas-phase electrophoresis to length classify CNTs grown in a continuous aerosol process. The separation process occurs at atmospheric pressure and involves electrostatic mobility separation which classifies fibers on the basis of equivalent projected surface area. This implies that one can for diameter controlled CNTs, obtain an on-the-fly determination of the CNT length distribution during CNT synthesis, or alternative y have a method to produce size separated CNTs. The method should be generic to any fiber based material.

11:45 AM S3.12

Environmental Remediation Using Nanoporous Materials. Tarek Abdel-Fattah, Department of Biology, Chemistry and Environmental Science, Chrisotpher Newport University, Newport News, VA.

Nanoporous materials characterized by well-defined pores in nanometer scale with unique molecular sieving capabilities and ultrahigh surface area are attractive to use as adsorbents for environmental remediation. We will discuss different synthesis strategies to produce effective adsorbents for environmental remediation. For example, we will present the use of organo-silicate nanocomposite materials for the remediation of chlorinated phenols from aqueous media. Also, we will present a study to support worldwide research efforts to obtain drinking water with arsenic levels below 10 part per billion (ppb) using different nanoporous adsorbents modified with different iron species. Furthermore, lead ions in soils and stormwater run-off from small arms firing range (SAFR) is a major concern. Various nanomaterials as adsorbents have been studied to remediate the problem of lead species releases to the environment. These nanomaterials can be used as barrier liners and point of use water treatment.

SESSION S4/G4: Joint Session: Nanomaterials: Biological and Environmental Interactions

Chairs: Vicki Stone and David Warheit
Tuesday Afternoon, November 29, 2005
Room 203 (Hynes)

1:30 PM *S4.1/G4.1

Toxicological Profiles of Nanomaterials. Erik Rushton, Gunter Oberdorster and Jacob Finkelstein; University of Rochester, Rochester, New York.

With the passage of the National Nanoscale Initiative in 2001 there has been increasing attention and funding given to nanomaterial research. This has led to a number of new materials developed at the nanoscale (< 100 nm) level, which often possess chemical and physical properties distinct from those of their bulk materials. These unique qualities are proving to be quite useful in a number of new applications. For example, biological applications in imaging, treatment, and drug delivery are particularly promising as well as the increasing engineering potential of nanocircuitry and materials science. As the number of applications increases however, so too does the potential for human exposure to nanomaterials through a number of routes: dermal, ingestion, inhalation, and even injection. Interestingly some of the properties of these nanomaterials that make them useful in these emerging technologies are the same properties that can increase their toxic potential. This is leading to an emerging discipline - nanotoxicology, which can be defined as safety evaluation of engineered nanostructures and nanodevices. Nanotoxicology research will not only provide information for risk assessment of nanomaterials based on data for hazard identification, dose response relationships and biokinetics, but will also help to further advance the field of nanoresearch by providing information to alter undesirable nanomaterials properties. Although nanotoxicology is in its infancy, there are some preliminary studies with newly developed materials that provide some insight into potential effects, which when coupled with older studies provides some insight on how these nanomaterials impact the biological system. This presentation summarizes results of studies with nanosized particles with a focus on the respiratory system and skin as portals of entry. The ability of particles to translocate from their site of entry, their ability to elicit biological responses, and their presumed mechanisms of action will be highlighted. This will be an attempt to illustrate how pervasive these materials can be, which may or may not be detrimental. With proper toxicological assessment this potential may be harnessed leading to breakthroughs at the nanotechnology - biology interface.

2:00 PM *S4.2/G4.2

Pulmonary Effects in Rats of Exposure to Nanoscale Titanium Dioxide or Nanoscale Quartz Particles: Particle Size and Surface Area are not the Only Considerations. David B. Warheit[1], Kenneth L. Reed[1], Thomas R. Webb[1], Christie M. Sayes[2] and Vicki L. Colvin[2]; [1]DuPont Haskell Laboratory, Newark, Delaware; [2]Rice University, Houston, Texas.

Numerous pulmonary toxicology studies in rats have demonstrated that nanoscale particles (generally defined as particles in the size range < 100 nm) administered to the lung cause a greater inflammatory response when compared to fine-sized particles of identical composition at equivalent mass concentrations. Contributing to the effects of nanoscale particles is their very high size-specific deposition when inhaled as singlet ultrafine particles rather than as aggregated particles. Some evidence suggests that inhaled nanoparticles, after deposition in the lung, largely escape alveolar macrophage surveillance and clearance and gain access through translocation to the pulmonary interstitium. In addition, in vitro studies suggest that nanoparticle-types are more toxic to pulmonary cells. However, some recent preliminary studies indicate that pulmonary exposures to nanoscale particulates may not always be more inflammogenic compared to macro/microscale particles. Indeed, data will be presented demonstrating that nanoscale quartz-crystalline silica particles (50 nm particle size) were less toxic to the lungs when compared to fine-sized quartz particles (1.6 um). However, when these studies were repeated with 10 nm quartz particles, the nanoscale quartz particles were as or more toxic than Min-U-Sil quartz. In another study, lung toxicity of intratracheally instilled Nano titania particles were compared to fine-sized particulates in rats. The effects of nanoscale TiO2 rods as well as Nano TiO2 dots (20 nm) were not significantly different from larger sized TiO2 particles (300 nm) at equivalent doses and this finding was confirmed in a second study. In another study with surface treatments on TiO2 particle-types, results demonstrated that surface coatings can modify the pulmonary toxicity of particles. In the aggregate, these studies indicate that a variety of factors beyond particle size and surface area serve to influence the pulmonary toxicity of nanoparticulates.

3:30 PM *S4.3/G4.3

Suggested Strategies for the Ecotoxicology Testing of New Nanomaterials. Vicki Stone, A. Ford and T. Fernandes; School of Life Sciences, Napier University, Edinburgh, United Kingdom.

Nanotechnology is a rapidly expanding and advancing field of research that has already yielded a variety of commercially available products including cosmetics, suntan lotions, paints, self cleaning windows and stain resistant clothing. The Royal Society and the Royal Academy of Engineering in their recent report ‘Nanotechnology and nanoscience: opportunities and uncertainties’ (http://www.nanotec.org.uk/finalReport.htm) concluded that nanotechnology is likely to have ‘huge potential’. While this report indicated that ‘many applications of nanotechnology pose no new health or safety risks’, it also recognised that the health, safety and environmental hazards of nanoparticles (diameter less than 100nm) and nanotubes requires investigation. A significant body of data exists regarding the toxicological effects of nanoparticles (also termed ultrafine particles) in mammalian systems, particularly with respect to the lungs and cardiovascular system. Such studies suggest that smaller particles, with a larger surface area per unit mass, are more potent at inducing oxidative stress and inflammation leading to adverse health effects. However, very few papers have been published regarding the effects of nanoparticles on other phyla such as micro-organisms, invertebrates and vertebrates from terrestrial and aquatic habitats. Since nanoparticles from both domestic and industrial products will be released into the environment, eg. wastewater, it is essential to investigate the impact on such species and the ecosystem. This presentation will aim to discuss how existing knowledge regarding the mammalian toxicology of nanoparticles could be used to generate an effective, efficient and focused strategy for testing the ecotoxicolgy of nanoparticles.

4:00 PM *S4.4/G4.4

Case Studies for Environmentally-Conscious Materials Selection with the CES Eco-Selector. Ulrike G.K. Wegst[1] and Michael F. Ashby[2]; [1]Max-Planck-Institute for Metals Research, Stuttgart, Germany; [2]Cambridge University Engineering Department, Cambridge, United Kingdom.

Materials contribute to the environmental burden of products during all stages of their life-cycle: their creation, use and disposal. The minimisation of this burden requires the selection of materials which are less toxic, can give products which − without compromising product quality − have a longer life-time, are more easily recycled, are lighter and less energy intensive, and which, where possible, use renewable or non-critical resources. Presented in this contribution are case studies on material substitution for lightweight cars and high performance sports equipment to illustrate how the Cambridge Eco-Selector, a software-based design tool, can aid the environmentally-conscious selection of materials. It is unique in that it provides guidance in the design of new and improved products early in the "concept" and "embodiment" stages of the design process, allowing for the simultaneous optimisation of technical, environmental and cost performance.

4:30 PM S4.5/G4.5

Atomic force microscopy of CHO cells exposed to quantum dots. Minhua Zhao[1], Charudharshini Srinivasan[2], Jeunghoon Lee[1], Diane Burgess[2], Fotios Papadimitrakopoulos[1] and Bryan D. Huey[1]; [1]Institute of Materials Science, University of Connecticut, Storrs, Connecticut; [2]School of Pharmacy, University of Connecticut, Storrs, Connecticut.

Atomic force microscopy (AFM) can be uniquely employed for dynamic nano-indention to probe the viscoelastic material properties of living cells in culture. AFM elastography, which maps the spatial distribution of cell mechanical properties with nanoscale resolution, has been used to investigate a living CHO (Chinese Hamster Ovary) cell culture. Quantum dots (QDs) are able to cross the cell membrane and to act as a fluorescent label. In this work, AFM elastography is captured on living CHO cells before and after introducing CdSe QDs into the cultural media. The accumulation of QDs within the cell is confirmed by in situ epifluorescence equipped on the AFM. AFM elastography before and after the addition of QDs at various concentrations is reported.

4:45 PM S4.6/G4.6

Characterization, Imaging and Degradation Studies of Quantum Dots in Aquatic Organisms. Kenneth E. Gonsalves[1], Sireesha Khambhammettu[1] and Amy H. Ringwood[2]; [1]Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina; [2]Biology, University of North Carolina at Charlotte, Charlotte, North Carolina.

Nanoparticles may be introduced into aquatic environments during production processes and also as a result of release following their use in electronic and biological applications. The purpose of these studies was to characterize and image the behavior of quantum dots (QD) in seawater, and the accumulation of QDs and their toxicity to potential biological receptors. For these studies, oyster embryos as well as isolated hepatopancreatic cells were used. Fluorescent confocal microscopy, electron diffraction and electron microscopy were used to determine the size distribution and composition of quantum dots and also to verify the accumulation and cellular localization inside these cells. Furthermore, there are natural differences in environmental factors that may affect the degradation rates of QDs, including salinity and pH conditions, as well as seasonal differences in temperature. To determine the effects of salinity on degradation rates, nonfunctionalized QDs composed of a Cd/Se core surrounded by layers of Zn (Evident Technologies) were added to 0.22 filtered seawater samples of different salinities (10, 20, and 30 parts per thousand), and the changes in emission spectra over time were determined; likewise, the potential effects of pH were evaluated under a range of environmentally realistic pH conditions (e.g. pH 7, 7.5, and 8); and the impacts of temperature (10, 20, and 30 degrees centigrade) were determined. These kinds of basic studies are essential for addressing the potential impacts of nanoengineered particles on aquatic organisms. Analogous studies with InP nanoparticles will also be presented.

SESSION S5: Poster Session
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

S5.1
Self-Extinguishing Elvax Nanocomposites. Aryeh Sokolov[3], Daniel Hefter[2], Mayu Si[1], Jonathan Sokolov[1] and Miriam Rafailovich[1]; [1]Materials Science and Engineering, Stony Brook University, Stony Brook, New York; [2]DRS High School, Woodmere, New York; [3]HAFTR High School, Cedarhurst, New York.

Self-extinguishing Elvax (ethylene vinyl acetate)/clay nanocomposites combined with red phosphorous and Mg(OH)2 have been prepared by melt blending. The materials were characterized by DMA, Instron, TGA, cone calorimeter, LOI and UL-94 V0. The addition of clay can dramatically increase the modulus and strength of Elvax. TGA results indicate the clay involves the second step degradation of Elvax and the strong char clay layers effectively prevent the heat and mass transfer through the underline materials. During the burning, the clay can effectively prevent the dripping. The addition of clay can greatly decrease the amount of Mg(OH)2 necessary for UL-94 V0, which proposes a tendency that the combination of clay and phosphorus compounds can replace halogen flame retardant compounds in the future. Further the effect of concentration of clay, red phosphorus and Mg(OH)2 were studied. And cone calorimeter was used to investigate the mechanism of flame retardancy. Supported by NSF funded MRSEC at Stony Brook

S5.2
The Effect of Nanoparticles on Selective Gas Permeability of Thin Film Membranes Using Supercritical Fluid. John Jerome[1], Allyson Ho[2], Alex Thachara[3], Mordechai Bronner[4], Young-Soo Seo[1], Tadanori Koga[1], Kwanwoo Shin[1], Jonathan Sokolov[1] and Miriam Rafailovich[1]; [1]Materials Science, Stony Brook University, Stony Brook, New York; [2]William P. Clements High School, Sugar Land, Texas; [3]The Wheatley School, Old Westbury, New York; [4]Yale University, New Haven, Connecticut.

