Sustainable
Nanotechnology
Organization

Research | Education | Responsibility

ABSTRACTS
2012

Oral presentations in Green; Posters in Black
Alphabetical by last name of first author

LONG TERM STABILITY AND METAL LEACHING IN NATURAL WATER SYSTEMS OF COMMERCIAL SINGLE WALL CARBON NANOTUBES

ADEYEMI ADELEYE, Bren School of Environmental Science and Management, University of California

Samuel Bennett, Bren School of Environmental Science and Management, University of California

Arturo Keller, Bren School of Environmental Science and Management, University of California, Santa Barbara

Carbon nanotubes (CNTs) are currently used in the manufacture of consumer products such as textiles, sporting goods, bicycle frames, vehicle fenders, x-ray tubes, hydrogen storage media, sorbents etc. The unique properties of CNTs have made them one of the most commonly used building blocks in nanotechnology and therefore, receiving intense investigation towards the development of their application. The high production and application volumes of CNTs increase the likelihood of their chronic and acute environmental exposure at different stages of their life cycle. Research is needed to assess the risks associated with CNTs in the environment. In this study, five different single-walled CNTs were dispersed into nine different natural waters and their long term stability was monitored. Photoxicity, metal leachate, and toxicity to freshwater algae were also studied. The behavior between raw and purified variants of the CNTs differs considerably in the different natural waters used. Residual metal catalyst can also leach out from all the commercial CNTs studied at different levels in many natural waters. As much as 10% of the total nickel leached from a purified CNT after 72 hr and aqueous concentrations of molybdenum leached from a different purified CNT were nearly 0.060 mg L-1 after 72 hr.

STUDY OF THE IMPACT OF DYSPROSIUM NANOPARTICLES ON E-COLI BACTERIA :

Nelson Anaya, University of Rhode Island

Janna Eaves, University of Illinois at Urbana-Champaign

Vinka Oyanedel-Craver, University of Rhode Island

The recent increase of the exploitation of Dysprosium nanoparticles (nDy) has been driven by high demand for these materials in bio/health applications such as MRI screening and anti-cancer therapy. Due to the lack of appropriate recycling systems it is very likely that high concentrations of nDy will enter into the environment through various pathways. Studies regarding the exposure of living organisms to elevated concentration of nDy are limited or non-existent.Physiological (membrane permeation, growth and respiration) response and metabolic activity were quantified to study the effect

of nDy on *E. coli* bacteria. Preliminary results show a positive correlation between nDy and carbon source concentration on the target microorganism. Higher concentrations of nDy in environments with higher glucose concentrations are more toxic on the *E. coli* bacteria.

NANOMATERIALS IN ORGANIC PHOTOVOLTAICS

ANNICK ANCTIL, Clemson University

Callie W Babbitt, Rochester Institute of Technology

Brian J Landi, Rochester Institute of Technology

Increasing demand for renewable energy has resulted in a new interest for alternative technologies such as organic photovoltaics. With efficiencies exceeding 10% for both polymer and small molecule photovoltaics, organic photovoltaics are now being commercialized due to their flexibility and low weight which allow for their adoption in new applications such as portable electronics, smart fabrics, and building-integrated photovoltaics. To date, most research efforts have been focused on increasing power efficiency with little assessment of potential negative impacts associated with their large scale production. It is generally assumed that organic photovoltaics have low environmental impacts and are by nature inexpensive to produce since they are often solution processed. In the present work, a comprehensive analysis of the life cycle embodied energy for C60 and C70 fullerenes which are the most common acceptor molecules in organic photovoltaics, has been performed from cradle-to-gate, including the relative contributions from synthesis, separation, purification, and functionalization processes. The embodied energy of all fullerenes was calculated to be an order of magnitude higher than most bulk chemicals. These results have enabled the life cycle impact associated with the production of various types of organic photovoltaics to be calculated, including polymer, small molecule and multi-junction devices.

SUSTAINABILITY AND SAFETY OF PHOTOVOLTAIC METALLIZATION: A MULTI-CRITERIA APPROACH TO COMPARE CURRENT AND EMERGING METHODS

Annick Anctil, Clemson University

Alessandra Colli, Brookhaven National Laboratory

Silver nanoparticles have been increasingly introduced in engineering processes. In the photovoltaics (PV) industry the use of silver nanoparticles has become common practice for the metallization process, to reduce material costs and energy consumption. The increasing cost of silver in recent years has created also alternative interests, in particular copper, anticipated to replace silver by 2020.Technology choices usually chase economic benefits, however other aspect particularly important regarding nanomaterials, such as environmental and health impacts, need to be considered. This works presents a comparative life cycle assessment (LCA) of different metallization techniques for PV cells, from nano-silver screen and aerosol printing with/without lead, to new metallization concepts for copper such as plating on nano-silver seed layers or direct plating.LCA results provide useful information regarding resources and energy usage, which will be complemented with economics and health metrics to feed a multi-criteria decision analysis approach to compare the various metallization pathways at sustainability and safety level. Sustainable development and risk management are overlapping frameworks to evaluate socio-economic, occupational and environmental impacts of human actions in every engineering field.The approach proposed is flexible enough to be applied to other products in the future to facilitate an informed decision making process.

TEACHING SYSTEMS THINKING FOR SUSTAINABLE NANOTECHNOLOGY

CALLIE BABBITT, Rochester Institute of Technology

Gabrielle Gaustad, Rochester Institute of Technology

The ability to develop nanotechnology that achieves sustainability goals with minimal ecological or health risks requires a future workforce with strong technical skills and appreciation for social, economic, and environmental implications of nanotechnology. While traditional disciplines like engineering, science, policy, and economics provide essential theoretical foundations, it is necessary to integrate knowledge from these fields to create a systems-level understanding of sustainable nanotechnology. The PhD and MS degrees in Sustainability at RIT establish a program of study that links discipline-specific science with integrative sciences of sustainability, such as industrial ecology, ecological economics, risk analysis, and ethics. This curriculum is a natural forum for addressing complex problems like nanotechnology, but faces an educational conundrum: methods taught, like life cycle assessment, rely heavily on existing data that characterize production processes, environmental releases, and mechanisms of fate and transport, which are not fully developed for nanomaterials and nanoprocessing routes. This presentation provides both a general overview of “systems-level” sustainability curriculum at RIT and a specific review of educational approaches aimed at bridging data gaps when teaching on sustainable nanotechnology, including combined synchronous and asynchronous project-based learning and the integration of lab- and design-based research into life cycle assessment and risk analysis coursework.

CERIA NANOPARTICLES: PLANNED AND UNPLANNED PREPARATION, DELIVERY, AND ENVIRONMENTAL IMPACTS ON PARTICLE PROPERTIES

DONALD R. BAER, EMSL, Pacific Northwest National Laboratory

Cerium oxide nanoparticles are widely studied for their use in catalytic, energy, environmental protection and bio-medical applications. These applications often depend on the ability of cerium to switch between +3 and +4 oxidation states. Our research examines the impacts of sample preparation, storage, processing and environment on the properties of ceria nanoparticles as they apply to materials science and biological systems. Published biological impacts of ceria nanoparticles suggest that larger faceted ceria particles that have been heated are more likely to have adverse consequences, while smaller particles synthesized at room temperature and never removed from solution often have anti-oxidative behaviors. Smaller particles are highly dynamic in nature changing their oxidation state not just as a function of size, but also as a function of aging (time) and environmental conditions. During particle nucleation and growth in solution, both the particle size and oxidation state change with time. Because synthesis, analysis and operational conditions often place particles in different environments, understanding how particles change as a function of time in different environments is essential to predicting their properties. Aging time and environmentally induced changes in particles may play a significant role in the discrepancies reported in various studies.

APPLICATION OF RESPONSE SURFACE METHODOLOGY TO ANALYZE THE FATE AND TRANSPORT OF NC60 NANOPARTICLES IN THE SUBSURFACE :

Chunmei Bai, University of Nebraska-Lincoln

Kent M. Eskridge, University of Nebraska-Lincoln

Yusong Li, University of Nebraska-Lincoln

The toxicities of engineered nanomaterials are continuously revealed as their commercial applications keep increasing. Predicting the fate and transport of engineered nanomaterials in the subsurface is crucial for risk assessment and exposure modeling. The mobility of fullerene aggregates (nC60) was found to be sensitive to a series of interrelated factors, including release concentration, hydraulic gradient, aggregate size, and collision efficiency factor. In this work, efforts have been devoted to establish quantitative relationships that link these factors with some response variables representing the distribution of nC60 nanoparticles in the subsurface, such as far front of plume (C/C0=0.01), centroid of plume, etc. The Modular Three-Dimensional Multispecies Transport Model (MT3DMS) was modified to incorporate the transport and retention of nC60 nanoparticles. Hypothetical scenarios of nC60 released into a relatively homogeneous aquifer (mean K = 16.8m/d, variance (lnK) = 0.29) and a highly heterogeneous aquifer (mean K = 4.77m/d, variance (lnK) = 4.5) were simulated using the modified MT3DMS. A response surface methodology (RSM) based on statistical design of experiment was then used to develop the quantitative relationships between these key factors and the distribution of nC60 in the subsurface for both sites. The performance of RSM on the two sites will be discussed.