The addition of inorganic nanoparticles to polymer thin films can be highly beneficial to their lubrication, strength, and UV resistance. Since nanoparticles are rigid, they do not conform to the molecular order of the film, producing nano-scale voids. Consequently, the introduction of nanoparticles into polymer films alters their porosity and this phenomenon may be exploited to engineer selectively permeable membranes. Porosity can also be introduced by swelling the films in supercritical fluids and then rapidly removing the solvent by decreasing the pressure which converts the solvent to the gas state. Since the particle-chain interactions can also affect the swelling of the film, this can provide an additional mechanism for controlling porosity. In order to test this hypothesis, solutions were made of nanoparticles, clay or gold, with polystyrene or poly (methyl methacrylate) polymer to observe the change in porosity and to analyze its dependence on polymer structure and on polymer nanoparticles interactions. The solutions were spuncast onto glass slides with a thickness of 2000A. Two sets of samples for each solution were made, with one set exposed to supercritical CO2. Samples were exposed at two different temperatures and pressures of 36C, 1200psi and 50C, 1450psi. The polymer thin film was floated off the glass slide onto a metal washer support. We then measured the permeability of O2 and CO2 gas. We found that exposure to supercritical CO2 greatly increased the permeability to both O2 and CO2 gas. The degree of change in permeability in the nano-composite film depended on the particle aspect ratio and intensity in the matrix.

S5.3
Abstract Withdrawn

S5.4
Effect of Length on Cytotoxicity of Multi-Walled Carbon Nanotubes against Human Acute Monocytic Leukemia Cell Line THP-1 *inVitro* and Subcutaneous Tissue of Rats *inVivo*. Yoshinori Sato[1], Atsuro Yokoyama[2], Ken-ichiro Shibata[2], Shin-ichi Ogino[1], Yoshinobu Nodasaka[2], Takao Kohgo[2], Kazuchika Tamura[2], Tsukasa Akasaka[2], Motohiro Uo[2], Kenichi Motomiya[1], Balachandran Jeyadevan[1], Mikio Ishikuro[3], Rikizo Hatakeyama[4], Fumio Watari[2] and Kazuyuki Tohji[1]; [1]Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; [2]Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan; [3]Institute for Materials Research, Tohoku University, Sendai, Japan; [4]Graduate School of Engineering, Tohoku University, Sendai, Japan.

Since a number of graphite-coated plastic valves *invivo* have maintained an intact graphite surface with little or no clot present, and given that graphite has been found to be biocompatible with cells, artificial heart valves and dental implants consisting of carbon fiber-reinforced carbon composites have been developed. Carbon nanotubes (CNTs) possess outstanding properties such as morphology, nano-spaces and a large specific surface area. Consequently, recent investigations have utilized CNTs in the development of a probe tip for scanning probe microscope, a vector used to targeting therapies for drug delivery, vaccine delivery, gene delivery and selective molecular adsorption. On the other hand, CNTs were reported to be harmful to living organisms and consequently extensive nanotoxicological investigations are necessary to determine their biocompatibility and cytotoxicity before carbon nanotubes can be safely used as biomaterials [1]. Generally, metal dissolution, surface functional groups and size effects have been commonly cited as factors indicating cytotoxicity. In particular, biocompatible PTFE and Ti particles were found to be increasingly cytotoxic with decreasing particle size. In an effort to be successfully applied as drug delivery systems, a few micrometer-length CNTs should be shortened to less than one micrometer to facilitate entry into cells. CNTs are long thin structures that possess diameters of a few nanometers, while the length can be up to a few micrometers. These could have unusual toxicological properties, in that they share morphological characteristics of both fibers and nanoparticles. To date, although some researchers have reported the effect of CNTs on cytotoxicity in cells, no detailed study has been carried out to determine the effect of length on CNT cytotoxicity. In this paper, we investigated the activation of the human acute monocytic leukemia cell line THP-1 *invitro* and the response in subcutaneous tissue of rats *invivo* to CNTs of different lengths. We used 220 nm and 825 nm long CNT samples for testing, referred to as 220-CNTs and 825-CNTs, respectively. 220-CNTs and 825-CNTs induced human monocytes *invitro*, although the activity was significantly lower than that of microbial lipopeptide and lipopolysaccharide, and no activity appeared following variation in the length of CNTs. On the other hand, the degree of inflammatory response in subcutaneous tissue in rats around the 220-CNTs was slight in comparison with that around the 825-CNTs. These results indicated that the degree of inflammation around 825-CNTs was stronger than that around 220-CNTs since macrophages could envelop 220-CNTs more readily than 825-CNTs. However, no severe inflammatory response such as necrosis, degeneration or neutrophil infiltration *invivo* was observed around both CNTs examined throughout the experimental period. [1] V. L. Colvin, *NatureBiotech.*, **21**, 1166, 2004.

S5.5
Fouling resistant thin-film composite membranes by self assembly of poly(vinylidene fluoride) comb copolymers. Ayse Asatekin, Long Hua Lee, Jong Hak Kim and Anne M. Mayes; Material Science and Engineering, MIT, Cambridge, Massachusetts.

Due to the limited availability of fresh water resources, water purification is an important part of environmental policy today. Membrane processes play an important role, but their use is limited by two factors: Short membrane life due to fouling, and high energy costs due to the requirement of high pressure to obtain reasonable flux. This study is aimed at designing fouling resistant thin film composite membranes aimed at nanofiltration and reverse osmosis with high flux. Our strategy involves comb copolymers with a highly hydrophobic poly(vinylidene fluoride) (PVDF) backbone and hydrophilic side-chains as a non-porous coating on a porous base membrane. The polymer undergoes self-assembly, and nanometer sized channels of hydrophilic phase are formed upon microphase separation. The chemistry of the side-chains determine the application: When poly(oxyethylene) methacrylate side chains are used (PVDF-g-POEM), fouling-resistant nanofiltration membranes are obtained with high flux (about 3 times that of a commercial nanofiltration membrane). These membranes resist fouling by protein, natural organic matter (represented by humic acid) and polysaccharide (represented by sodium alginate) foulants in 24-hour tests. Charged side-chains can exclude ions and be employed for salt retention. Ion retention studies include monovalent and divalent salts.

S5.6
Preparation and Characterization of Polyamide Nanofiltration Composite Membranes with Photo-catalytic TiO2 Layers. Jonggeon Jegal and Seung Hee Son; Applied Chemistry Division, Korea Research Institute of Chemical

Technology, Daejon, South Korea.

Polyamide (PA) nanofiltration (NF) composite membranes are the ones that have been very often used especially for the water treatment such as wastewater treatment and drinking water production, due to their good permselective properties. However, membrane fouling by the contaminant of the wastewater is one big problem that should be solved for the better application of the PA NF membranes. In order to solve such problem, many people have tried, making the membrane surface hydrophilic, because people considered that the hydrophilic surface is better for antifouling. However, such tries have not been very successful yet, so the problem still remains. In this study, a PA NF composite membrane with photocatalytic TiO2 layer on its surface was developed to prepare a membrane with excellent anti-fouling properties, in which the TiO2 layer was chemically linked to the PA thin film. 3-aminopropyltrimethoxysilane (APTMOS) that can react with acylchloride groups remained in the PA thin film was used to form chemical bond between the both layers. To protect the polymeric layers of the membrane including the PA layer and the PSf support layer from the UV-degradation by the TiO2, while cleaning the membrane with UV-light irradiation, a silicone layer was formed between the layers of TiO2 and PA. The membrane prepared was characterized using SEM, ESCA, XRD and permeation test. From the characterization, it was found that the crystalline TiO2 particles were attached to the membrane surface in a stable form. By the long time tests with or without UV-light irradiation, the effect of TiO2 on the membrane fouling was studied: When the membrane with TiO2 layer was exposed to the UV-light after a certain period of time of separation process, the foulants adhered to its surface was effectively removed. The TiO2 crystal layer appeared to make the membrane surface hydrophilic, reducing membrane fouling and degrade the foulants adhered to the membrane surface at the same time.

S5.7

Micro fluidic Registration of Sub-Micron Pathogens for Quorum Detection. Nevil R. Shah and Shalini S. Prasad; Electrical Engineering, Portland State University, Portland, Oregon.

We have utilized the principle of lab-on-chip systems for detection of bacteria (E .coli) in a fluid medium. This is achieved by employing the adhesion properties of e-coli strains to nano-structured material by surface modification of the nano structured materials via chemical functionalization techniques. Carbon nanotubes are used as nano scale traps for the e-coli. The quorum of bacteria required for producing a biological perturbation was identified by detecting the intrinsic electrical activity that is obtained from the presence of a quorum. This quorum was detected by fabricating a device by integrating hard and soft lithopgraphy techniques. Transparent substrates were patterned with metallic micro electrodes on which functionalized carbon nanotubes were localized via fluidic means. The geometry of the device was designed to facilitate laminar flow of the fluid through the polymer (PDMS) channel due to capillary action. A good spread of the fluid is obtained over the electrode for better detection of E. coli. PDMS encapsulates the metallic micro electrodes for providing stable chemical microenvironment for sensing. Samples containing the pathogens were circulated on the substrate via micro fluidic channels that are fabricated to encapsulate the substrate. Selective binding of the pathogens to the functionalized nanoscale materials occurred. This resulted in the spatial localization of the pathogens on the metallic micro electrodes. The metallic micro electrodes were probed to record the in situ electrical changes. Thus quorum sensing is achieved in a rapid high throughput manner.

S5.8

CO Adsorption and Oxidation on Silica-Supported Metal and Alloy Nanoparticle Catalysts. Derrick Mott, Andrew Smith, Jin Luo and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

The understanding of the surface properties of supported metal and alloy nanoparticle catalysts is essential for exploiting their unique catalytic properties for environmental monitoring and remedy. This paper reports findings of an investigation of CO adsorption and oxidation on silica-supported metal nanoparticles. The metal nanoparticles were prepared by core-shell synthesis. Au/SiO2, Pt/SiO2 and AuPt/SiO2 with nanoparticles of 2-5 nm sizes and controlled alloy compositions were studied as model catalyst systems. Using CO as a probe molecule, the catalytic ability of the nanoparticles was characterized using transmission FTIR. The catalytic ability for CO oxidation on the catalysts was also monitored using GC with a fixed bed reactor. Results are compared with those for traditionally prepared Au/SiO2 catalysts. The results revealed some initial insights into the understanding of the relationship between the catalytic activity and the surface characteristics of the metal nanoparticles. New insights into the correlation between the surface composition and binding properties, along with their implications to the design of nanostructured catalysts for environmental monitoring and remedy, are discussed.

S5.9

Study of nanostructured materials by magnetic resonance methods. Natalia Noginova[1], Marsha King[2], Donald White[3] and Tracee Harris[1]; [1]NSU, Norfolk, Virginia; [2]SCSU, Orangeburg, South Carolina; [3]Tuskegee University, Tuskegee, Alabama.

Magnetic resonance methods were used to investigate the effects of particle size and magnetic impurities in nanostructured solid state materials. 27Al NMR spectra, and nuclear spin relaxation have been studied in powder samples with different size of particles with and without ferromagnetic nanoparticles, and compared to those in single crystals. Proton NMR and spin dynamics was also studied in liquid and solid suspensions of Fe2O3 nanoparticles and analyzed together with ESR data in the same materials. Significant changes in the shape of the line and relaxation kinetics were observed with decrease of particle size and explained by taking into account the effect of the surface distortions. Studies of the spectra and spin dynamics in solid and liquid suspensions with magnetic nanoparticles in different concentrations allow us to estimate local fields and parameters of nanoparticles interactions.

S5.10

Preparation and Characterization of Electrospun Poly(4-methyl-1-pentene) (P4M1P) Fibers. Keun-Hyung Lee[1], Steven Givens[1], D. Bruce Chase[2] and John F. Rabolt[1]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Central Research and Development, Experimental Station, Dupont, Wilminton, Delaware.

A electrospinning study utilizing isotactic poly(4-methyl-1-pentene) (P4M1P) in a mixed solvent system was performed. P4M1P, a member of the polyolefin family, has not been electrospun previously from solution due to its low solubility. No organic solvent can dissolve any significant amount of P4M1P at room temperature. In this study, the effects of a mixture of good solvent and/or non-solvent(s) on the electro-spinnability and morphological appearance of P4M1P electrospun fibers have been investigated. Various fiber morphologies such as circular, twisted circular, curled and twisted ribbon structures were found depending on the solvents used. FT-IR and Raman spectra of P4M1P (bulk, film, and E-spun fibers) revealed interesting differences as a function of processing conditions. In addition, the effect of heat treatment as a function of the temperature and time was analyzed using FT-IR, Raman and wide angle X-ray scattering.