SURFACE MODIFICATION OF NANOAG WITH “BENIGN” SURFACE COATINGS LIMITS ITS TRANSPORT THROUGH BIOLOGICAL BARRIERS. :

Barita Baruwati, Hindustan Unilever Limited

Raj Varma, US EPA

Bellina Veronesi, US EPA

Nanosilver (nanoAg) is used in medical imaging, food packaging and aseptic wound dressings. Surface coating of the parent nanoAg ensures retention of its size and efficacy. Greener synthesis of nanomaterials and their coatings promotes environmental sustainability. This study investigates if coatings with anti-oxidant properties (green tea GT; glutathione, GSH), affects anoAg’s movement through in vitro models of human epithelia (Caco-2) and rat endothelial (RBEC4) cells. Physicochemical (PC) characterization of as-synthesized nanoAg, nanoAg-GT and nanoAg-GSH included X-ray diffraction, UV absorbance, transmission electron microscopy, surface charge (zeta potential) and aggregate size. These measures indicated that nanoAg samples retained <50 nm size in aqueous solutions, but aggregated (>500-1500 nm) when suspended in culture media. Confluent monolayers of Caco-2 or RBEC4 cells were exposed to the nanoAg samples and transcellular resistance (TEERS) measured. Unmodified nanoAg moved through both barriers within 30 min. However, the coated nanoAg showed marginal transport, suggesting that surface coating limited nanoAg's movement through biological barriers. Cell culture models of oxidative-stress sensitive dopaminergic neurons (N27) indicated that non-cytotoxic (1.0 ppm) concentrations of each nanoAg material significantly stimulated NFkb reporter genes in transfected neurons after 18 hr exposure, suggesting that surface coatings do not diminish nanoAg's potential neurotoxicity.

LEGAL ASPECTS/POLICY CONSIDERATIONS

LYNN L. BERGESON, Bergeson & Campbell, P.C.

Governance and policy issues pertinent to nanotechnology are very much a part of a vigorous domestic and international debate concerning how best both to foster and to manage effectively emerging technologies. An essential component of the legal, regulatory, and policy implications of nanoscale materials and their varied applications is the concept of sustainability. While the term is generally well understood as an aspirational goal, the meaning of sustainability in a legal and policy context is less clear and less developed as a governance parameter.

This presentation will focus on the legal, regulatory, and policy implications of sustainable nanotechnology. It will explore domestic and international legal frameworks, their capacity and elasticity to reflect and achieve the goals of sustainability, and the utility of other governance tools, including regulatory provisions, financial incentives (credits, accelerated approvals), and related tools to foster and achieve sustainability.

MULTIFUNCTIONAL POLYMER NANOCOMPOSITES FOR SOLID STATE LIGHTING APPLICATIONS

Michael R. Bockstaller, Carnegie Mellon University

Clare Mahoney, Carnegie Mellon University

Solid-state lighting (SSL) technologies are expected to revolutionize energy efficient lighting. A key challenge in the realization of cost-efficient design of SSL device architectures is the removal of excess heat that is generated during emission processes in solid state devices. Current strategies to address thermal management primarily center on the integration of heat sinks that present a barrier to cost efficient fabrication. Polymer nanocomposites combining high thermal conductivity with high transparency hold the promise to significant cost reduction by alleviating the need for heat dissipation.

FATE OF NANOMATERIALS IN MUNICIPAL SOLID WASTE LANDFILLS

STEPHANIE C. BOLYARD, University of Central Florida

Debra R. Reinhart, University of Central Florida

Swadeshmukul Santra, University of Central Florida

Given the increase in nanomaterial (NM) use in consumer products and the large fraction of waste placed in landfills worldwide, the probability of these products reaching municipal solid waste (MSW) landfills at the end of their useful life is high. Since nanotechnology use is still in its early stages, there are currently no regulations pertaining to the disposal of NMs and their fate in MSW landfills is still unknown. Understanding the fate of NMs in MSW landfills is vital to ensure the proper handling of these novel materials from cradle to grave; such research will provide information on how these NMs can be safely introduced into the environment. This research seeks to understand the fate of NMs within waste environments by examining the interactions between NMs and landfill leachate components. The primary focus of this study is the effect of Zinc Oxide (ZnO), Titanium Dioxide (TiO_2), and Silver (Ag) on biological landfill processes, solids aggregation, and chemical speciation of Zn, Ag, and Ti in landfill leachate following the addition of coated ZnO, TiO_2, and Ag.

RATIONAL DESIGN OF CARBON NANOTUBE DISPERSIONS AND TOXICITY ELIMINATION

JEAN-CLAUDE J. BONZONGO, University of Florida

Kirk J. Ziegler, University of Florida

Environmentally benign manufacturing is an important goal for the emerging nanomaterial industries, ensuring that risks to human health and the environment are minimal. For instance, nanotube processing has a tremendous opportunity to evolve as a "green" process, benefiting from the experience of previous industrial enterprises. We hypothesized that the environmental and human health impacts of single-walled carbon nanotubes (SWCNTs) can be reduced or eliminated through intimate coupling of toxicity testing and manufacturing during the production process. To test this hypothesis, engineering, chemistry, and toxicology were integrated into a preemptive experimental approach using model aquatic organisms. Obtained results point to the types of surfactants used to prepare SWCNT dispersions on one hand and the abundance of metallic and semi-conductive fractions within a SWCNT mixture on the other hand as key factors controlling the biological responses of exposed organisms. Manipulation of these factors resulted in toxicity mitigation/elimination. Overall, the results of this study point to the potential of “green” manufacturing of carbon nanotubes, in that the eco-toxicity of SWCNT can be eliminated through coupling of bioassays and manufacturing during the production process.

EXPOSURE ASSESSMENT AND HEALTH OUTCOMES ATTRIBUTABLE TO THE NANO FRACTION OF FAMILIAR POLYDISPERSE AEROSOLS

JOSEPH BRAIN, Harvard University, Center for Nanotechnology and Nanotoxicology at the Harvard School of Public Health

Nanotoxicology benefits from decades of research on the deposition, clearance, and health effects of airborne particulate matter (PM). Many familiar aerosols which are polydisperse in size have particles in the nano range. For example, there is abundant evidence that diesel particles and welding fume contain nanoparticles. Moreover, hundreds of millions of individuals are exposed to either active or passive tobacco smoke. In fact, everyone on the planet breathes ambient PM, both indoors and outdoors. With appropriate technology, it can be demonstrated that all PM exposures include nanomaterials. Interestingly, what we now refer to as nanomaterials (particles with a dimension smaller than 100 nm) is comparable to the historic EPA definition of ultrafines (particles smaller than 0.1 microns).What is the contribution of nanoparticles in these aerosols by number, surface area, or mass? What is the relative contribution of these smallest particles to health and environmental outcomes? Data will be presented demonstrating the particle size distributions of common polydisperse particles. Evidence in regard to the extent to which health effects from this nano particle fraction will also be presented. A challenge is to understand the importance of the nano fraction of these familiar polydisperse aerosols and to delineate what data are applicable to new and more complex engineered nanoparticles (ENPs). We must learn as much as possible from the past.

TITANIUM DIOXIDE PHOTO-OXIDATION EFFICIENCY IN SMALL-SCALE PHOTOTHERMAL WASTE DEGRADATION REACTORS

CHRISTOPHER N. BREMER, Arizona State University

With the increase in demand for industrial production and efficiency, comes the demand for increasingly efficient downstream treatment of toxic waste. Nanoscale titanium dioxide (anatase titania) is very promising in fulfilling this role because it requires no support processing units, requires no non-natural energy input and titania requires no heat input, making it safer and greener than incineration. A prototype photothermal reactor which uses only concentrated solar energy was tested using methylene blue as the waste. The gaseous products were identified and the reaction efficiency was determined to prove the validity of using a throughput photodegradation reactor for small scale industrial settings. The issues of (a) nanoparticle separation, (b) light penetration, and (c) reaction dependence upon light concentration are addressed. Nanoparticle separation is made possible through a phase separation, the reactor core is calculated to be of the proper diameter to enable ultraviolet penetration through the entirety of the titania fluid, and the optimum light concentration to promote (a) and (b) is also determined. While titania reactor systems do not treat as much waste (mass per unit time) as traditional methods, it is still a nascent technology; future research into functionalized nanoparticles show great promise in increasing the reaction rate.

UNDERSTANDING MAST CELL ACTIVATION IN THE DEVELOPMENT OF SAFE NANOTECHNOLOGIES

Jared Brown, East Carolina University, Brody School of Medicine

Concern about the use of engineered nanomaterials (ENMs) has increased significantly in recent years due to potentially hazardous impacts on human health. Mast cells are critical for innate and adaptive immune responses, often modulating allergic and pathogenic conditions. Mast cells act in response to environmental danger signals such as IL-33 and the IL-1 like receptor ST2. We have examined the involvement of mast cells and the IL-33/ST2 axis in adverse responses to ENMs. Mice with normal mast cell populations exhibit significant ENM directed systemic and pulmonary inflammation, fibrosis, altered lung function and exacerbated cardiac IR injury. In contrast, these toxicological effects of ENMs were not observed in mice deficient in mast cells or mice with mast cells unable to respond to IL-33. Lastly, we have established that certain ENMs are capable of inducing mast cell activation in vitro. Our findings establish for the first time that mast cells orchestrate adverse immune effects to ENMs giving insight into a previously unknown mechanism of toxicity and thereby providing a realistic therapeutic target. Lastly, the use of mast cells and the IL-33/ST2 axis as a screening tool for ENM safety and in the preclinical development of nanomedicines will be presented.