S5.11

Comparison of Structural and Optical Properties of ZnO Nanostructures Fabricated by Thermal Evaporation and Pulsed Laser Deposition. Jong Hoon Kim, Kyung Ah Jeon, Hong Seong Kang and Sang Yeol Lee; Yonsei University, Seoul, South Korea.

The structural and optical characteristics of ZnO nanostructures fabricated by simple method of thermal evaporation and pulsed laser deposition (PLD) are investigated. A mixture of ZnO and graphite powder and ZnO ceramic target were used as sources, respectively. Influence of the preparation conditions on the luminescent and structural properties is discussed. Temperature and sample position are critical parameters to form different morphologies of ZnO nanostructures. Photoluminescence spectra show that the ZnO nanostructures have an ultraviolet emission at around 380 nm and a green emission at around 520 nm.

S5.12

Green Synthesis of Zinc Oxide Film with Vacuum Ultra Violet Light. Junko Hieda[1], Nagahiro Saito[1], Yasushi Inoue[2] and Osamu Takai[2]; [1]Graduate School of Engineering, Nagoya University, Nagoya, Japan; [2]EcoTopia Science Institute, Nagoya University, Nagoya, Japan.

Zinc Oxide (ZnO) is well known as a semiconductor with wide bandgap. The material has various properties such as piezoelectric property, ultraviolet emission and transparency in the range of visible light. Thus it can be utilized as a transparent electrode, ultraviolet emission diode and surface acoustic wave (SAW) device. ZnO films has been fabricated through chemical vapor deposition (CVD), sputtering, and sol-gel process. In particular, the sol-gel process is one of low-cost process, which has high efficient productivity, however, the synthesis generally requires a calcination process at high temperature to crystallize amorphous metal oxide. This high temperature process does not allow us to fabricate the film on various substrates, in particular, polymer ones. Moreover the high temperature process is not environmentally-benign one. In this report, the crystalline ZnO films are attempted to be fabricated by vacuum ultraviolet (VUV, the wavelength of 172 nm) irradiation onto ZnO gel films based on the reaction of the films with radicals such as ozone and atomic oxygen obtained by VUV irradiation. Zinc chloride was used as a precursor. A surfactant (Pluronic P123 block copolymer) was added into sol solution due to uniformity of films. Thin films were fabricated by spin coating on ITO and silicon substrates. VUV light was irradiated onto the ZnO gel films at 10^5 Pa. The VUV-irradiated gel films were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FT-IR). Furthermore, we observed the VUV-irradiated gel films by scanning electron microscopy (SEM). XRD patterns show that the gel films were changed into crystalline Zn $(OH)_2$ and ZnO. Hexagonal structure was observed in images. In summary, crystalline ZnO films can be fabricated through the photocalcination without heat treatment or with the lower temperature treatment. We believe that this is generally one of green process for ceramics.

S5.13

Nanometer-scale dissolution of single particlulate smectite observed with a phase-shift interferometer microscope.
Hisao Satoh[1,2], Yoshihiro Nishimura[1,2], Katsuo Tsukamoto[1], Akira Ueda[2], Shinzo Ueta[2] and Koichi Kato[2]; [1]Department of Mineralogy, Petrology and Economic Geology, Tohoku University, Sendai, Japan; [2]Central Research Institute, Mitsubishi Materials Corporation, Saitama, Japan.

Direct measurement of nanometer-scale growth and dissolution occurred on crystal surface has recently been enabled by optical interferometrical method as well as scanning probe microscope. However, rate determination of very slow dissolution by in-situ observation is still difficult because it takes very long time to detect the change in the height successfully. As a challenging approach, we conducted measurement of the dissolution rates of smectite in neutral to highly alkaline solutions using a modified Michelson-type phase-shift interferometer (PSI) microscope (height resolution, 6 nm for smectite in solution). Using gold-sheet as an insoluble reference in the reaction-cell, interferogram (203×151 μm^2) can be continuously obtained for 1000 min. The interferograms were calculated into phase and height maps based on phase-shift image-processing and optical indices of the solutions. Dissolution experiments of smectite were made on single particle of Na-montmorillonite ($\sim$40-100 μm; Kunipia-P, Kunimine Industry Co.) fixed by a gold-sheet on the titanium holder in the cell filled with NaCl-NaOH solutions (I = 1.0 M) at pH = 7 to 14 at 22 °C with flowing at the rates of 9 to 175 μm/s. The minimum retreat ($\sim$ 6 nm) was successfully detected at basal plane (001) of smectite particles during experiments at pH = 7 after 1000 min. The resultant dissolution rates at pH = 7, 10, 13, and 14 were measured to be 9.56E-14, 1.27E-13, 1.46E-12, and 3.40E-12 m/s, respectively, at a flow rate of 175 μm/s. Based on molar volume of smectite as 138.39E-6 m^3/mol, the rate equation showed rate (mol/m^2/s) = $10^{-10.97} + a\mathrm{H}^{+-0.23}$ ($R^2 = 0.89$). This result suggests that smectite can solely be dissolved in the three-orders faster rate than that previously reported on flow-through experiments (rate = $10^{-14.11} + a\mathrm{H}^{+-0.25}$; Sato et al., 2003). In order to confirm the rate variations, we further proceeded the dissolution experiments with changing the flow rates of NaOH solution (pH = 14) and doping of Si (Na_2SiO_3; 5E-3 to 5E-4 M of Si). Slower flow rates (FR) effectively reduced the dissolution rate of smectite (001) as parabolically expressed with rate (m/s) = 3.04E-13$\times$FR$^{0.5}$ - 6.32E-13 ($R^2 = 0.99$). Si-doped NaOH solution further reduced the dissolution effectively as expressed with rate = 2.63E-14$\times$FR$^{0.5}$ - 1.12E-13 ($R^2 = 0.84$). The slowest dissolution observed was 1.5E-13 m/s in an experiment at flow rate of 9 μm/s and Si concentration of 5E-3 M. These results imply that dissolution of smectite is diffusion-controlled at pure NaOH and slightly interface-controlled at Si-bearing NaOH systems. Thus, the dissolution of single particulate smectite exposed importance of basic process at dissolution interface involving step development, etch pit generation, and adsorption. This study leads to better constructive design of the long-term endurable barrier, which is composed of smectite clay, for high-level radioactive waste in the underground repository.

S5.14

NO2 gas adsorption on (10,0) Carbon nanotube.
Deepti Phatak[1], H. B. Schlegel[2], E. Goldfield[2] and J. Choi[1]; [1]Electrical and Computer Engineering, Wayne State University, Detroit, Michigan; [2]Department of Chemistry, Wayne State University, Detroit, Michigan.

The interaction between NO2 and a finite length semi-conducting (10,0) carbon nanotube (C200H20) is studied at PM3 semi-empirical, Hartree-Fock and density functional level of theory. Semi-empirical calculations show that NO2 adsorbs on to the carbon nanotube; however, the spin-unrestricted calculations have a very large spin contamination and therefore quantitatively give wrong values for band gap after NO2 adsorption. Spin restricted open shell Hartree-Fock (ROHF) calculations give more reasonable energetics and charge distributions. DFT calculations done using the LSDA and B3PW91 functionals give near zero homo-lumo gap for finite length nanotube. Interaction of 2 NO2 molecules with naphthalene and pyrene is studied at B3LYP level of theory in chemisorbed as well as physisorbed configuration. A mechanism for formation of NO3 on these surfaces is also investigated at B3LYP level, which will be subsequently investigated on the (10,0) finite sized nanotube.

S5.15

Nanoparticle Hydroxyapatite Derived from Bovine Bone as a Remediation Agent. Stephen J. Florczyk and Matthew M. Hall; BMES Program, Alfred University, Alfred, New York.

While hydroxyapatite (HA) is a commonly used biomaterial, it has also been shown to have potential environmental applications. Previous research has illustrated the ability of hydroxyapatite and other calcium phosphate materials to remove heavy metal cations such as Pb, Cd, and Ni from water and soil. The utilization of bovine bone as a source material for HA nanoparticles is also a type of waste remediation. The production of HA nanoparticles from bovine bone will be optimized to produce a narrow particle size distribution by varying conditions such as suspending medium, milling method, and milling time. The optimized HA nanoparticles will be studied for their ability to immobilize heavy metal cations. The study will feature solutions containing heavy metal cations being filtered through HA nanoparticles. The concentrations of heavy metal cations will be determined using inductively coupled plasma-optical emission spectroscopy.

S5.16

Field Emission Properties of Carbon Nanotubes Grown on AAO Templates with and without Catalysts.
Chien-Sheng Huang, Bohr-Ran Huang and Kun-Ting Hung; Department and Institute of Electronic Engineering, National Yunlin University of Science and Technology, Touliu City, Yunlin, Taiwan.

The uniformity of carbon nanotubes (CNTs) was improved while growing on a porous aluminum template, which had been processed by anodization and pore widening procedures at lower temperatures. Contrasting to the normal situation, the catalytic metals were optional during the synthesis of CNTs. The cobalt catalysts were electrochemically deposited at the pore bottom of the anodic aluminum oxide (AAO) nano-template. By using plasma enhanced chemical vapor deposition (PECVD) with a gaseous mixture of methane/hydrogen (CH_4/H_2), the CNTs were grown within nano-channels of the AAO template at 550 °C. The Raman spectroscopy was performed to inspect the I_D/I_G of as-grown CNTs with or without catalysts, respectively. The field emission characteristics were also measured. It was found that the tube density and the quality of CNTs grown on the AAO template played important roles on the turn-on voltage. Owing to the field screening effect on the emission current, an optimal ratio between the nano-channel spacing and the outside length of CNTs could be found to near 2, which revealed a key factor in field emission array applications.

S5.17

Interaction of Semiconductor Nanoparticles with *Pseudomonas Aeruginosa*. Peter K. Stoimenov[1], John H. Priester[2], Galen D. Stucky[1] and Patricia A. Holden[2]; [1]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California; [2]Bren School of Environmental Science & Management, University of California, Santa Barbara, California.

Very little is known regarding the environmental behavior of nanomaterials. The possible environmental impacts of nanomaterials is of increasing concern as the number of applications of different nanomaterials is steadily increasing. Particularly interesting is the widely studied fluorescent semiconductor nanoparticles such as CdSe, its analogues and core/shell nanoparticles. Studying the environmental responses of nanomaterials is of importance because it is likely that the specific chemical and physical properties of the nanomaterials will trigger bioresponses that differ from the constituent metals. We are studying the environmental strain *Pseudomonasaeruginosa* PG201, both in liquid culture and in biofilm, to understand its interactions with water based solutions of semiconductor nanoparticles CdSe and CdTe. The interactions were studied by viability studies, transmission and scanning electron microscopy (TEM and SEM), and fluorescence microscopy. A summary of the results will be presented. A parallel study was conducted involving cadmium and selenium salts separately and in combination to determine if possible toxicity effects can be explained simply by the presence of the toxic cadmium and selenium oxidation products generated in the course of nanoparticle oxidative decomposition. It was observed that *P.aeruginosa* generates spherical selenium nanoparticles from Se salts under aerobic conditions, but the process is inhibited by any amount of Cd. Curiously, strong fluorescence is observed when the bacteria are incubated in the presence of both Se and Cd salts yet elemental selenium is not generated.

S5.18

Interactions of PAMAM Dendrimer Nanoparticles with Cells: Dependence of Surface Groups and Relationship with Lipid Raft Mediated Endocytosis. Seungpyo Hong[1,2], Jennifer L. Peters[2], Istvan J. Majoros[2], James R. Baker[2], Bradford G. Orr[2,3] and Mark M. Banaszak Holl[1,2,4]; [1]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan; [2]Michigan Nanotechnology Institute of Medicine and Biological Sciences, University of Michigan, Ann Arbor, Michigan; [3]Physics, University of Michigan, Ann Arbor, Michigan; [4]Chemistry, University of Michigan, Ann Arbor, Michigan.

It was recently found that amine-terminated PAMAM dendrimers induce membrane permeability consistent with the presence of nanoscale holes in living cell membranes[S. Hong et al. Bioconjugate Chem. 2004, 15, 774]. The PAMAM induced membrane permeability appears to depend on size and surface groups of the nanoparticles as well as temperature. Higher generation dendrimers have been reported to be more effective in membrane permeabilization than smaller dendrimers. In this study we prepared amine, acetamide, and carboxylate terminated G7 PAMAM dendrimers with chemically well defined structure. Further the dendrimers were conjugated with AlexaFluor 488 enabling us to employ confocal microscopy and flow cytometry. Positively charged amine-terminated dendrimers internalized into KB and Rat2 cells causing spontaneous LDH leakage. Neither the acetamide nor the carboxylate terminated dendrimers exhibited similar behavior. The internalization of the amine-terminated PAMAM dendrimers was further investigated in vitro by employing metabolic inhibitors, including reduced temperature and cytochalasin D (CD; an actin filament disruption agent). Low temperature reduced but did not prevent G7 dendrimer internalization and LDH leakage. Rat2 cells pre-treated with CD still exhibited LDH release and dendrimer internalization. Two endocytic markers (Cholera Toxin for lipid raft mediated endocytosis and Transferrin for clathrin dependent pathways) were also employed. G7 PAMAM dendrimers appeared to co-localize with cholera toxin suggesting that the internalization mechanism follows lipid raft mediated endocytosis. However, by depleting cholesterol using methyl-β-cyclodextrin, enhanced LDH leakage caused by dendrimers was observed. This is inconsistent with the lipid raft mediated endocytosis hypothesis.

S5.19

Biocompatibility of Carbon Nanotubes with Vascular Smooth Muscle Cells. Natalia Varaksa, Tammy Oreskovic and Paul Rice; Materials Reliability Division, National Institute of Standards and Technology, Boulder, Colorado.

Development of bioceramics and devices based on carbon nanotubes (CNTs) and nanofibers is one of the most active areas in nanotechnology/biology interface. However, the lack of sufficient knowledge about compatibility of carbon nanotubes with biological systems prompts the investigation of their effects on cell viability. Most of the reported studies have shown the impact of large agglomerations of CNTs on specific systems in animals, such as pulmonary and dermatological effects, but only a few have investigated these effects at a cellular level. In our work, we report the response of vascular smooth muscle cells (VSMCs) to multi-walled CNTs to assess their potential use as tissue engineered vascular grafts. The exposure of cells to CNTs was performed by two different methods. These methods were: - growth of VSMCs on CNTs deposited on glass substrates, - suspensions of CNTs in aqueous biological media. Due to the hydrophobicity of CNTs, biocompatible surfactants were used as dispersion agents for aqueous CNT suspensions. The viability of cell growth was evaluated using optical and electron microscopies as well as Alamar Blue, a cell proliferation assay. Results indicated that in a liquid suspension of CNTs cells had been growing as well as the controls, while carbon nanotubes deposited on glass substrates retarded cell proliferation, as compared to the controls. However, most of the cells remained viable and attached to the substrates. These results demonstrate the biocompatibility of CNTs with VSMCs, permitting us to further consider CNTs as possible candidates for tissue engineered vascular grafts.

S5.20

Flame Retardant High Impact Polystyrene Nanocomposites. Mayu Si[1], Jonathan Sokolov[1], Miriam Rafailovich[1], John Oh[2], Wonwoo Lee[2], Kiwoong Yoo[2] and Ryan Saunders[2]; [1]Materials Science and Engineering, Stony Brook University, Stony Brook, New York; [2]Jerico High School, Jericho, Pennsylvania.

High impact polystyrene flame retardant nanocomposites with conventional flame retardant agents, brominated polystyrene (Br-PS) and antimony trioxide (AO), were prepared by melt blending. The combustion behavior was investigated by subjecting slabs of the polymer to UL-94 V0 testing. We found that the polymers with only the retardant agents or the clay could not pass UL-94 V0 standard. On the other hand, all polymers with both components were self-extinguishing. TEM images indicated that the clay is very effective in improving the dispersion of Br-PS and AO in HIPS, which further increase the efficiency of conventional flame retardants. The phosphate compounds combined with clay were under investigation to try achieve UL-94 V0. Based on TEM and combustion test, the general mechanism is proposed that the introduction of clay can improve the compatibility between polymers and fire-retardant agents, the synergy between the char formed by the clay and gas phase isolation due to the conventional flame-retardant agents make the material become fire-retardant. ? Supported by NSF funded MRSEC at Stony Brook

S5.21

Flame Retardant Polymer Blend Nanocomposites. Mayu Si[1], Jonathan Sokolov[1], Miriam Rafailovich[1], Tohru Araki[2] and Harald Ade[2]; [1]Materials Science and Engineering, Stony Brook University, Stony Brook, New York; [2]Physics, NC State University, Raleigh, North Carolina.

We investigated the flame retardant performance of polymer blends, PS/PMMA, PC/SAN, with organoclay, conventional flame retardant agents such as decabromodiphenyl oxide (DB) and antimony trioxide (AO). These polymer blends were characterized by TEM, STXM, LOI and UL-94 V0. TEM and STXM photographs show that the addition of organoclays into polymer blends drastically reduces the average domain size of the component phases and improves the dispersion of DB and AO. Further, UL-94 V0 results indicate that the polymer blends with DB and AO can not achieve self-extinguishing in the absence of clay. The amounts of flame retardants and clay used were varied to try to achieve the optimal formula. Clay functions as a compatibilizer and char former in flame retardant polymer blend systems, which provides great potential for the future application. Supported by NSF funded MRSEC at Stony Brook

S5.22

The Effects of Supercritical Carbon Dioxide (scCO2) on the Phase separation of PS and PMMA Blend Thin Film under Confinement. John Jerome, Young-Soo Seo, Tadanori Koga, Devinder Mahajan, Jonathan Sokolov and Miriam Rafailovich; Materials Science, SUNY-STONY BROOK, Stony Brook, New York.

Thin film thickness dependence of a silicon oxide (SiOx) capping layer to control the morphology of polystyrene/poly(methyl methacrylate) PS/PMMA and deuterated polystyrene/poly(methyl methacrylate) dPS/PMMA was investigated. Theoretical investigation predicted that polymer blend films confined in between two walls where both walls preferentially adsorb the same component are expected to be laterally phase-separated with large separation distance where preferential component completely wets the substrate surface. In the case of PS/PMMA, PMMA domain formed a vertically phase-separated " rod " structure surrounded by PS domain after annealing. In the case of dPS/PMMA, long phase-separated domains associated with the increase of SiOx capping layer were also observed. By adding 10% Polystyrene-diblock-poly(methyl methacrylate) (PS-b-PMMA) diblock to dPS/PMMA blend, a lamellar morphology was formed at the interface. A combination of x-ray reflectivity (XR) and atomic force microscopy (AFM) measurements were employed to explain the difference in morphology between PS/PMMA and dPS/PMMA. X-ray showed that X value between PS/PMMA increased by a factor of approximately 2 compared to that of dSP/PMMA. In addition to interfacial interaction, the morphology also depends on the polymer rigidity. Hence we will also report on particle-reinforced polymers.

S5.23

Photocatalytic Surface Based on Mesoporous TiO2 Thin Film. Liang Hong, Zhaolin Liu, Bin Guo and Huixin Jiang; Institute of Materials Research & Engineering, Singapore, Singapore.

Polyethylene glycol (PEG) oligomer has been identified to be a crucial additive in the TiO2 colloidal dispersion generated from the sol-gel reaction. The colloidal dispersion was spin-coated on a glass plate, and the coating layer was converted to a consolidated thin film via calcinations at 550oC. PEG plays a key role in assuring a crack-free nano-porous TiO2 matrix through calcination. Heavy cracks over the entire film would be otherwise unavoidable without the presence of PEG in the colloidal dispersion. PEG is deemed to play a role in controlling hydrolysis rate of Ti(i-OPr)3, namely, PEG polymer coils in the sol-gel system could steadily release catalyst H3O+ for the hydrolysis reaction, which leads to more uniform and dense TiO2 nuclei. In addition, PEO is also believed to act as a so-called lubricating agent among TiO2 particles in the colloidal coating layer before calcinations, this helps to homogenize the density in the sol-gel coating layer in the drying course. Nanoporous TiO2 thin films, resulted ultimately from the above sol-gel coating and thermal curing procedure, are transparent and comprise primarily by the anatase phase. The photocatalytic activity of the TiO2 thin films was evaluated by the photooxidized extent of iodide and methyl orange, and the outcomes showed the favorable a trend with increasing PEG content in the antecedent colloidal dispersion systems.

S5.24

Electrical Breakdown and Ballistic Transport Study of Various Carbon Nanotube Structures. Bangalore K. Rao[1], Do Hyun Kim[1], Jun Huang[1], Wanjun Park[2], Donghun Kang[2] and Wong Bong Choi[1]; [1]Mechanical and Materials Engineering, Florida International University, Miami, Florida; [2]Materials and Device Lab, Samsung Advanced Institute of Technology, Yongin-Si, Gyeonggi-Do, South Korea.

In order to employ the nanotube as building block of future interconnect in electronic circuit its transport mechanism like ballistic and breakdown limits must be clearly understood. Resent studies on the CNT have given some insight into the transport mechanism. Here we demonstrate the result of low and high bias measurement on singlewall carbon nanotube (SWNT), multiwall carbon nanotube (MWNT), CNT-Mat and CNTs in anodized aluminum oxide (AAO). Not much study has been carried out on SWNT and CNT-Mat break down mechanism. Experimental result on MWNT nanotube have demonstrated that they breakdown between 3 to 4 V and the breakdown current in between 100- 600microA. Ballistic transport takes place only in the nanotube with length not more that 500-900nm and at voltage bias less that 0.1V.Electromigration, an important phenomenon that explains the breakdown in conventional metal wire, does not explain breakdown in nanotube. It is important to know and compare the mechanism and factor that control the ballistic transport and breakdown in different nanotube. A systematic comparison of these values coupled with the mathematical calculation gives an outlook on the transport mechanism of the CNT. By knowing the properties of SWNT and MWNT we can tailor the properties of the CNT-Mat to suit our requirement as it shows unique properties like high current densities, semiconducting behavior, and can be applied in the real devices application. Future work involves using the particular type of nanotube for specific device, like CNT-Mat for sensor application, MWNT for Field emission and interconnects.

SESSION S6: Nanomaterials for Treatment and Remediation

Chairs: Dionysios Dionysiou and Wei-xian Zhang
Wednesday Morning, November 30, 2005
Room 203 (Hynes)

8:00 AM S6.1

Filtration and Separation Applications for Nanoporous Carbide-Derived Carbon. Elizabeth N. Hoffman, Gleb Yushin, Michel W. Barsoum and Yury Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Carbide derived carbon (CDC) contains tunable nanoscale pores and high specific surface areas. Nanoporous CDC has been synthesized from selected ternary carbides via chlorination reactions over the temperature range of 400 °C - 1200 °C. X-ray diffraction, Raman spectroscopy, electron microscopy, and sorption analysis were used to reveal the CDC microstructure. Sorption isotherms obtained using a variety of adsorbate gases have shown controlled variations in adsorption properties of the synthesized samples. CDC offers a unique capability to design materials with increased adsorptive selectivity for a given gas or aqueous mixture through the ability to tailor the porosity, specific surface area, and surface termination. Initial sorption results show tremendous potential for CDC in separation applications such as air and water purification, as well as fuel purification, such as methane, for increased fuel economy.

8:15 AM S6.2

Functionalized nanotubes for space exploration air revitalization. Ramakumar Allada[1], Padraig Moloney[2], Chad Huffman[3], Olga Gorelik[3], Pasha Nikolaev[3], Sivaram Arepalli[3] and Leonard Yowell[2]; [1]National Research Council/NASA Johnson Space Center, Houston, Texas; [2]NASA Johnson Space Center, Houston, Texas; [3]ERC Inc./NASA Johnson Space Center, Houston, Texas.

Removal of carbon dioxide from closed atmospheres has a number of environmental control applications including manned space flight systems and various defense and civilian uses. Given the challenges of missions to the Moon and Mars, NASA Johnson Space Center is interested in designing a regenerable CO2 removal system (RCRS) for use in spacecraft and extravehicular mobility units (EMU). The previous solid-amine system developed in the late 1980s consisted of polymer beads coated with an amine compound that sequesters carbon dioxide from an air stream [1]. The main drawback encountered with its operation included poor adherence of the amine to the support phase, mediocre surface area and poor thermal conductivity. Single-walled carbon nanotubes (SWCNT) have been proposed as a new amine support material for the RCRS because of their higher surface area and thermal conductivity [2]. Initial research demonstrated the need for functionalization of SWCNT to obtain optimal adherence of the amine to the SWCNT support phase [3]. The chemical binding between the support phase and the amine insures that the medium will have a longer cycle life since it has greater thermal stability. Recent investigations show that SWCNT can be functionalized with primary and secondary amines. The extent of functionalization and thermal stability is monitored by XPS and TGA. We will present equilibrium CO2 adsorption capacity data for several versions of SWCNT supported amine-based CO2 scrubber materials. We will correlate this data with their surface area and porosity as well as the relative amine contents. [1] F.A. Ouelette, H.E Winkler, G.S Smith, The Extended Duration Orbiter Regenerable CO2 Removal System. SAE paper # 901292, 20th International Conference on Environmental Systems. 1990. [2] J. Hone, M. C. Llaguno, N. M. Nemes, A. T. Johnson, J. E. Fischer, D. A. Walters, M. J. Casavant, J. Schmidt, R. E. Smalley, Appl. Phys. Lett., 77, 666 (2000). [3] P. Moloney, C. Huffman, O. Gorelik, P. Nikolaev, S.Arepalli, R. Allada, M. Springer, L. Yowell, NN2.4, Materials for Space Applications MRS Proceedings Volume 851

8:30 AM S6.3

Investigation of nitrate reduction in neutral medium on Rh-modified pyrolytic graphite electrodes. Oleg Brylev[1,2], Daniel Belanger[1] and Lionel Roue[2]; [1]Department of Chemistry, University of Quebec in Montreal, Montreal, Quebec, Canada; [2]INRS - Energie, Materiaux et Telecommunications, Varennes, Quebec, Canada.