SIZING NANOPARTICLES FOR A SUSTAINABLEFUTURE – STATUS, LIMITATIONS AND OPPORTUNITIES

SCOTT C. BROWN, E.I. du Pont de Nemours

David B Warheit, E.I. du Pont de Nemours

Nanoparticles, by definition, areidentified by their size; however, harmonized methods for identifying nanomaterialsby size for real world samples are lacking. Furthermore, the limitations and validity of different sizing approaches are often overlooked. While particle size remains the discriminating factor for classifying a materialas ‘nano’, inconsistencies in nanoparticle size metrology will continue to challenge policy and decision-making. Moreover, the lack of rigorously evaluated nanoparticle metrology methods will inhibit the safe and judicious implementation of sustainable nanoparticle-based products. With increasing regulatory actions from governments across the world, it is important that enhanced efforts are placed in the area nanoparticle size metrology for identifying nanomaterials, and also when reporting and considering nanotoxicology and ecotoxicology data. This presentation will highlight current challenges in nanoparticle size metrology as well as research needs and opportunities in this area.

NANOMATERIALS-BASED SUSTAINABLE NANOMANUFACTURING FOR ELECTRONICS, ENERGY AND BIOTECHNOLOGY APPLICATIONS

AHMED BUSNAINI, Northeastern University

Present fabrication facilities that manufacture nanoscale devices such as consumer electronics costs $5-10 billion. This high cost of entry barrier completely shuts out small and medium sized businesses. A directed assembly based sustainable nanomanufacturing factory could be built for as low as $25-$50 million, a fraction of today’s cost, making nanotechnology accessible to millions of new innovators and entrepreneurs and unleash a wave of creativity in the same way as the advent of the PC did for computing. The NSF Center for High-rate Nanomanufacturing (CHN) is developing tools and processes to conduct fast massive directed assembly of nanoscale elements by controlling the forces required to assemble, detach, and transfer nanoelements at high rates and over large areas. The center has developed templates with nanofeatures to direct the assembly of carbon nanotubes (CNTs) and nanoparticles (down to 10 nm) into nanoscale trenches in a short time (in seconds) and over a large area (measured in inches). The center has demonstrated that nanotemplates can be used to assemble naoscale structures (polymers, CNTs and nanoparticles) and transfer them onto a second substrate. Recently, a fast and highly scalable, material-independent, aqueous, room-temperature and pressure manufacturing process of 3-D nanoscale features was developed for fabricating interconnects using nanoparticles.

RESPONSES TO PULMONARY EXPOSURE TO CARBON NANOTUBES IN NIOSH ANIMAL STUDIES

VINCENT CASTRANOVA, National Institute for Occupational Safety and Health

Workplace exposure studies indicate that carbon nanotubes (CNT) can be aerosolized upon agitation associated with activities such as: weighing, transferring, mixing, blending, and sonication. Since worker exposure is feasible, the possible adverse health effects of CNT inhalation are of concern. In animal models, pulmonary exposure to single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) causes the following pulmonary reactions: 1) acute pulmonary inflammation and injury, 2) rapid an persistent formation of granulomatous lesions at deposition sites of large CNT agglomerates, and 3) rapid and progressive alveolar interstitial fibrosis at deposition sites of more dispersed CNT structures. Pulmonary exposure to SWCNT induces oxidant stress in aortic tissue and increases plaque formation in an atherosclerotic mouse model. Inhalation of MWCNT depresses the ability of coronary arterioles to respond to dilators. These cardiovascular effects may be due to neurogenic signals from sensory receptors in the lung. Indeed, pulmonary exposure to MWCNT induces upregulation of mRNA for inflammatory mediators in selected brain regions. In light of measured airborne CNT in the workplace and animal studies indicating adverse health effects of pulmonary exposure, NIOSH has conducted risk assessment using available animal exposure-response data. As a result, NIOSH has developed a recommended exposure limit for CNT of 1 ug/m3.

DEVELOPMENT AND FIELD EVALUATION OF THE THERMOPHORETIC PERSONAL SAMPLER (TPS)

GARY CASUCCIO, RJ Lee Group, Inc.

John Volckens, Colorado State University

Understanding the risks that engineered nanomaterials pose to humans and the environment requires measurement technology that is capable of quantitative identification of nanoparticles in ‘real world’ environments (i.e., in the presence of interferences). Current nanoparticle air sampling and measurement technologies (i.e., direct reading and filter-based methods) have significant shortcomings: most existing air A personal sampler incorporating thermal precipitation has been developed to assess exposures to engineered nanoparticles. The thermophoretic personal sampler (TPS) captures airborne particles onto an electron microscope (EM) grid. EM analytical techniques are used to quantify the size, number and composition of airborne nanoparticles. The use of EM permits engineered nanoparticles to be distinguished from other incidental (anthropogenic) and naturally occurring ultrafine particles that are ubiquitous in workplace and ambient atmospheres.sampling technologies are not well suited for the collection, measurement and speciation of nanoparticles, and there are no standard quantitative methods for personal exposure to engineered nanoparticles. The presentation will provide an overview of the TPS and results obtained in field evaluations.

NANOPARTICLE ELECTROSPRAY FACILITATES THE BREAK OF COAT-IMPOSED SEED DORMANCY

DA-REN CHEN, Washington University, St. Louis

Stephen G. Wu, Washington University, St. Louis

Yinjie J. Tang, Washington University, St. Louis

We will present a novel technique to promote plant seed germination through the electrospray (ES) of trace amounts of nanoparticles (NPs). Via the ES process, sprayed TiO_2 NPs carrying with high electrical charges can be accelerated and used to penetrate lettuce (Lactuca sativa) seed coats. After a brief pretreatment of seeds (~15 each try) with the NP electrospray (4~5 min, 6 μL NP solutions), the germination percentage and seedling size of the lettuce seeds was significantly improved. Such enhancement was more pronounced when lettuce seeds showed low activity in germinating. For example, the germination of the lettuce seeds under stress conditions (i.e., acidic environment) was improved by fivefold after the NP electrospray treatment. In the shelf life study, the lettuce seeds continued to have improved germination one month after the NP spray treatment. TEM and SEM-EDX images suggest that the ultra-fine TiO2 particles created “nano-holes” in the lettuce seed coats, resulting in the breaking of coat-imposed seed dormancy. To test the broad application of this technique, we used the same electrospray protocol to treat several recalcitrant plant seeds, and discovered significant improvement (3~4 folds) of recalcitrant seeds in germination percentage subsequent to the NP treatment.

INTERACTION OF MULTIWALLED CARBON NANOTUBES WITH MODEL CELL MEMBRANES

KAI LOON CHEN, Department of Geography and Environmental Engineering, Johns Hopkins University

Peng Yi, Department of Geography and Environmental Engineering, Johns Hopkins University

Carbon nanotubes (CNTs) are widely used in consumer products and industrial and research applications because of their unique mechanical, chemical, and electronic properties. Recent studies have shown that CNTs can exhibit toxic effects on bacterial and mammalian cells. A proposed mechanism for the cytotoxicity of CNTs is that the nanotubes can damage cell membranes and result in the inactivation of the cells. To better understand the interaction between CNTs and cell membranes, the adsorption and desorption of multiwalled CNTs (MWNTs) on model cell membranes is investigated in solution chemistries that are relevant to environmental and biological systems using a quartz crystal microbalance (QCM). Supported lipid bilayers (SLBs) comprising 1, 2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) formed on QCM crystal surfaces are employed as model cell membranes. MWNTs are subsequently deposited on the SLBs over a range of CaCl2 concentrations at pH 7.3. Our results show that the deposition kinetics of MWNTs on SLBs increases with increasing $CaCl_2$ concentrations due to the neutralization of charges on the nanotubes and SLBs. In addition, some of the deposited MWNTs can be released from the SLBs when the solution CaCl2 concentration is decreased. Similar deposition and release experiments will be conducted in the presence of NaCl.

YES, I SEE.” – BRINGING NANOTECHNOLOGY EDUCATION TO UNDERGRADUATE CLASSROOMS

Hyoungjin Cho, University of Central Florida

Sudipta Seal, University of Central Florida

Lei Zhai, University of Central Florida

Through NSF-NUE program, NUE: Preparing Undergraduates for Careers in Nanotechnology (0741508), simple but effective nanotechnology teaching modules as well as multimedia content which connect the students’ interest to nanotechnology in relation to their current major were developed and used in regular lecture-based classes for the undergraduate curriculum at the University of Central Florida. Considering the limited resources and time in conventional engineering courses, creative but condensed delivery of basic concepts of nanotechnology was attempted. Then based on the hypothesis that instructors could further develop students’ interest in this emerging area through the introduction of teaching modules and a career module, the evaluation of the effectiveness of the modules in selected engineering courses was conducted. The results suggested that adoption of modular lectures in regular engineering courses influenced attitude towards nanotechnology – overall the invited lectures with adopted teaching modules could pique student’s interest (albeit in the short-term) in the subject."

TRACKING TRANSLOCATION OF INDUSTRIALLY RELEVANT ENGINEERED NANOMATERIALS (ENMS) ACROSS ALVEOLAR EPITHELIAL MONOLAYERS: THE EFFECT OF PARTICLE PROPERTIES ON SIZE AND SURFACE CHEMISTRY AFFECT PARTICLE

Joel Cohen, Harvard School of Public Health

Joseph Brain, Harvard School of Public Health

Phil Demokritou, Harvard School of Public Health

Relatively little is known about the fate of industrially relevant engineered nanomaterials (ENMs) in the lungs. These interactions are important when considering inhalation exposure and subsequent translocation of ENMs across the thin epithelial lining layer of the lung. We present a novel method for tracking well-characterized industrially relevant metal oxide ENMs made radioactive. Nano-sized CeO_2 of various primary particle diameter (27 and 119nm), and SiO_2-coated-CeO_2 particles generated by flame spray pyrolysis were neutron activated in a nuclear reactor, forming the gamma emitter 141Ce. ENMs were characterized in dry powder form using state of the art methods (XRD, BET, XPS, TEM). Liquid ENM suspensions were prepared and characterized by DLS following a previously described protocol. Calu-3 lung epithelial cells were cultured on transwell inserts with 3 μm pores. Transepithelial electrical resistance (TEER) was measured over time to confirm the development of a monolayer and the formation of tight junctions between cells. Toxicity was evaluated for all ENMs using a standard LDH and MTT assay to determine an appropriate dose for tracking particle translocation without killing the cells.

ENM dispersions were applied to cells below the pre-determined killing dose, and trafficking was evaluated following 4, 24, and 48 hours of exposure by gamma spectrometry. A mass balance of particles was determined for nondeposited ENMs, ENMs internalized by cells, and ENMs that translocated across the cellular monolayer into the basal compartment of the transwell system. Our results demonstrate the influence of particle size and surface chemistry on ENM delivery to cells, cellular uptake, and translocation of the particles across the alveolar epithelium following inhalation exposure.

A NOVEL METHOD FOR MEASURING EFFECTIVE DENSITY OF NANO-AGGLOMERATES IN LIQUID SUSPENSIONS: IMPLICATIONS FOR IN VITRO DOSIMETRY AND NANOTOXICOLOGY

JOEL COHEN, Harvard School of Public Health

Glen DeLoid, Harvard School of Public Health

Phil Demokritou, Harvard School of Public Health

With the ever-increasing number and variety of engineered nanomaterials (ENMs) entering the consumer market, efficient and inexpensive in vitro toxicity assays are needed to correlate ENM properties with biological activity. However, results reported for in vitro assays often vary substantially among different studies and from in vivo data. In many cases these discrepancies may be attributable to inadequate characterization of ENM transformations in liquid suspension and the subsequent effects on particle delivery to cells in culture. Specifically, agglomeration results in large particles with an effective density significantly lower than that of raw material, thereby slowing particle delivery to cells, as well as reducing the surface area available for interactions with biological substrates. Here we present a novel method, based on volumetric centrifugation, for measuring the effective density of ENM agglomerates. Using effective densities determined by this method, and agglomerate sizes measured by dynamic light scattering, we calculated the dose of ENMs delivered to cells over time for a large panel of nano-sized metal oxides. Finally, we investigated the implications of effective density and particle kinetics in an in vitro cytotoxicity assay using Calu-3 lung epithelial cells. Our results suggest that the dose delivered to cells is a superior predictor of cytotoxicity than administered mass concentration.

SOIL GROWN CLARKIA (ONAGRACEAE) EXPOSED TO METAL OXIDE NANOPARTICLES EXHIBIT LIMITED NANOPARTICLE UPTAKE AND PHOSPHATE LIMITATION

Jon R. Conway, Bren School of Environmental Science & Management, UC Santa Barbara

Susan J. Mazer, Department of Ecology, Evolution and Marine Biology, UC Santa Barbara

Arturo A. Keller, Bren School of Environmental Science & Management, UC Santa Barbara

Despite growing concerns about the potential adverse effects of nanomaterials on the environment, few studies have examined the interactions of soil-borne nanoparticles and plants. Plants are the basis for many food webs, and so it is necessary to understand how the presence of man-made nanoparticles in the environment may affect plant performance and/or generate cascading effects on their pollinators or herbivores to properly manage nanoparticle use and disposal. In this study, Clarkia unguiculata were

grown in soil with excess or limited nutrients and watered with TiO_2 or CeO_2 nanoparticle suspensions of varying concentrations. Tissue and soil samples were taken at regular intervals and nanoparticle and phosphorous concentrations were measured using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Growth and chlorophyll measurements were also collected. Little or no uptake of either nanoparticle was seen, but phosphorous deficiency, stunted growth, and chlorosis were seen in unfertilized treatments. In a separate experiment, metal oxide nanoparticles were shown to sorb phosphate over several other macronutrients ($N0_3$, NH_4, Mg, K). Together these results suggest these nanoparticles may reduce phosphorous bioavailability in the environment.

SUSTAINABLE ENERGY FROM POLYMER NANOCOMPOSITES

MARK DADMUN, University of Tennessee

Polymer nanocomposites are an important class of materials that are suitable for the conversion of sunlight to electricity, as well as novel thermoelectric materials. In these applications, the specific distribution of the nanoparticle in the polymer matrix plays an important role in the performance of the nanocomposite for energy conversion. In this talk, we will discuss recent results in our lab that have sought to control and accurately characterize the morphology of conjugated polymer:fullerene, as well as conjugated polymer:carbon nanotube nanocomposites, and to correlate the specific domain structure and interfacial area to energy conversion efficiency. These results then serve to guide the design of sustainable manufacturing and fabrication processes that will allow for the reproducible production of polymer nanocomposites for optimal sustainable energy production.

WHEN NANOPARTICLES ENTERS THE HOUSE OF MICROBES – IMPORTANCE OF BIOFILMS IN FATE AND TRANSPORT OF NANOMATERIALS

ALAN W. DECHO, Department of ENHS, University of South Carolina, Columbia, SC

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Sorption of nanoparticles (NPs) on different environmental surfaces has important implications on their fate and transport in aquatic systems upon environmental release. Recent investigations have established that significant accumulations of NPs occurred in aquatic biofilms, which point to the emerging and important role of biofilms for influencing the overall environmental partitioning of NPs. Extracellular polymeric substances (EPS), a major biofilm component, account for an important portion of the sorptive capacity of a biofilm. EPS is composed of polymers having different charges and hydrophobicity due to the different exposed functional groups, which will influence the binding of NPs. Hematite ($?\text{-}Fe_2O_3$) and lead sulfide (PbS) quantum dots were chosen, respectively, as model natural and engineered NPs for this study. With the characterization by surface-sensitive/nano-scale tools (e.g., quartz crystal microgravimetry and atomic force microscopy), our preliminary results suggested that the extent and rate of NP adsorption onto substrate coated with EPS-related compounds are influenced by: 1) the physical structure and chemical composition of EPS and 2) the capping agent of NPs. Overall, our initial findings highlighted the critical role of surface modification in NP-biofilm interactions. Further research on this topic is necessary to better understand how biofilms could impact the environmental health and safety of NPs.

CRITICAL ISSUES IN RISK ASSESSMENT OF ENGINEERED NANOMATERIALS: THE WAY TOWARDS A SUSTAINABLE NANOTECHNOLOGY INDUSTRY

PHILIP DEMOKRITOU, Harvard University, Center for Nanotechnology and Nanotoxicology

While there are challenges to face and barriers to take down, for the first time in the history of new technology, there is an opportunity here to develop a sustainable industry which safeguards public health and protects the environment.Numerous reports and commissions have documented the explosion of discoveries in nanotechnology. Moreover, these discoveries are quickly moving out of the laboratory into commercial products. It has become apparent that the environmental health and safety implications of nano-enabled products need to be assessed in parallel with nanotechnology and its applications. This will require a drastic change in the current modus operandi and requires joint efforts by all stakeholders involved – academia, industry and regulators. This sessions aims to discuss the current risk assessment paradigm, present the state of the art and identify critical issues for future research in this area. What are the historical data and lessons learned from incidental particles such as ambient ultrafine particles, diesel exhaust, welding fume, fire smoke, etc that can guide us ? What are the critical issues which can pave the way towards a sustainable industry? What is the industry's prospective on nano-EHS matters? Those are some of the important questions the session will try to address.