The catalytic activity of rhodium films in many reactions of environmental importance is very well known, particularly for nitrate reduction in waste water. Due to the high cost of Rh it is of weighty importance to obtain thin rhodium films and the electrodeposition remains one of the most efficient methods for this purpose. Compared with other methods, the electrodeposition parameters can be much more easily controlled to produce the required deposit properties. The electrodeposition of metallic Rh on pyrolytic graphite electrodes was performed from a Na3RhCl6 aqueous solution in potentiostatic mode involving the double-pulse technique. The influence of deposition potential and deposition time as well as the properties of Rh deposits (Rh loading, surface area, specific catalyst area) were determined. The application of short potential nucleation pulse allows to obtain enhanced surface coverage in comparison with usual potentiostatic deposition and to decrease the mean particle size from 70 to 30 nm. In this case the specific catalyst surface area can attain 32 m2/g. For the investigation of NO3- reduction the neutral medium was chosen as the most appropriate to the industrial needs. The electrodes were subsequently tested for H2 evolution reaction in 1 M NaCl aqueous solution and then in the presence of NO3- anions (1 M NaCl + x M NaNO3 (x=0.02-1)), so the contributions from hydrogen evolution and nitrate reduction could be split up. The potential limits were from -0.35 to -1.25 V vs.Ag/AgCl. In 1 M NaCl + 0.1 M NaNO3, a peak appearing at approximately -0.85 V proves the catalytic efficiency of Rh modified electrodes towards NO3- reduction. The adsorption equilibrium constant and the activation energy for nitrate reduction were then determined. The current at -0.85 V (5th cycle, cathodic scan), when one can neglect hydrogen evolution, could be used as a quantitative characteristic of the catalytic efficiency of Rh deposits. It can be normalized to the geometrical surface area of graphite electrode, to the Rh real surface area or to the mass of deposited Rh. Taking account of high Rh price, the mass activity should be considered as an especially important for its commercial use as a catalyst. The double-pulse technique proved its efficiency at positive deposition potentials and small deposition time. The increase in the nucleation pulse duration from 20 to 100 ms results in enhancing the mass catalytic activity towards NO3- reduction, which attains 175 A/g for the best sample (nucleation pulse of 100 ms, deposition time of 60 s at -172 mV vs. Ag/AgCl). However, for significant deposition times (>240 s) the difference of electrochemical properties between non-pulse and pulse obtained samples vanishes. The authors are greatly indebted to NanoQuebec, the Natural Sciences and Engineering Research Council of Canada (NSERC) and Enpar Technologies for supporting this work and to R. Mineau (UQAM) for taking SEM micrographs.

8:45 AM S6.4

In-situ Treatment and Remediation of Groundwater Using Nanotechnology. Harch Gill[1] and Thomas Mallouk[2]; [1]Princeton Nanotech LLC, Robbinsville, New Jersey; [2]Penn State University, University Park, Pennsylvania.

A successful, high profile, full-scale NanoFeTM Technology application was performed to treat chlorinated hydrocarbons contaminated groundwater at a former landfill site in Hamilton

Township, New Jersey. NanoFeTM consists of supported submicron (<10-6 meter), bacteria-sized, nanoparticles of zero valent iron (Fe0) and trace amounts of a noble metal catalyst. NanoFeTM is an extremely versatile remediation tool given its high reactivity and extremely small particle size (typical particle sizes are on the order of 10-100 nanometers). The remediation goal for the site was to inject NanoFeTM slurry into the most contaminated portion of the dissolved chlorinated contaminant plume within a shallow perched water aquifer, to significantly reduce the contaminant concentrations. The primary groundwater contaminants targeted for reduction consisted of 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE), and trichloroethylene (TCE). The NanoFeTM Technology full-scale application was initiated in June 2004 and applied to approximately a one-half acre area of the site in two phases of injection. A total of 4,500 pounds of NanoFeTM was injected using direct-push technologies and was applied in a 20-foot injection grid pattern in the treatment area. A baseline groundwater monitoring event was conducted a month prior to NanoFeTM injection and four post-injection groundwater monitoring events were conducted over a five month period. The monitoring program included the measurement of field geochemical parameters and the laboratory analyses of collected groundwater samples for VOCs, total and dissolved iron, and selected contaminant degradation indicators (ethane, ethene, and chloride concentrations). The NanoFeTM Technology application at the site demonstrated that the primary project objective was successfully achieved to effectively treat the hotspots of the perched water zone. The dissolved chlorinated contaminants were reduced by over 90% over a five month period. Additional reductions in the dissolved chlorinated contaminant concentrations continued to be observed in succeeding quarterly monitoring events.

9:00 AM *S6.5
Environmental Applications of Zero-valent Iron Nanoparticles: Fundamental Issues. Wei-xian Zhang, Civil & Environmental Eng., Lehigh University, Bethlehem, Pennsylvania.

Nanotechnology is the engineering and science of manipulating matter at the nanoscale (<100 nm). For environmental applications, nanotechnology offers the potential of novel materials and processes with unique reactivity toward targeted contaminants, enhanced mobility in environmental media, and application flexibility. Many nano-based environmental technologies (e.g., sensors, sorbents, reactants) are under active research and development, and are expected to play a leading role for the next generation environmental technologies, with the potential to significantly improve and/or replace various conventional environmental technologies in the near future. Iron nanoparticle technology represents perhaps one of the first nanoscale environmental technologies. Since 1995, work at Lehigh University has systematically examined iron nanoparticles for environmental remediation. The first synthesis of iron particles with the borohydride method was developed in 1997. Studies on the hydrodechlorination with bimetallic nanoparticles have been reported. In 2001, the first field demonstration was conducted. Recent work has expanded the applications to the remediation of perchlorate, heavy metal ions such as Cr(VI) and Cd(II), and organochlorine pesticides such as DDT and lindane. Interests on the iron nanoparticle technology have been growing rapidly over last 3-4 years. Recent field tests have further demonstrated promising prospective for in situ remediation. Currently, this technology is being used at more than 20 sites in U.S. In this presentation, fundamental issues related nanoparticles synthesis, characterization, fate and transport, and environmental impact will be discussed.

10:00 AM S6.6
Nanosized Photocatalysts for Environmental Applications. Billie Lynn Abrams, Jess P. Wilcoxon, Steven G. Thoma and Paula P. Provencio; Sandia National Labs, Albuquerque, New Mexico.

Traditionally, TiO_2 has been the most commonly used catalyst in the photooxidation of toxic chemical waste as well as in water splitting reactions. On the nanoscale (∼25nm), it has been shown to be more effective than in bulk form due to the increased surface area. Unfortunately, bulk and nanosized TiO_2 have the major drawback of a very large band gap (3.2eV) requiring the use of UV excitation (only ∼3% of the solar spectrum). The development of new nanosized photocatalysts capable of utilizing the visible region of the solar spectrum will allow for higher efficiency photocatalytic reactions. We will present a detailed study of nanosized MoS_2 (n-MoS_2) photocatalysts whereby high pressure liquid chromatography (HPLC) in combination with dynamic light scattering (DLS) and HRTEM are used to probe the relationship between surface chemistry and photocatalytic activity. HPLC is shown to be particularly useful for studying fully dispersed clusters and their chemical changes during catalytic reactions. The use of n-MoS_2 is based on research by Wilcoxon et al. [1-3]showing the complete photo-oxidation of organic chemicals with visible light. N-MoS_2 and its isomorphs have the potential to photooxidize a wide variety of toxic pollutants. Another promising application is as a photocatalyst for the production of H2 by splitting either H_2O or H_2S. The implications of this for contributing to a H_2 economy will be discussed. 1. Wilcoxon, J. P. "Photooxidation Method Using Mos2 Nanocluster Materials". 6,245,2000, 2001. 2. Thurston, T. R.; Wilcoxon, J. P., Photooxidation of Organic Chemicals Catalyzed by Nanoscale MoS2. *JournalofPhysicalChemistryB*, 103, (1), 11-17(1999). 3. Wilcoxon, J. P.; Newcomer, P. P.; Samara, G. A., Synthesis and Optical Properties of MoS2 and Isomorphous Nanoclusters in the Quantum Confinement Regime. *JournalofAppliedPhysics*, 81, (12), 7934-44(1997). Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

10:15 AM S6.7
Evolution of the core-shell structure of metallic iron particles as a function of time and environment. Donald Baer[1], Chongmin Wang[1], Mark Engelhard[1], Dean Matson[1], James Amonette[1], Vaishnavi Sarathy[2], John Linehan[1], James Nurmi[2], You Qiang[3], Jiji Antony[3], Klaus Pecher[1], R. Lee Penn[4] and Paul Tratnyek[2]; [1]Pacific Northwest National Laboratory, Richland, Washington; [2]Department of Environmental and Biomolecular Systems, Oregon Health and Sciences University, Beaverton, Oregon; [3]Department of Physics, University of Idaho, Moscow, Idaho; [4]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

The high reactivity of metallic iron nanoparticles with contaminants such as chlorinated hydrocarbons, the possibility of solution based delivery to contamination zones and evidence of an ability of the nanostructure to alter reaction pathways have stimulated considerable research into the potential use of iron metal nanoparticles for environmental remediation. As part of our examination of the chemical properties of nanoparticles, we are exploring the stability of nanoparticles and how they evolve with time in different environments. Iron nanoparticles containing metallic iron and exposed to any reactive environment invariably have a core/shell structure where the shell slows the oxidation rate of the particle. Iron nanoparticles, synthesized by borohydride reduction (Fe^{BH}), by thermal reduction of oxide particles under a hydrogen atmosphere (Fe^{H2}), or produced by a vacuum based cluster process (Fe^{sp}) are characterized by a variety of methods before and after exposure to different environments. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and x-ray diffraction (XRD) are routinely used to examine the particles. In some circumstances, x-ray adsorption spectroscopy (XAS) or other methods are used to characterize the particles. The influence of formation and processing conditions on the nature of the core/shell structure has been examined in some detail. The oxides shells formed on Fe^{sp} particles have been examined for different particle sizes and exposures to oxygen. The room temparature oxidation of these nanoparticles shows the formation of voids and in some circumstances hollow oxide nanoparticles. Although the formation and processing are significantly different, the presence of interfacial voids below an iron oxide shell is found both in the Fe^{sp} particles and Fe^{H2}. The shells on the Fe^{BH} particles are rich in boron an significantly different from those on the other particles. Studies measuring the reductive dechlorination of carbon tetrachloride (CT) have shown differences in the branching ratio for the Fe^{H2} and Fe^{BH} nanoparticles. The reaction branches between a pathway that yields chloroform (CF) as its primary product and one or more pathways that yield other products. For an initial CT concentration of 4 μM, the yield of CF (YCF) was typically < 0.4 for the Fe^{H2} form and > 0.4 for Fe^{BH}. In this circumstance the non-CF pathway was favored when the Fe^{H2} form was used. To help understand the impact of time and sample type on reaction pathway, a series of experiments using electron paramagnetic resonance (EPR) spectroscopy spin trap studies to nondestructively probe the reactivity of Fe^{H2} and Fe^{BH} particles over time has been initiated. The EPR measurements on Fe^{H2} show differences in the nature of the electron transfer reduction process as a function of time. These measurements are matched with TEM, XPS and XRD particle characterization after similar time and solution exposures.

10:30 AM S6.8
Promoting Effect of a Carbon Coating on CF2Cl2 Decomposition over Nanocrystalline MgO.
Alexander F. Bedilo[1], David S. Heroux[2], Vladimir V. Chesnokov[1], Ilya V. Mishakov[1], Maxim S. Mel'gunov[1], Alexander M. Volodin[1], Vladimir I. Zaikovskii[1] and Kenneth J. Klabunde[3]; [1]Boreskov Institute of Catalysis, Novosibirsk, Russian Federation; [2]Department of Chemistry, University of Maine, Farmington, Maine; [3]Department of Chemistry, Kansas State University, Manhattan, Kansas.