FATES OF METALLIC NANOPARTICLES INTERACTING WITH BIOLOGICAL SYSTEMS

Christian Dimkpa, Biology Department, Utah State University

Joan McLean, Utah Water Research Laboratory, Utah State University

Anne Anderson, Biology Department, Utah State University

Nanoparticles (NPs) of CuO and ZnO are among the most toxic in the environment. Our group is tracking the environmental fate and impact of CuO and ZnO NPs in biological systems. We find shape modification of ZnO, but not of CuO NPs, to elongated structures in plant-free sand matrices. However, the elongated structures were not generated when wheat was planted in the sand. Both the ZnO and CuO NPs aggregated to sub-micron structures in the planted sand. The NPs dissolved in the sand, but the presence of plants increased metal release. Colloidal materials visible from the NP-amended sand, especially in the presence of plants, had surface charge distinct from those developed from NPs in water suspensions. We demonstrate that NPs suspended in materials washed from the wheat roots form colloids with altered surface charge, indicative of particle coating and aggregation. AFM analysis suggests that coating of the NPs with materials from the wheat root may be part of the protective mechanism. The CuO NPs reduced wheat root elongation to a greater extent than the ZnO NPs, although both NPs enhanced root branching, a common plant response to metal-induced stress. Cu and Zn from

CuO and ZnO NPs accumulated in wheat shoot tissues; Cu from the CuO NPs was present mainly as CuO, and to a lesser extent as a Cu(1)-sulfur complex, while Zn from the ZnO NPs was found as Zn phosphate. These differences seem to indicate the significant role that release of metal from the metal oxide NPs play in phytotoxicity. Our findings illustrate that the properties of NPs are influenced strongly by factors from sand and plant components. NPs may be transformed, coated, aggregated and subjected to different rates of dissolution. Each of these changes may have a differential impact on a target organism.

PHOTOCATALYTIC REDUCTION OF NITRATE USING WATER AS A HOLE SCAVENGER

Kyle Doudrick, Arizona State University

Natalie Geiger, Arizona State University

Paul Westerhoff, Arizona State University

Nitrate contamination of drinking water sources remains a problem and it can be costly for treatment facilities to remove. Photocatalysis is an emerging water treatment technique that holds promise for reducing nitrate efficiently. However, there are some limitations to this technology, such as the requirement of an organic hole scavenger (e.g., formic acid) or acidic pH, that keep it from being used for direct water treatment. Removing the need of an organic hole scavenger reduces the risk of effluent contamination and eliminates the need to adjust pH post-treatment. In this study we evaluated a number of photocatalysts that are capable of using water as a hole scavenger (i.e., oxidize water) for nitrate reduction, and then optimized successful candidates with appropriate co-catalysts. Sodium tantalate reduced nitrate using water as a hole scavenger, but the rate was slow and by-product selectivity was to nitrite. Iridium oxide and palladium nanoparticle co-catalysts were loaded onto the surface of sodium tantalate to catalyze the water oxidation reaction and the reduction of nitrite, respectively.

SYNTHESIS MATTERS: PHOSPHATASE ACTIVITY OF CeO_2 NANOPARTICLES MAY UNDERLIE THEIR TOXICITY

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Sudipta Seal, Nanoscience Technology Center University of Central Florida

William Self, University of Central Florida

The study of the chemical and biological properties of CeO_2 NPs (nanoceria) has expanded over the recently. Although most of the focus has been on the ability of these materials to reduce reactive oxygen and nitrogen species in biological systems, there are reports that claim that nanoceria are toxic. Unfortunately, the material synthesis of these studies varies significantly. Thus we must first determine whether nanoceria made by different methods are similar or different in their chemical properties. In this work, we investigated two water-based nanoceria with varying surface ratios of Ce^{3+}/Ce^{4+} (CNP1 and CNP2) and one hexamethylenetetramine based nanoceria (HMT-CNP1). HMT-CNP1 are readily taken into endothelial cells and their aggregation can be visualized using light microscopy. CNP1 and CNP2 were also taken up but to a lesser extent. Exposure to HMT-CNP1 also reduced cell viability (MTT) at a 10-fold lower concentration than CNP1 or CNP2. Surprisingly, exposure to HMT-CNP1 led to substantial decreases in ATP level. In addition we found that HMT-CNP1 exhibited robust phosphatase activity. Though CNP2 also exhibits ATPase activity, CNP1 lacked phosphatase activity. These results suggest increased uptake and ATPase activity of HMT-CNP1 may underlie the mechanism of their toxicity.

UPTAKE AND BIOACCUMULATION OF TiO_2 NANOPARTICLES IN THE BLUE MUSSEL (*MYTILUS EDULIS*) AND THE EASTERN OYSTER (*CRASSOSTREA VIRGINICA*)

John J. Doyle, University of Connecticut

Robert Mason, University of Connecticut

Evan Ward, University of Connecticut

The purpose of this work is to study the uptake and bioaccumulation of ~30 nm TiO2 particles in two commercially relevant species of bivalves. Nanoparticles are delivered to the animals either freely suspended or incorporated into marine snow at a concentration of 5 ppm. Animals feed for two hours, and then depurate for a maximum of 120 hours. During depuration, feces are collected and groups of animals are sacrificed at 0, 6, 24, 72, and 120 hours post-exposure. The gills and digestive glands are isolated by dissection, and all samples are analyzed with an inductively coupled plasma mass spectrometer (ICPMS) to obtain an estimate of titanium concentration. Analyses revealed that TiO_2 nanoparticles readily agglomerated in natural seawater, artificial seawater, and MQ-water forming larger aggregates. The hydrodynamic diameter of these aggregates was similar in all fluid media. TiO_2 nanoparticles were cleared from the gills and the digestive gland almost immediately, and were completely depurated from the digestive system after 72 hours. The interactions between nanoparticles and suspension-feeding bivalves are critical as these organisms are consumed by, and may transfer nanomaterials to, humans. This research will provide insight into how a potential anthropogenic contaminant could affect living, marine resources and human health.

MESOPOROUS SILICA NANOPARTICLES AS COMPLEX BIOACTIVE DELIVERY VEHICLES

KATHLEEN EGGLESON, University of Notre Dame

This paper will offer multi-faceted consideration of mesoporous silica nanoparticles (MSNs) as candidates for medical applications. MSNs have been increasingly investigated as potential drug delivery vehicles and theranostic devices. MSNs vary in size and shape of both particle and pore and are amenable to modification, allowing structural customization for different cell target and cargo combinations. With relatively large pore volumes, MSNs can: transport large payloads of one or more bioactive molecules, enhance solubility of hydrophobic pharmaceuticals, target drug release to specific cell types, and control release kinetics through multiple mechanisms. Mechanized MSNs have been elegantly designed and shown promise as complex engineered nanomedicines in early in vitro experiments. Design concepts and functional data for multiple specific MSN applications will be presented. Composed of the two most abundant elements in Earth's crust, limits to the sustainable use of MSN vectors in vivo may come in the form of hemolytic, inflammatory, and/or other toxicities. While some forms of silica can cause severe pathology in humans (especially with occupational exposures), initial studies regarding MSN toxicology have been contradictory and inconclusive. A life cycle-based approach will be used to frame analysis of potential risks and benefits of MSNs for medical applications.

UNINTENTIONAL EXPOSURE TO NANOPARTICLES VIA AN INDUSTRIAL SILICON PROCESSING ACCIDENT

Sheryl H. Ehrman, University of Maryland College Park

Orion Wenrich, University of Maryland College Park

As the nanotechnology industry has grown so have the concerns regarding nanoparticle exposure. Nanoparticles may also form and be released as unwanted byproducts of industrial accidents. While research has been performed regarding health and ecological effects of nanoparticle exposure, there has been surprisingly little research using regional transport modeling software to develop and study exposure event scenarios. Chlorosilanes are used in the Siemens process for silicon purification. Silicic acid and silica nanoparticles are an unwanted side effect of chlorosilane processing into solar grade silicon. Given the global increase in start-up companies in the silicon and solar industries, we investigate the regional effect that a silicon processing accident might have using Hysplit and ALOHA software. Results from ALOHA indicate an AEGL-1 toxic air hazard up to 3.9 km away for a release of trichlorosilane alone, from a plant that produces 1,600 metric tons annually of solar grade silicon. For a plant that produces ten times as much the AEGL-1 hazard level could extend up to 10 kilometers from the plant when the source amount is scaled up accordingly. Additional results incorporating chemical reactivity will be discussed.

METHODS TO EVALUATE THE EFFECTIVENESS OF NANOPARTICLE CONTROL TECHNOLOGIES

MICHAEL ELLENBECKER, University of Massachusetts Lowell

Su-Jung Tsai, University of Massachusetts Lowell

Kevin Dunn, National Institute for Occupational Safety and Health

In the occupational environment, the most effective method for reducing exposures to airborne engineered nanoparticles (ENPs) is the use of engineering controls. Tsai and others, however, have found that engineering controls, such as local exhaust ventilation, that are very effective in controlling other contaminants and that appear to be controlling ENP release, can in fact allow the release of significant numbers of airborne ENPs. Such releases are not detectable by conventional occupational hygiene techniques, such as gravimetric sampling, or by the workers' senses. In such cases, the workers will have a false sense of security, believing that the engineering controls are protecting them from exposure. A combination of traditional and advanced assessment methods are needed for the evaluation of engineering controls. This paper will review available techniques used in our laboratory, such as computational fluid dynamics (CFD) modeling, flow visualization using fog and laser light sheets, and sophisticated particle source monitoring. In addition, the advantages and disadvantages of these methodologies will be discussed. Standardized protocols for engineering control evaluation will be presented and discussed.