Nanocrystalline metal oxides prepared via a sol-gel route from the corresponding alkoxides have small average crystallite sizes (4-8 nm), unusual crystallite shape, superior adsorption and catalytic properties [1]. Aerogel-prepared (AP) alkaline earth metal oxides have been shown to be efficient destructive sorbents in reactions with halogenated hydrocarbons, hazardous compounds and air pollutants containing phosphorous, sulfur, etc. In particular, we have recently reported the existence of an intriguing induction period phenomenon during CF2Cl2 decomposition over AP-MgO [2]. Current presentation will be devoted to the effect of an intelligent carbon coating on the reaction of MgO nanocrystals with CF2Cl2. As we have recently shown, if the metal oxide nanoparticles are coated with a porous carbon, the water problem often deteriorating the adsorbent performance is minimized, while destructive sorption of target pollutants is still allowed [3]. The carbon coating of nanocrystalline MgO was carried out by heating it in butadiene flow at 500°C. The carbon concentration was varied by variation of the reaction time. The initial carbon formation occurred at a rate of approximately 2 wt. % per hour. The formation of carbon structures on AP-MgO has been studied by HTEM, XRD, ESR and adsorption techniques. The structure of the MgO core is not affected by the carbon deposition, but is covered by carbon "nanoislands" or three-dimensional structures, depending on the amount of deposited carbon. Despite the fact that the carbon coating covers certain percentage of the surface active sites and, thus, was expected to decrease the AP-MgO reactivity, it was found to improve its reactivity in destructive adsorption of CF2Cl2. The kinetics of the process over AP-MgO is characterized by a prolonged induction period, which is as long as 8.5 h at 325°C and nearly 1 h long at 400°C. The addition of only 1 wt.% carbon significantly shortens the induction period, while 10% C/AP-MgO has a 3 times shorter induction period than AP-MgO. Further studies are required to understand how the carbon coating affects the processes taking place on he MgO surface during the induction period. The financial support of the US Army Research office, Presidium of the Russian Academy of Sciences (Project 8.23), and Russian Foundation for Basic Research (Grant 05-03-33000) is acknowledged with gratitude. [1] K. J. Klabunde, J. V. Stark, O. B. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic and D. Zhang, J. Phys. Chem. 100 (1996) 12142. [2] I. V. Mishakov, V. I. Zaikovskii, D. S. Heroux, A. F. Bedilo, V. V. Chesnokov, A. M. Volodin, I. N. Martyanov, S. V. Filimonova, V. N. Parmon and K. J. Klabunde, J. Phys. Chem. B, 109 (2005) 6982. [3] A.F. Bedilo, M.J. Sigel, O.B. Koper, M.S. Melgunov and K.J. Klabunde, J. Mater. Chem., 12 (2002) 3599.

10:45 AM S6.9

Carbon Nanotubes as Superior Adsorbents for Trichloroethylene. Saikat Talapatra[1], Reena Srivastava[2], Robert Vajtai[1], Gunaranjan Viswanathan[1], James E. Kilduff[2], Anchal Srivastava[3], Onkar N. Srivastava[3] and Pulickel M. Ajayan[1,4]; [1]Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; [2]Department of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, New York; [3]Department of Physics, Banaras Hindu University, Varanasi, U.P., India; [4]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Adsorption is an important unit process for water quality control, and increasingly stringent water quality standards have stimulated a search for new, better adsorbents. Organic compounds comprise a major class of contaminants, both in potable water sources (e.g., rivers) and hazardous waste sites. In this research, we evaluate the efficacy of carbon nanotubes (CNTs) for adsorbing trichloroethylene (TCE) from water. TCE is a chlorinated aliphatic synthetic organic chemical (SOC), which because of its widespread use as an industrial solvent, is one of the most frequently detected ground water contaminants in the United States (National Research Council, 1994). TCE has been designated as a priority pollutant by the United States Environmental Protection Agency, and is regulated by the Safe Drinking Water Act Amendments of 1986 (U.S. EPA, 1986). The present state of the art for removing TCE and many other SOCs from water and air uses fibrous, powdered, or granular activated carbon (ACF, PAC, and GAC, respectively). Whereas an important feature of activated carbons governing their capacity is the surface area or pore volume accessible to the adsorbate, the adsorption energy is governed by the presence of micropores. When a molecule adsorbs in pores not too much larger than molecular dimensions, overlapping surface forces increase adsorption energy. Therefore, as micropore volume is filled, and adsorption occurs in larger pores, adsorption energy decreases. If the solution phase concentration is sufficiently high, micropores will become saturated and the activated carbon will reach its capacity. In contrast, carbon nanotubes exhibit high adsorption energies by virtue of their surface characteristics, not due to the presence of micropores. Therefore, adsorption energy should not be sensitive to loading; at least until monolayer coverage is attained. Because of these features, carbon nanotubes have significant potential as highly efficient adsorbents for water purification purposes. In this presentation we demonstrate the efficacy of CNTs for adsorbing TCE from aqueous solution. By comparing measured uptake of TCE by two different activated carbons (wood-based WVB and coal-based F400), and by single- and multi-walled carbon nanotubes (SWNT and MWNT, respectively) we demonstrate the high affinity of TCE for carbon nanosurfaces. Our data provide convincing evidence for the promise of CNTs as adsorbents for water treatment.

11:00 AM *S6.10

Self-assembled nanostructured crystalline TiO_2 thin films and TiO_2/Al_2O_3 composite membranes with simultaneous photocatalysis, disinfection, separation, and antifouling properties. Hyeok Choi[1], Anna C. Sofranko[2] and Dionysios D. Dionysiou[1]; [1]Civil and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio; [2]Chemical Engineering, University of Virginia, Charlottesville, Virginia.

Nanocrystalline titanium oxide (TiO_2, titania) has been extensively studied due to its outstanding physical and chemical properties in photocatalytic applications for environmental remediation. Titania is usually used in the form of nanoparticles in suspension for high catalytic surface area and activity. However, nanosize TiO_2 particles in suspension are difficult to remove after their application in water and wastewater treatment. Recently, many research studies have been carried out to immobilize TiO_2 catalyst onto various substrates as thin films and membranes for use in a variety of applications. In particular, photocatalytic membrane reactors are of great interest because of their multiple functions such as (i) decomposition of recalcitrant organic contaminants, (ii) destruction of biological toxins (microcystin-LR), (iii) inactivation and killing of pathogenic microorganisms (*E.coli*), (iv) physical separation of parent contaminants and intermediate products, and (v) self-antifouling action. However, to accomplish the development of such TiO_2 photocatalytic membrane reactors, there is a great need to apply novel material synthesis procedures to tailor-design the structural properties and enhance the catalytic properties of the photocatalytic TiO_2 thin films and membranes. The properties include active anatase crystal phase, high crystallinity, small crystallite size, high surface area and porosity, narrow pore size distribution, and film homogeneity and reproducibility. The development of nanoscience and nanotechnology, especially for modern material synthesis, makes it possible to develop new types of TiO_2 photocatalysts with improved properties and functionalities for environmental applications. In order to synthesize highly efficient nanostructured crystalline TiO_2 photocatalytic films and membranes, we have investigated a novel chemistry method employing surfactant molecules as a pore directing agent along with acetic acid-based sol-gel route. In this synthesis method, we can control hydrolysis reaction of titanium precursors for controlled and stable nanostructure of TiO_2 material and manipulate its nanoporous structure. Here, we report the synthesis procedure and mechanism and the characterization of the photocatalytic TiO_2 films and membranes. Furthermore, the multiple functions mentioned above from water decontamination, disinfection, separation to antifouling action are discussed for their environmental applications and implications.

11:30 AM S6.11

Innovative and Cost-Effective Nanocomposite Adsorbent for Removal of Heavy Metal Ions from Drinking Water. Huimin Amy Chen[1], Dennis A. Clifford[2] and Gautam Samanta[2]; [1]Inframat Corporation, Willington, Connecticut; [2]Civil and Environmental Engineering, University of Houston, Houston, Texas.

Contamination of arsenic, lead, and other heavy metal ions in drinking water is affecting health of billions of people world-wide. There is urgent need of innovative and cost-effective adsorbents for the removal of heavy metal ions from drinking water. Inframat Corporation is developing unique nanocomposite granules that are efficient in removing both arsenic and lead contaminants from drinking water. Each composite granule contains thousands of nanofibers interwoven with thousands of nanoparticulates, creating high volume of porosity and increasing specific surface area. The high porosity structure allows quick penetration of water through the media and the quick removal of contaminants from water through adsorption process. The removal of arsenic and lead from drinking water by Inframat media was studied by isotherm adsorption tests. It demonstrated significant removal efficiency and Inframat is currently working with industry partner to commercialize the media for point of use water treatment device.

11:45 AM S6.12

High Flux Ultrafiltration Membranes Based on Electrospun Nanofibrous Scaffolds. Kyunghwan Yoon[1], Kwangsok Kim[2], Xuefen Wang[1], Dufei Fang[1], Benjamin S. Hsiao[1] and Benjamin Chu[1]; [1]Chemistry, Stony Brook University, Stony Brook, New York; [2]Polymer Science and Engineering, Inha university, Incheon, South Korea.

Conventional ultrafiltration filters for water treatments are based on porous membranes, typically manufactured by the phase immersion method. The microstructures of the substrate in these membranes usually result in a relatively low flux rate. In this study, we demonstrate a new type of high-flux ultrafiltration medium based on an electrospun nanofibrous scaffold (e.g. polyacrylonitrile, PAN) coupled with a thin layer of hydrophilic, water-resistant, but water-permeable coating (e.g. chitosan). Such nanofibrous composite membranes exhibit a much higher flux rate for ultrafiltration. The interconnected nanofibrous scaffold can be controlled partially by varying the fiber diameter (from less than ~100 nanometers to a few micrometers) by means of electrospinning processing. An example membrane, containing an electrospun PAN scaffold with an average fiber diameter from 124 ~ 720 nm and a porosity of about 70 %, together with a chitosan top layer having a thickness of 1 μm, although not yet fully optimized, exhibited a 7-time higher total thickness-normalized flux rate and 23-time higher coating thickness-normalized flux rate than commercial ultrafiltration membranes, while maintaining the same rejection efficiency (> 99.9 %) for oily waste-water filtration. *Work supported by the Office of Naval Research

SESSION S7: Nanotechnology Enabled Sensors for Environmental Monitoring II

Chairs: Joydeep Dutta and Chuan-Jian Zhong
Wednesday Afternoon, November 30, 2005
Room 203 (Hynes)

1:30 PM *S7.1

Chemical Sensor Applications using Polymer Nanojunctions. N. J. Tao[1], Erica Forzani[1], Alvaro Aguilar Diaz[1], Xiulan Li[1], Larry A. Nagahara[2], Ishamshah Amlani[2] and Raymond Tsui[2]; [1]Electrical Engineering, Arizona State, Tempe, Arizona; [2]Motorola Labs, Tempe, Arizona.

A basic requirement for a chemical or biological sensor is to convert a molecular binding event into a measurable signal. Conducting polymers are attractive for sensor applications because they can directly covert the binding event into an electrical signal. They can be modified chemically with appropriate functional groups for specific detection of different analytes. An additional advantage is that conducting polymers can be scaled all the way down to nanoscale or even to single molecule dimension, which provides one with a unique opportunity to study molecular binding events on the nanoscale. In the present work we demonstrate chemical sensor application of functionalized conducting polymer nanojunctions. Each nanojunction is formed by bridging a pair of gold electrodes separated with a small gap (20 to 60 nm) of polyaniline (PANI) and recognizing molecules like peptides, an enzyme and a copper complex are use for detection of heavy metal ions in drinking water, glucose and a nerve agent simulant, respectively. The signal transduction mechanism of the sensor is based on the change in the nanojunction conductance as a result of a specific recognition reaction. These sensors offer several distinctive features: (1) By reducing the junctions down to nanoscale, the conductance of even a poorly conductive polymers is measurable. (2) The nanojunctions have a very large surface to volume ratio and gives rise to extremely high sensitivity. (3) The reduced dimension requires only small amounts of probes and samples and promises a highly integrated device.

2:00 PM *S7.2

Nanostructured Array Sensing Materials and Pattern Recognition for Environmental Monitoring. Chuan-Jian Zhong[1], Nancy N. Kariuki[1], Lingyan Wang[1], Mark Schadt[1], Xiajing Shi[2], Jin Luo[1], Derrick Mott[1], Susan Lu[2] and Jian Q. Wang[3]; [1]Chemistry, State Univ. of New York at Binghamton, Binghamton, New York; [2]System and Industrial Engineering, State Univ. of New York at Binghamton, Binghamton, New York; [3]Physics, State Univ. of New York at Binghamton, Binghamton, New York.