OCCUPATIONAL HEALTH & SUSTAINABILITY; OEHS AS A TOOL FOR INNOVATION

DONALD EWERT, nanoTox, Inc.

Chemical development has been an integral part of human nature since the beginning of time. As a result, we've come to expect an ever-increasing continuum of change. This demand, however, has potential for unwarranted risk and on occasion, excessive illness and death. Thus, we've learned to balance the benefits of innovation with a portfolio of protections; all designed to guard human health and the environment. This common voice toward protection creates a backdrop for regulation which now governs the actions of all producers and chemical end users. Companies no longer have the freedom to introduce new products without first tempering their process through a myriad of health & safety considerations. By establishing tough regulatory oversight, we control the processing, marketing, transportation, and disposal of nearly every chemical in existence. Having taken lessons learned to a new level, Nanotechnology is much more than a simple acronym. Regulatory agencies nationwide and across the globe have begun to initiate regulations controlling nearly every facet of activity, from occupational exposure to production, use, and waste management. This presentation provides participants with a survey of current nanotechnology OEHS regulation and offers tools to support sustainable expansion in Occupational, Environmental, Health and Safety.

TRANSPORT AND DEPOSITION OF NON-SPHERICAL NANOMATERIAL IN SUBJECT-SPECIFIC LUNG AIRWAYS

Yu Feng, NCSU

Clement Kleinstreuer, NCSU

Most naturally occurring and man-made nanoparticles are non-spherical. As part of nanotechnology, their exponential growth in fabrication, handling and use for, say, cosmetics, cleaners, composites and nanomedicine make them increasingly ubiquitous in the air we breathe. The unique lung deposition patterns of nanoparticles, their level of toxicity and their ease-of-migration into the blood stream may cause severe health problems, as discussed by Oberdoerster et al. (2005). In contrast, non-spherical nanomaterial, e.g., carbon nanotubes, is also being used as drug carriers for cancer treatment (Zhang et al., 2011; Kleinstreuer et al., 2012). While the transport and deposition of spherical nanoparticles ($0<d_p<100$nm) has been analyzed (see Kleinstreuer & Zhang, 2010; among others), the fate of needle-like particles in subject-specific lung airways has hardly been addressed.To simulate inhaled non-spherical particle transport, orientation and deposition, the Euler-Lagrange fluid-particle modeling approach has been employed in Fluent 14.0 (ANSYS, Canonsburg, PA) with user-supplied C-programs.

The computer simulation results have been compared to fiber transport and deposition in a circular tube (Tian et al., 2012) and further validated with experimental data sets for a subject-specific airway configuration provided by Su & Cheng (2006). Additionally, the accuracy and effectiveness of using equivalent spheres to approximate non-spherical particle dynamics have been investigated. Specifically, equivalent volume, Stokes, and aerodynamic diameters were considered, and the Stokes equivalent-sphere hypothesis was improved. The numerical results expand the basic understanding of the dynamics of non-spherical particles in realistic shear flows, and can be used to investigate the fate of inhaled toxic or therapeutic nanomaterials.

GUIDING EMERGING TECHNOLOGIES: APPLYING PRINCIPLES OF SUSTAINABILITY AND ANTICIPATORY GOVERNANCE

RIDER FOLEY, Center for Nanotechnology in Society, Arizona State University

Daily, products enhanced or enabled by nanotechnology enter the physical and social fabric of our lives, yet little is known about who "governs" emerging technologies. Two approaches are attempting to solve this problem. First, descriptive studies on emerging technology can be very specific to actors and responsibilities. Second, sustainable governance introduces values intended to broaden the criteria upon which an actor's decision-making is based. However, descriptive studies rarely address what actors should do and values-based sustainability principles are not connected to the practice of actors. The goal is to synthesize sustainability principles and anticipatory governance for evaluative purposes. This goal informs our research questions: (i) which actors are currently occupied in the nanotechnology innovation process? (ii) what responsibilities do they express as theirs and which do they assign to others? and (iii) how do those responsibilities align (or contrast) with the synthesized framework? Literature reviews and interviews (n=45) with key actors will provide the requisite data. Results indicate economic-based values guide decision-making. Yet, evidence suggests that broader values are also considered. We offer empirical evidence to evaluate strengths, weaknesses, and gaps in the current governance regime, as a means to contemplate alternative designs of future governance.

CHALLENGES IN STUDYING THE FATE AND EFFECTS OF NANOPARTICLES IN AQUATIC SYSTEMS

VALERY E. FORBES, University of Nebraska, Lincoln

Increasing use of metal-bearing nanoparticles (NPs) is likely to result in their release to the aquatic environment. However, the extent to which metal-bearing NPs are more or less bioavailable and/or toxic than other forms of metals to aquatic organisms remains unclear. This talk will address the particular challenges involved in studying the fate and effects of metal-bearing NPs in aquatic systems with particular emphasis on sediments. The properties of metal-bearing NPs are likely to change substantially following addition to aquatic and sedimentary media (e.g., through dissolution, agglomeration, and/or sedimentation), and our results suggest that their bioavailability and toxicity to aquatic organisms are not easily predictable. The reasons are partly due to the specific nature of the particles themselves, partly due to the properties of the exposed organisms, and partly due to our current inability to completely characterize NPs in certain media (e.g., sediments). The results that I will describe represent part of the outcome of a large EU 7th Framework Project (NanoReTox), which has involved a multidisciplinary team of physical chemists, human toxicologists, and ecotoxicologists. An important take-home message from this work is that we need better methods for detecting and characterizing NPs at environmentally-realistic concentrations, particularly in sediments.

SYNCHROTRON CONFIRMATION OF THE UPTAKE AND TRANSLOCATION OF TiO_2 NANOPARTICLES IN CUCUMBER PLANTS

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Nanotechnology includes the fabrication and use of different nanomaterials (NMs), including nanoparticles (NPs). Properties derived from NPs surface area, chemistry, shape, and surface charges, among others, allow their utilization in numerous goods and consumer products. Reports indicate that the number of nanoproducts worldwide increased by 521% since March 2006 to August 2011. TiO_2 NPs are among the most used nanomaterials . These NPs are used in sunscreens, surface antibacterial and antiviral disinfectants , organic pollutant removers, gas sensors, solar cells, food coloring in powdered doughnuts, skim milk as a fat substitute to provide the white color, and in paints. However, this variety of uses and the release of TiO_2 NPs from paints by weather conditions, increase the possibility of environmental dispersion of TiO_2 NPs with unknown consequences. Thus, advances in nanotechnology have raised concerns about possible effects of NMs in the environment, especially in terrestrial plants. In this research, the impacts of TiO_2 nanoparticles (NPs) were evaluated in hydroponically grown cucumber (Cucumis sativus) plants. Seven day old seedlings were treated with TiO_2 NPs at concentrations varying from 0 to 4000 mg L-1. At harvest, the size of roots and shoots were measured. In addition, micro X- ray fluorescence (micro-XRF) and micro X-ray absorption spectroscopy (micro-XAS), respectively, were used to track the presence and chemical speciation of Ti within plant tissues. Results showed that at all concentrations, TiO_2 significantly increased root length (average >300%). By using Synchrotron micro-XRF it was found that Ti was transported from the roots to the leaf trichomes, suggesting that trichomes are possible sink or excretory system for the Ti. The micro-XANES spectra showed that the absorbed Ti was present as TiO_2 within the cucumber tissues, demonstrating that the TiO_2 NPs were not biotransformed.

REGULATING NANO-CONTAINING PRODUCTS: IDENTIFYING GAPS IN CHARACTERIZING RISKS

THERESE GARVEY, Rochester Institute of Technology

Gabrielle Gaustad, Rochester Institute of Technology

Callie Babbitt, Rochester Institute of Technology

Nanomaterials have been introduced into a array of consumer products and their rapid implementation looks to continue. While the benefits these smaller materials afford are clear, their life-cycle environmental impacts remain largely uncharacterized and the risk of particulate exposure is uncertain. In the pursuit of quantifying risk, there have been many studies done to understand the ecotoxicological impacts of nanomaterials; however, comparing results between these studies is difficult as methodologies range greatly between disciplines. There is a clear need to synthesize the work between the engineering, environmental health and safety, medical, and ecology communities. Due to disparity between disciplines, it is difficult to undertake either a life-cycle assessment or risk assessment with current knowledge and differing metrics. This work outlines key results and methodologies from impact and exposure literature in a range of disciplines and provides an initial assessment of key gap areas within the life-cycle of several case study products. Integrated metrics are explored in this context. Implementation of risk-reducing strategies (regulations, product design, etc.) is discussed in the framework of a life-cycle perspective to identify which may have the highest potential impact within that stage.

SAFE BY DESIGN: DEMONSTRATING THE EFFICIENCY OF A SAFER FORMULATION CONCEPT FOR FLAME-GENERATED ENGINEERED NANOMATERIALS (ENMS)

Samuel Gass, Harvard University

Georgios Pyrgiotakis, Harvard University

PHILIP DEMOKRITOU, Harvard University

In this study, a safer formulation concept for flame-generated nanomaterials was demonstrated. It is based on the encapsulation of potentially toxic nanomaterials by a biologically inert nanothin amorphous SiO_2 layer. The core-shell particles maintain their intrinsic optical, magnetic or plasmonic properties of the core material but exhibit surface properties of their SiO_2 shell. The SiO_2-coating process was performed using the recently developed flame spray pyrolysis (FSP)-based Versatile Engineered Nanomaterial Generation System (VENGES). We first demonstrate the versatility of the proposed SiO_2-coating process by applying it to several ENMs (CeO_2, Fe_2O_3, ZnO, Ag) marked by their prevalence in consumer products as well as their range in toxicity. We quantified the thickness of the SiO_2-coating (TEM, XPS), evaluated its efficiency (Chemisorption) and its effect on the core material structure, composition and morphology (XRD, BET, and TEM). Furthermore, we examined their behavior in physiological fluids and compared to those of pure silica nanoparticles. Finally, we provide valuable in-vitro toxicological evidence for the safety of this novel formulation concept by evaluating the relative toxicity of SiO_2-coated vs. uncoated ENMs using a number of cellular assays and several cell-lines. Our results show that the proposed method can be used to effectively and uniformly coat flame generated ENMs with a nanothin layer of amorphous SiO2 that significantly reduces their toxicological effects. This scalable method can be applied in nanomanufacturing of nanomaterials developing safer by design nanoparticles.

INTERACTIVE EFFECTS OF NANO-TiO_2 AND SOIL WATER ON SOIL MICROBIAL COMMUNITIES

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John H. Priester, University of California, Santa Barbara

Laurie C. Van De Werfhorst, University of California, Santa Barbara

Manufactured nanomaterials (MNMs) are used in impermanent goods (e.g. paints, and personal care products), making it likely that MNMs are building up in soil. To date, studies show few effects of carbonaceous MNMs on soil microbial communities; however, we have shown that some high production metal oxide MNMs alter soil microbial community diversity including the proportion of functionally-narrow taxa. Here, we asked: does nano-TiO_2 change soil water relations, and thereby indirectly affect soil microbial communities? To test, we amended a natural grassland soil with a nano-TiO_2 concentration based on predicted (yr.2025) environmental release levels, and equilibrated the soils for 9 months at various relative humidities. The time course of soil water content increase was diffusional, and neither the wetting rate nor final soil water relations varied with nano-TiO_2 addition. However, nano-TiO_2-induced soil microbial community dissimilarities increased, but tended to approach a maximum, when soils became drier, indicating that soil water mediates nano-TiO_2 effects on soil bacterial communities. Taken together, nano-TiO_2 effects on soil bacteria are likely due to direct toxicity which is affected by soil environmental factors. This study contributes to our understanding of the mechanisms of MNM effects on soil bacterial communities, including such effects under varying environmental conditions.

COHERENT VIBRATIONAL AND ELECTRONIC SPECTROSCOPY OF ENGINEERED AND NATURAL NANOPARTICLES

FRANZ M. GEIGER, Northwestern University

Understanding the physical and chemical processes occurring at the surfaces of nanoparticles is important for understanding, controlling, and predicting how nanoparticles interact with the environment. This presentation will show how nonlinar optical coherent electronic and vibrational probes access the surfaces of engineered and natural nanoparticles directly, in real time and space, at room temperature, under aqueous solution and flow conditions or at one atmosphere of air, and without the necessity of external labels. Example are presented that focus on nm-sized CdSe quantum dots as an example of engineered nanoparticles and on highly size resolved organic aerosol particles from tropical and boreal forests as an example of natural particles.

OIL SPILL REMEDIATION USING BIOCOMPATIBLE DENDRITIC POLYMERS

Nicholas K Geitner, Clemson University

David Ladner, Clemson University

Pu-Chun Ke, Clemson University

This research examines the potential of both polyamidoamine (PAMAM) dendrimers and poly(ethyleneimine) (PEI) hyperbranched polymers, or dendritic polymers in short, to act as novel oil dispersants. As such, we seek to understand their ability to enhance the solubility of oil hydrocarbons in water in a biocompatible manner. The first stages of the project examine the fundamental interactions between these dendritic polymers and both linear and poly-aromatic hydrocarbons. In the studies we find that these dendritic polymers, especially the hyperbranched polymers, do significantly enhance the solubility of hydrocarbons in pure water and thus have significant potential as oil dispersants. Studies planned or in progress include computational modeling of hydrocarbon-polymer complexes as well as biocompatibility studies of these complexes.

METALLIC OXIDE NANOPARTICLES HAVE SIGNIFICANT NONLETHAL EFFECTS ON THE METABOLISM OF SOIL MICROBES

Jordan Goodman, Utah State University, Department of Biological Engineering

Christian Dimpka, Utah State University, Department of Biology

Anne Anderson, Utah State University, Department of Biology

The extensive involvement of nanoparticles (NPs) in commerce means that their entry into the environment is inevitable. Our research focuses on the potential impact of metallic oxide nanoparticles in agriculture. One impact of CuO and ZnO NPs is their antimicrobial activity for pathogens. However the soil bacterium, Pseudomonas chlororaphis O6 (PcO6) has high resilience to killing by both NPs. This bacterium represents bacteria that colonize plant roots improving their resilience to both biotic and abiotic stress. At sublethal levels, the CuO and ZnO NPs differentially remodel PcO6 metabolism. Whereas CuO NPs reduce the formation of a Fe-chelating siderophore, ZnO NPs enhance production. Also CuO NPs increase and ZnO NPs repress synthesis of indole acetic acid, a plant-growth regulator. Formation of other secondary compounds, phenazines, also is strongly inhibited by ZnO NPs. A role of NPs as a point source for metal release is involved in these processes. Siderophore, IAA and phenazines each are beneficial in plant interactions. Thus, the effects of the sublethal concentrations of NPs could affect plant performance. Our findings suggest that the release of NPs into the environment may generate more subtle effects through modification of microbial metabolism that could influence interspecies involvement.

ELECTRONIC STRUCTURE-DEPENDENT TOXICITY OF SWCNT REVEALED BY TOXICOGENOMIC ANALYSIS

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Chad D. Vecitis, School of Engineering and Applied Science, Harvard University

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The chirality-dependent electronic structure of SWCNTs i.e., metallic or semiconducting, affect their reactivity and interactions with microorganisms, therefor exhibit different toxicity effects. Cellular stress response pathway ensemble-based toxicogenomic approach using recombinant E.coli K12 strains with GFP fusions were used for investigation the toxicity of these SWCNTs. Oxidative stress and membrane stress are showed to be the two major pathways whose transcriptional level were affected by SWCNTs exposure. The metallic SWCNTs induced significantly higher transcriptional level changes in oxidative stress (6 folds), membrane stress (2.5 folds) than the semiconducting SWCNTs. The compromise of membrane integrity and presentence of oxidative stress may disrupt the function of the membrane-bound electron carriers. For sub-categorized membrane stress functions, metallic SWCNTs induced higher altered gene expression of those involved in electron transfer, membrane structure related macromolecular metabolism, flagella biosynthesis, and antibiotic resistance. Metallic SWCNTs produced more ROS, which may resulting from the stronger ability on electron transport, than semiconducting SWCNTs. The significantly higher stress response caused by the metallic SWCNTs than the semiconducting SWCNTs seemed to suggest that the toxicity level and mechanism of SWCNTs are related with the electronic structure and electron transfer ability of the SWCNTs.

APPLICATIONS OF SP-ICP-MS: EXTRACTION AND DETECTION FROM BIOLOGICAL MATRICES

Evan Gray, Colorado School of Mines

Manuel Montano, Colorado School of Mines

Christopher Higgins, Colorado School of Mines

Assessing the potential for adverse biological effects of engineered nanoparticles (ENPs) relies in part on reliable detection, characterization and quantification methods. Several of the current challenges include: low ENP concentrations, polydispersity arising from aggregation/partial dissolution, and the presence of interfering particles. For many inorganic-based ENPs, single particle inductively coupled plasma-mass spectrometry (spICPMS) has recently been shown to be a promising approach for detection and quantitation. In particular, the elemental specificity of ICPMS provides a means to detect and quantify ENPs in complex matrices. Although much of the reported work has focused on method development, spICPMS applications are growing. Application of spICPMS to biological systems is the subject of this presentation. In examining Au and Ag nanoparticles spiked into a variety of tissues, we have obtained high (> 80 %) particle recoveries, and were able to determine particle size, using a tetramethylamonium hydroxide extraction procedure. In laboratory exposures of D. magna to Au and Ag ENPs, we were able to use spICPMS to examine ENP translocation from the gut into the body fluids. SpICPMS also allowed examination of particle depuration from L. variegatus exposed to these same particles. Furthermore spICPMS analysis allowed to differentiation of the original ENPs from other forms.

ARMS CONTROL FOR NANOTECHNOLOGY

Mark A. Gubrud, Department of Physics and Astronomy, University of North Carolina, Chapel Hill

If nanotechnology is to be sustainable, it must not become the engine of a resurgent and out-of-control global arms race which generates an unlimited stream of new threats to international and human security. The emergence and further development of nanotechnologies in electronics, sensors, information and artificial intelligence, materials, miniaturized systems, and bionanotechnologies, is expected to create many opportunities for evolutionary and revolutionary advances in the performance of military systems, as well as qualitatively new types of weaponry (1). Avoidance of a nanotechnology-powered arms race therefore requires a preventive approach to arms control (2), embodying three principal aspects: the identification of new threats enabled by nanotechnologies, proposal of credible arms control and international security measures which can be taken to limit these threats, and identification of verification, enforcement and hedging measures which can be used to implement an arms control and cooperative security approach to managing the global security risks of nanotechnology, including the potential uses of nanotechnologies within such an approach.