Nanostructured sensing arrays combined with pattern-recognition analysis are expected to provide new opportunities for enhancing the design of sensor materials in terms of sensitivity and selectivity. Such sensing properties are tunable by several design parameters such as particle size, interparticle distance and dielectric medium constant. This presentation will focus on the recent development of an investigation of molecularly linked core-shell nanoparticle assemblies as sensing array materials on chemiresistor and piezoelectric transducers for the detection of volatile organic compounds (VOCs) and the data analysis based on pattern recognition using principle component analysis (PCA) and artificial neural networks (ANN) techniques. The nanostructured array elements consist of thin film assemblies of monolayer-capped metal and oxide nanoparticles which were formed by molecularly-mediated assembly with tunable structures and functional groups. Each array element displayed linear responses to the vapor concentration. The observed high specificity constitutes an unprecedented example resulting from the unique combination of hydrogen-bonding donor/acceptor and hydrophobicity in the interparticle structure. A set of ANNs along with PCAs was used for the analysis of a series of vapor responses. The PCA technique was used to cluster data and feature extraction. A hierarchical BP neural networks system was employed as the pattern classifier. Implications of our findings to the delineation of the design criteria of nanostructured sensing arrays and the device integration for environmental monitoring will also be discussed.

3:30 PM *S7.3

Heavy-Metal Ion Sensing with Gold Nanoparticles. Abhilash Sugunan[1], Joydeep Dutta[1], Chanchana Thanachayanont[2] and Jons Hilborn[3]; [1]Microelectronics FOS, Asian Institute of Technology, Pathumthani, Thailand; [2]National Metal and Materials Technology Center, Pathumthani, Thailand; [3]Polymer Chemistry, Materials Chemistry, Uppsala University, Uppsala, Sweden.

The chemical inertness and resistance to surface oxidation make gold an important material for use in nano-scale technologies and devices. This property is crucial when particle size approaches the nano-scale and the dominance of surface atoms results in an enhanced chemical reactivity. Though the resistance to surface oxid ation is maintained in nanoparticles of gold, the chemical inertness of bulk gold is lost, and a heightened catalytic behavior is observed. Gold nanoparticles synthesized by using organic solvents are reported to offer excellent control and uniformity of size and can be dried and re-dispersed easily, since the protective capping agent (usually a thiol) is chemically bound by a coordinate bond to the surface of gold nanoparticles, unlike the physical adsorption of excess ions as in the case of the Turkevitch process. However, the organic solvents used in these techniques render them unsuitable for solution-based sensors for detection of bio-molecules like proteins, and saccharides. Applications of gold nanoparticles as sensors are usually based on detecting the shifts in SPR peak, due to either change in the dielectric constant around the nanoparticles as a result of adsorption of analyte molecules, or due to analyte-induced agglomeration of the nanoparticles. Both these effects rely on the selectivity provided by the functionalized capping agents (in the form of ions or specific polymers), highlighting the significance of the chemical methods of synthesis and stabilization of these nanoparticles for use as solution based sensors. We will report a novel strategy for using gold nanoparticles capped with chitosan for sensing ions of heavy metals. Acidic anions (glutamate ions in our case) are expected to cap the nanoparticle surfaces similar to conventional methods of stabilization of gold nanoparticles by citrate ions. The polycationic nature of chitosan enables attachment of the polymer to the negatively charged gold nanoparticle surfaces through electrostatic interactions. Use of chitosan serves dual purpose of providing sufficient steric hindrance ensuring stability of the colloid and also to functionalize the nanoparticles for use as sensors. The well-documented chelating properties of chitosan and the sensitivity of the optical properties of gold nanoparticles to agglomeration have been employed to detect low concentrations of heavy metals ions (Zn2+ and Cu2+) in water. A comparison of the optical absorption spectra of the colloidal suspension before and after exposure to metal ions is a good indicator of the concentration of the heavy metal ions.

4:00 PM *S7.4

Mercury detection with monodispersed and size-controlled Au/Ag nanoparticle arrays synthesized on deposited nanostructured Si films. A. Kaan Kalkan and Stephen J. Fonash; Center for Nanotechnology Education and Utilization, Penn State University, University Park, Pennsylvania.

Mercury is a severe neurotoxin whose contamination in the environment has jumped threefold since the beginning of the industrial revolution. Coal-fired power plants are the major emitters of mercury, which enters the food chain via the air and water. With the emergence of surging economies around the globe and the resulting demands on oil supplies, coal usage and, therefore, the potential for further mercury contamination are increasing. To monitor mercury levels, quick reliable means of both elemental and ionic mercury detection are needed. We demonstrate a novel surface plasmon resonance mercury sensor capable of detecting both elemental and ionic mercury in air and water down to ppb levels in minutes. Our sensor consists of a 3-dimensional array of Au/Ag nanoparticles, which are synthesized on plasma deposited nanostructured columnar Si films simply by film immersion into pure Au/Ag salt solutions. In addition to functioning as a reducer, the nanostructured Si provides immobilization and monodispersion of the Au/Ag nanoparticles due to its systematic nanoscale topography without the requirement of a surfactant, capping agent, or linker. The absence of such agents on the nanoparticle surfaces is a substantial benefit that provides unlimited access for the adsorption of mercury accounting for the ultrasensitive and ultrafast detection we observe. The plasmon extinction peak increases in intensity, broadens, and shifts towards lower wavelengths in response to mercury's adsorption. In particular, at 20 ppb mercury, the shift is 4 nm in the first 5 minutes with Au nanoparticles (average size is 20 nm). The total shift (at saturation) as well as the kinetics of the shift has a dependence on mercury concentration which can be readily used to measure mercury levels. Unlike our nanostructured columnar Si, flat Si surfaces lead to Au/Ag nanoparticle synthesis (only in the presence of HF) with no control over particle size and aggregation resulting in multiple resonances of the plasmon extinction which are less susceptible to frequency shift upon mercury adsorption.

4:30 PM S7.5
Behavior of CNTs in Bio Systems. Evgenia Buzaneva, Radiophysical faculty, National Taras Shevshenko University of Kyiv, Kiev, Ukraine.

The combination of DNA molecules and carbon nanotubes (CNTs) opens a new perspective in the self-assembly of nanomaterials and nanodevices. Our main subject is CNTs and their interaction with DNA biomolecular gel. The electronic properties and vibration modes of CNT and DNA/CNT systems were investigated by TEM and Raman spectroscopy. From UV-VIS-NIR absorption spectra the principal electronic absorption bands have been evaluated. The role of the DNA is revealed by the existence of the 2.5-3eV and 2 eV bands and shifting of the minima at 2.96 eV, 3.05, 3.34 eV. Using these results we assert that system of electron levels is self-formed at the DNA/CNT interface. Some separate projects that design the organization of CNT/DNA blocks are reviewed.

4:45 PM S7.6
Redox Cycling and DNA Damage Induced by Fe-Containing Carbon Nanomaterials. Lin Guo[1], Daniel Morris[1], Robert Hurt[1], Charles Vaslet[2], Margaret Tsien[2] and Agnes Kane[2]; [1]Engineering Division, Brown Univerisity, Providence, Rhode Island; [2]Pathology Department, Brown University, Providence, Rhode Island.

Carbon nanotubes and nanofibers are now being synthesized and used in significant quantities, but their potential health risks have yet to be fully assessed. Nanotubes/fibers have some properties in common with asbestos, a group of crystalline, iron-containing mineral fibers that are known human carcinogens. One hypothesis for asbestos-related disease involves redox catalyzed generation of reactive oxygen species leading to DNA damage and cytotoxicity. The redox-active species in asbestos is iron, which can be mobilized from the crystal lattice by natural chelators. Iron is the single most common element used in nanotube/fiber catalyst formulations and, despite purification procedures, most samples contain significant quantities of residual catalyst. This study examines the potential cytotoxicity of iron-containing carbon nanomaterials using a variety of molecular and cellular endpoints, including iron mobilization, induction of plasmid DNA single strand breaks, reactive oxygen species production, cell death, lysosomal membrane permeability, and phagocytosis using F-actin staining by rhodamine-conjugated phalloidin and scanning electron microscopy. The iron in catalytically-grown nanotubes varies in chemical composition and can be partially or wholly encapsulated by carbon. To manage this complexity, experiments were first carried out on a pair of model carbon nanomaterials in which the amount, form, and accessibility of iron were carefully controlled. The model materials are non-catalytic, template-fabricated carbon nanofibers in two forms: (a) high-purity (Fe-free), and (b) surface doped with fully accessible iron nanoparticles. A second set of experiments were conducted on commercial multiwall nanotubes in four forms: (a) raw, (b) vendor purified (reduced iron content), (c) purified then partially oxidized, (d) purified then ground, to test the effects of post-synthesis handling and processing. The experiments on model materials clearly demonstrate the importance of iron in nanofiber toxicity. The doped fibers showed significant Fe mobilization by ferrozine in the presence of ascorbate, a higher frequency of DNA single-strand breaks, elevated oxidative metabolism in cells by DCFDA, frustrated phagocytosis, and increased cell death. The experiments on commercial materials showed strong effects of purification and weaker effects of processing. The raw commercial nanotubes showed similar results to the Fe-doped model nanofibers. The purified nanotubes had much lower Fe mobilization and DNA single strand break frequency. Partial oxidation of the purified sample restored some of the iron mobilization and DNA damage, suggesting that additional iron was made accessible by oxidative tube damage. Overall, these results suggest practical guidelines for fabricating, purifying, and handling iron-containing carbon nanomaterials to minimize toxicity.

SESSION S8: Policy and Legal Approaches for Nanotechnology

Chair: Melissa Hoffer
Thursday Morning, December 1, 2005
Room 203 (Hynes)

8:15 AM S8.1
Abstract Withdrawn

8:30 AM S8.2
Approaches for Informing Risk Assessment of Nanoscale Materials. Jo Anne Shatkin, The Cadmus Group, Inc., Watertown, Massachusetts.

The ability to engineer novel materials and products at a nanoscale requires a paradigm shift in the way we analyze and manage risks. We know from past experience that every new technology has presented unintended consequences-some beneficial-effects that are not easily predicted because they are so far downstream. Nanoscience and technology-the ability to measure, manipulate, create, and organize molecules, structures and machines at a quantum level-is likely to create significant changes in our economy, and in our daily lives. From the small but growing body of evidence, we may not able to predict the behavior of nanosize particles from their bulk equivalents. We don't even have agreed upon measurement methods, or adequate terminology. The basic research now being undertaken by many governments is a logical and necessary step. But the development and implementation of nanoscience and technology is proceeding too rapidly to wait for the data needed for regulators and risk managers to fully quantify risk to inform the analytical and decision process of how to evaluate and address small and novel particles. Understanding the toxicity of nanomaterials will take time, as will the development of regulatory frameworks, while numerous applications for nanoscale materials are rapidly developing and beginning to enter the marketplace. The development of risk science over the last decades has significantly improved decision making under uncertainty. An adaptive risk framework can allow critical and precautionary decision making under uncertainty. As new information develops, key assumptions are revisited, and risk estimates revised. Risk is a function of both the toxicity and exposure of a material. A risk-informed evaluation framework shifts the focus from hazard potential to risk, and considers how and under what conditions human and environmental exposure may occur. Exposure considerations include intended and unintended uses, and the potential for human and environmental exposure to nanomaterials and to products throughout the life cycle. Amid uncertainties about the biological and environmental attributes of nanoscale materials, defining and analyzing the key variables for exposure assessment centers on the potential areas of concern and control points. Risk analyses can inform the broad field of nanoscale science and technology.

8:45 AM *S8.3
Risk Algorithms and Emerging Nanotechnologies. D. M. Berube, NanoSTS, University of South Carolina NanoCenter, Columbia, South Carolina.

Generally, risk assessment is about hazards and probabilities. On the other hand, risk is perceived and additional variables are relevant when laypersons are the intended audience. More and better communicated scientific data are not sufficient to counteract lay biases. Assessment becomes more problematical when dealing with an emerging technology that has not generated hazard data. It becomes more convoluted when the costs and benefits of a technology involve speculation from variable contexts and over very different time frames. It becomes thornier when the public intuits toxicology. This presentation will investigate some of the variables pertinent to building a risk algorithm for emerging nanotechnologies that does the following: (1) treat risk assessment as a concept grander than simple probability of hazard; (2) incorporate public biases and heuristics as legitimate variables;(3) factor in characteristics of new media, such as blogging, wikipedia, podcasting, etc., and (4) discount technological speculation against different context and times frames.

9:15 AM S8.4
Nanotechnology - Emerging Issues for Environmental Protection. Nora Savage and Barbara Karn; EPA, Washington DC, District of Columbia.

The mission of the United States Environmental Protection Agency (U.S. EPA) is to protect human health and the environment. EPA conducts and supports research to ensure that there is a sound scientific basis for its actions to carry out this mission. Agency scientists at laboratories and centers located throughout the country conduct intramural research. The EPA's Office of Research and Development (ORD) sponsors extramural research through awarding of grants and contracts. The National Center for Environmental Research (NCER) handles these as part of the Science to Achieve Results (STAR) and Small Business Innovation Research (SBIR) programs. Research on human health, environmental effects, exposure, and risk assessment is utilized to inform decisions on risk management. As one of the few federal agencies that focuses on the environment, the EPA is interested in nanotechnologies that will assist in the remediation and treatment of pollutants, improve detection and monitoring capabilities, and enable manufacturing and synthesis techniques that result in a reduction or elimination of wastes. In addition, the Agency is interested in the environmental implications of nanotechnology and of the convergence of technologies (nano, info, bio and cogno). Nanotechnology may offer the promise of improved characterization of environmental problems, significantly reduced environmental impacts from "cleaner" manufacturing approaches, and reduced material and energy use. However, the potential impact on human health and the environment of nanoparticles that are manufactured for and utilized in various applications must also be evaluated. The development and use of nanotechnology could have a dramatic impact on modern society, as a result of its potential to substantially improve the characteristics and/or performance of a number of commercial product applications including, but certainly not limited to, cosmetics, microelectronics, energy generation and distribution, food processing, and building construction. Government agencies around the world are supporting the use of this technology in a number of ways to improve environmental and public health protection, as well as to increase economic benefits and enhance quality of life. This presentation will focus on the nanotechnology extramural research sponsored by the Agency, several coordinated activities and meetings, and critical issues and perspectives of nanotechnology within the Agency.

9:30 AM S8.5
Nanotechnology and the Environment: In Search of a Consistent Regulatory Approach. Mark C. Kalpin and James G. Votaw; Wilmer Cutler Pickering Hale and Dorr LLP, Boston, Massachusetts.

The United States, the European Union, China, and Japan are all poised to develop new, or adapt existing, environmental regulatory programs to specifically address nanomaterials. While some parts of those programs share common foundations, other portions utilize a different, and potentially inconsistent, approach to the regulation of nanomaterials and nanocomposites. Because the market for nanomaterials and nanocomposites is global, it is critical that steps be taken now to ensure that the potential inconsistencies that exist in these approaches do not stifle the development and distribution of those materials and composites. At the same time, independent voluntary standards-setting entities, such as the ASTM International (ASTM) and the International Standards Organization (ISO), propose to develop standards for terminology and nomenclature, safe handling and environmental control of nanoscale materials, measuring and evaluating toxicity effects, environmental impact, exposure assessment, metrology, and methods of analysis for nanomaterials. Because these voluntary standards likely will form the basis of any regulatory programs that are developed for nanomaterials, they could significantly influence the environmental regulatory programs that ultimately are developed in the United States, the European Union, and in Asia.

10:15 AM PANEL DISCUSSION I – Policy and Legal Approaches to Nanotechnology

Panel I will focus on (i) overview of potential and likely environmental regulatory schemes applicable to nanomaterials in the US; (ii) overview of environmental regulatory approach and international emerging markets; and (iii) the "back door" regulatory impact of standards development.

Session Chair: Melissa Hoffer
Moderator: Mark Kalpin
Panelist/Topic:
Julio Rivera - National nanotech policy development
Jo Anne Shatkin - Risk assessment
Fred Klaessig - Public perception of nanotech and impact on technology
Nora Savage - Environmental protection
James Votaw - Divergent int'l regulatory approaches
Kevin Ausman - Standards development process

SESSION S9: Regulation of Nanotechnology and Nanomaterials

Chair: Nora Savage
Thursday Afternoon, December 1, 2005
Room 203 (Hynes)

1:30 PM S9.1
LAWS - 'L'egislation, 'A'pplications, 'W'earables: 'S'ocietal Implications of Nano & Smart Materials. Sonia E. Miller, [1]Converging Technologies Bar Association, New York, New York; [2]S.E. MILLER LAW FIRM, New York, New York.

Nanostructures measuring 100 nanometers or less have special properties due to their size. Because of their tiny size, there is fear that they may enter cells, interfere with normal biological function, and potentially lodge themselves in the lungs or brain. Can the specific characteristics of nanoparticles pose a risk to the workplace? If so, how can nanoparticles be handled safely? The potential and concern for environmental, health, and safety risks and harm is oftentimes linked to nanotechnology. Debate continues regarding the measures that should be taken to assure the safety of its innovative development. Should nanoparticulate materials be subjected to further regulatory measures? Are the laws currently in place sufficiently flexible to adapt to nano and smart materials? What are the societal implications of the continued advance of nanotechnology without conclusive evidence of its risks? This presentation will explore the issues of LAWS.

1:45 PM S9.2
Regular Chemistry, Regulatory Chemistry, and Rhetorical Chemistry: Innovation in a Period of Public Dialog. Frederick Cameron Klaessig, Aerosil & Silanes, Degussa Corporation, Piscataway, New Jersey.

There are several national and international initiatives focusing on nanotechnology with the National Nanotechnology Initiative coordinated through the National Science Foundation being prominent to those of us in the United States. Each of these intiatives is encouraging scientific discovery, obtaining public funding, and promoting subsequent commercialization (all a form of rhetorical chemistry). More recently, a number of national environmental agencies, such as the Environmental Protection Agency in the U.S., have expressed concerns that these scientific advances may represent new chemical functionality (a form of regular chemistry) that is not readily encompassed in the concepts behind the various national chemical inventories. In essence, the legal categorizations of regulatory chemistry is possibly being challenged by advances in regular science. As a supplier of nanostructured materials for longer than the word "nano" has been in the English language, Degussa's AEROSIL business line has a historical perspective to bring to the public dialog on nanotechnology, especially the interaction of definitions with well known surface science phenomena. More importantly, we at Degussa continue to innovate in this period of public dialog, which places new demands on packaging concepts, toxicity testing, and life cycle analyses during the new product development process.

2:00 PM S9.3
Environmental & Public Health Regulation of Nanomaterials: An Interdisciplinary Approach. Ahson Wardak[1,2], Michael Gorman[1] and Nathan Swami[2]; [1]Systems and Information Engineering, University of Virginia, Charlottesville, Virginia; [2]Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia.

The full consequences of introducing a broad range of nanotechnologies into the global environment cannot be anticipated in advance, because perturbations in complex systems have non-linear consequences. As the National Nanotechnology Initiative's annual funding approaches one billion dollars, nanomaterials will be increasingly commercialized in the marketplace, and the environmental implications will be immense and not entirely predictable. The challenge is to shape nanotechnology responsibly and adapt regulation, as necessary, by focusing on the most likely risks, as substantiated by scientific data. The lack of extensive data on the toxicology of nanomaterials has greatly hampering the field of environmental risk perception and its communication to the general public. This paper explores the application of an interdisciplinary approach based on a "trading zone" metaphor within the Earth Systems Engineering Management framework to identify environmental impacts and risks posed by nanomaterials. This approach uses the context of the environmental regulatory structure in a complementary manner with the fundamental science, production technology, and environmental toxicity of engineered nanoparticles to develop scenarios for nanoparticle release and interaction with the environment, and thereby identify and possibly rank potential risks that may characterize the transport of anthropogenic nanoparticles within specialized environments. This paper will focus on regulatory challenges posed by particular nanomaterials within pertinent scenarios during their life cycle, and discuss the kind of additional data that ought to be collected to achieve a systems-level view of environmental and health impacts. REFERENCES Allenby, B. R. (2000/2001). "Earth Systems Engineering and Management." Technology and Society, 19(4), 10-24. Gorman, M. E. (2003). "Expanding the Trading Zones for Convergent Technologies." In M. C. Roco & W. S. Bainbridge (Eds.), Converging Technologies for Improving Human Performance: Nanotechnology, Biotechnology, Information Technology and Cognitive Science (pp. 424-428). Dordrecht, Netherlands: Kluwer. Gorman, M.E., Groves, J.F. and Catalano, R.K. (2004). "Collaborative Research into the Societal Dimensions of Nanotechnology: A Model and Case Study," IEEE Technology and Society Magazine, 23(4): 55-62. Wardak, A., & Rejeski, D. (2003). "Nanotechnology & Regulation - A Case Study using the Toxic Substance Control Act (TSCA) (No. 2003-6)."

Washington, D.C.: Foresight and Governance Project, Woodrow Wilson International Center for Scholars.

2:15 PM S9.4
Nanotechnology: Ensuring a Safe and Healthful Workplace. Vladimir Murashov, National Institute for Occupational Safety and Health, Washington, District of Columbia.

The fast pace that characterizes the development of nanotechnology, an emerging technology in which matter is manipulated on the nanoscale, poses novel challenges for occupational safety and health in this strategic sector of U.S. economy. Because this technology is relatively new, and because nanomaterials can have unique properties that differ significantly from those of traditional materials, scientific data are scarce for predicting whether job-related exposures could result in adverse health effects. Likewise, additional data are needed to identify appropriate exposure-control strategies. Developing new data needed to answer those questions offers new opportunities in occupational safety and health research at this early stage of nanotechnology growth. The National Institute for Occupational Safety and Health (NIOSH), is the Federal agency established to help assure safe and healthful working conditions for working men and women by performing research, experiments, and demonstrations necessary to explore new problems, including those created by new technology in the field of occupational safety and health. NIOSH addresses the research challenges of nanotechnology through strategic internal and external collaborations, and active engagement of stakeholders. NIOSH's accomplishments and current research activities in nanotechnology will be highlighted in this presentation.

2:30 PM S9.5
Regulation of Nanotechnology in the Environment and Workplace: Comparative Approaches. Melissa Hoffer[1], Barbara D. Beck[2] and Lorenz R. Rhomberg[2]; [1]Wilmer Cutler Pickering Hale and Dorr LLP, Boston, Massachusetts; [2]Gradient Corporation, Cambridge, Massachusetts.

Environmental applications of nanotechnology have been deployed in the US to remediate constituents of hazardous waste. Engineered nanoparticles, increasingly incorporated into available products, offer many benefits. Little is known about environmental or worker risk, if any, posed to those exposed to these materials, raising important legal, economic, and ethical considerations for all stakeholders. Emerging regulatory schemes in the EU and US reflect different approaches to addressing those uncertainties. EPA recently proposed a cleanup for the Nease Chemical Superfund site using nanoscale zero-valent iron (ZVI) particles to treat deep groundwater. Nanoscale ZVI treatment for chlorinated VOC contamination at three Naval facilities has shown promising results. Yet last year, the UK Royal Society recommended a total ban on environmental releases of nanoparticles until more is known about their fate, transport and potential effects on human health and the environment. NIOSH estimates that three million people in the US will be regularly exposed to nanomaterials in the workplace by 2015. While production of nanoscale materials is rising, the paucity of toxicological data has led NIOSH to characterize nanomaterials as "a unique, immediate, and unquantified potential health hazard to workers." The European Commission's proposed new chemical registry system - REACH - would incorporate the precautionary principle by shifting to industry the burden of proving that a chemical substance introduced to the EU market is "safe." This approach may be more protective in preventing exposure to potentially harmful substances; it also may prevent mitigation of known harmful exposures. US regulation places the burden on public agencies to demonstrate potential risk before imposing restrictions. Manufacturers may be under a duty to disclose known hazards, but they need not demonstrate the absence of risk prior to introducing products to market. This approach has encouraged development of useful materials, however it may also result in potential harm and/or liability for manufacturers when products enter the market prior to sufficient data development. The Nease Site remedy was selected based on an assessment of the remedy criteria set forth in the US Code of Federal Regulations. We examine the application of those criteria to the use of nanoscale ZVI to determine how risks associated with nanomaterials were addressed, and how that assessment may have differed under a precautionary principle rubric. We then examine the process by which OSHA determines that a workplace exposure presents a risk subject to regulation, and how that assessment would differ if the precautionary principle were applied.

3:15 PM PANEL DISCUSSION II – Ethical and Legal Aspects of Nanomaterials and the Environmental Regulation

Panel II will focus more in depth on the rationale for the differences in regulation of nanomaterials in the Europe and US. This panel will present hypotheticals framed to elicit discussion of relevant legal and ethical issues involving (i) workplace safety and (ii) the use of nanomaterials for remediation.

Session Chair: Nora Savage
Moderator: Melissa Hoffer
Panelist/Topic:
Sonia Miller - Societal implications of nanomaterials
Ahson Wardak - Environmental and public health regulation
Vladimir Musharov - Workplace safety
Barbara Beck - Comparative hypothetical models for regulating use of nanomaterials in remediation and in workplace
Nicholas Ashford - Legal and ethical implications
Wei-Xian Zhang - Nanoscale ZVI
David Warheit and/or Fred Klaessig - Industry perspective