GRAPHENE-BASED ENVIRONMENTAL BARRIERS

FEI GUO, Brown University

Vivek Shenoy, Brown University

Robert Hurt, Brown University

Many environmental technologies rely on containment by engineered barriers that inhibit the release or transport of toxicants. Graphene is a new, atomically thin, two-dimensional sheet material, whose aspect ratio, chemical resistance, flexibility, and impermeability make it a promising candidate for inclusion in a next generation of engineered barriers. Here we show that ultrathin graphene oxide (GO) films can serve as effective barriers for both liquid and vapor permeants. First, GO deposition on porous substrates is shown to block convective flow at much lower mass loadings than other carbon nanomaterials, and can achieve hydraulic conductivities of 5×10-12 cm/s. Second we show that ultrathin GO films of only 20 nm thickness coated on polyethylene films reduce their vapor permeability by 90% using elemental mercury as a model vapor toxicant. The barrier performance of GO in this thin-film configuration is much better than the Nielsen model limit, which describes ideal behavior of flake-like fillers uniformly imbedded in a polymer. The Hg barrier performance of GO films is found to be sensitive to residual water in the films, which is consistent with molecular dynamics (MD) simulations that show lateral diffusion of Hg atoms in graphene interlayer spaces that have been expanded by hydration.

NANOTECHNOLOGY FOR SUSTAINABLE ENERGY

RAM B. GUPTA, Auburn University

Today’s world is facing two critical challenges: (1) high fuel prices, and (2) climatic changes. Both of these are linked to the over-dependence on the fossil fuels: petroleum, natural gas, and coal. The transport is almost totally dependent on fossil particularly petroleum based fuels such as gasoline, diesel fuel, liquefied petroleum gas, and natural gas. The combination of rising oil prices, issues of security, climate instability and pollution, and deepening poverty in rural and agricultural areas, is propelling governments to enact powerful incentives for the use of renewable energy. Key to the supply of sustainable energy is economic and environmentally benign conversion of the solar, wind, biomass, and geothermal energies into the usable electricity and fuels. The use of nanotechnology is playing an important role in many of these conversion technologies. In additional, nanotechnology is helping with

lowering of the energy use in many of the new consumer products. This talk will provide an overview of how nanotechnology is being applied to the sustainable energy and challenges what are remaining.

DEVELOPMENT OF NANOSCALE REFERENCE MATERIALS AT NIST: CHALLENGES AND CONSIDERATIONS FOR SUSTAINABLE NANOTECHNOLOGY

VINCENT A. HACKLEY, National Institute of Standards and Technology

The proliferation of manufactured nanoscale materials, principally in the form of nanoparticles (NPs), and their subsequent incorporation into a growing number and variety of consumer, biomedical and industrial products, has increased concern regarding their potential risk to human health and the environment. This in turn is generating a negative impact on the commercialization and public adoption of nanotechnology. Understanding the relationship between intrinsic material properties and NP interactions with biological and ecological systems is key to establishing long term sustainability of this emerging technology. Studies are also required to assess occupational and environmental exposure to NPs as part of a risk assessment framework. The lack of adequate material characterization and the need for relevant reference materials (RMs), to provide traceability and benchmark data, have been highlighted as significant factors limiting the value of nanotoxicity studies and the capacity to compare data obtained on similar materials in different laboratories. In this presentation I summarize recent and on-going efforts at the National Institute of Standards and Technology to develop RMs intended for use by the biomedical, environmental health and safety, and other research and regulatory communities. I will discuss considerations and challenges that impact the prioritization and development of RMs.

MECHANISMS OF CUO NANOPARTICLE TOXICITY TO SACCAROMYCES CEREVISIAE

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Nanomaterials are used in many commercial products and new applications in biomedicine, yet their fate, potential toxicity, and mechanisms of internalization in biological cells have not been well defined. The main objective of this study is to identify the pathways and mechanisms underlying interactions between metal oxide NPs and eukaryotic cells. S. cerevisiae provides an ideal model system in which to study the NP toxicity, particularly as many genes involved in metal homeostatsis, cellular defense, and regulation show near-complete conservation between yeast and humans. Exposure to CuO NPs resulted in a higher percentage of cells with membrane damage and higher intracellular Cu levels than exposure to the molar equivalent of CuSO4. In experiments with S. cerevisiae endocytosis mutants, we observed lower percent membrane damage from CuO NPs and $CuSO_4$ in the two mutants in comparison to the wild type. The results suggest that endocytosis might play an important role in NPs uptake and toxicity. We also have found that generation of reactive oxygen species in the mitochondria may be responsible for observed toxicity associated with metal NP exposure. On the basis of these data, we postulate that metal nanooxides exhibit a significant toxicity while triggering different mechanisms of cell response.

CENTER FOR CHEMICAL INNOVATION: THE CENTER FOR SUSTAINABLE NANOTECHNOLOGY

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Franz Geiger, Northwestern University

Rebecca Klaper, University of Wisconsin-Madison

The Center for Sustainable Nanotechnology is a new, multi-institutional partnership devoted to investigating the fundamental molecular mechanisms by which nanoparticles interact with biological systems. The CSN is funded by the National Science Foundation Division through the Centers for Chemical Innovation Program. Using a chemistry-centered approach, we aim to understand the molecular-level chemical and physical principles that govern how nanoparticles interact with living systems, in order to provide the scientific foundations that are needed to ensure that continued developments in nanotechnology can take place with the minimal environmental footprint and maximum benefit to society. Participating institutions include the University of Wisconsin-Madison, the University of Minnesota, the University of Illinois, the University of Wisconsin-Milwaukee, Northwestern University, and the Pacific Northwest National Laboratory. In this poster presentation we will described some of ongoing and planned research, education, and outreach activities of the CSN.

PHOTOTOXICITY OF TiO_2 NANOPARTICLES

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Metal oxide semiconductors such as TiO_2 are capable of inducing toxicity when illuminated by light, creating reactive oxygen species (ROS) such as hydroxyl radicals and superoxide ions. We have investigated the phototoxicity of TiO_2 nanoparticles in the presence and absence of different ligand capping groups, using zebrafish (Danio rerio) embryos as a model system. All nanoparticles are synthesized and characterized in our laboratories to enable comparisons of the influence of size and surface terminations. Our results show that for a given total mass concentration as the nanoparticles become smaller they become more toxic, commensurate with the increase in nanoparticle surface area and measurements of ROS species. More surprisingly, however, in vivo fluorescence imaging studies using fluorescent indicators of oxidative stress show that there are quite substantial differences in where the oxidative stress is observed when comparing otherwise-identical nanoparticles of different sizes (6 nm, 12.4 nm, and 15 nm diameter). The influence of ROS is also affected by the presence of organic ligands, which can block access of water/O_2 to the nanoparticle core and can stabilize nanoparticles in solution. Recent results on ligand effects will be presented.

INNOVATIVE BIOSENSORS USING A MULTI-WALLED CARBON NANOTUBE ARRAY FOR MONITORING CYANOTOXINS IN WATER

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Amos Doepke, University of Cincinnati

Dionysios D. Dionysiou, University of Cincinnati

An innovative electrochemical biosensor using a multi-walled carbon nanotube (MWCNT) array was developed for monitoring a potent cyanotoxin, microcystin-LR (MC-LR) in sources of drinking water supplies. To fabricate biosensor electrodes, mm-long MWCNT arrays were grown on patterned Si substrates by water-assisted chemical vapor deposition. Scanning electron microscopy and high-resolution transmission microscopy methods were employed and revealed that the electrodes consisted of vertically well-aligned MWCNTs arrays with a narrow size distribution. To enhance the graphitization of synthesized MWCNTs, high temperature thermal treatment (2500 oC) in an Ar atmosphere (an inert environment) was used. To produce oxygen-containing functional groups on the surface of the MWCNT array, the MWCNT array was functionalized with electrochemical activation in alkaline media. MC-LR was immobilized onto the functionalized MWCNT array by cross-linking between MC-LR and produced functional groups on the MWCNT. To provide specificity of biosensors, monoclonal antibodies specific to MC-LR were added in the incubation solutions. The performance of the MWCNT biosensor was evaluated by electrochemical impedance spectroscopy (EIS). The electrochemical impedance remarkably increased upon MC-LR and antibody conjugation. The electrochemical response for MC-LR was inversely proportional to the MC-LR concentration (0.05 to 20 ?g•L-1). The biosensor detected concentrations much lower than the World Health Organization (WHO) provisional concentration limit of 1 ?g/L for MC-LR in drinking water.

MONODISPERSE TiO_2 PHOTOCATALYTIC FILMS FOR TREATMENT OF MICROCYSTIN-YR

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The removal of natural toxins from sources of drinking water is important because their presence may severely affect humans and animals’ health. In particular, the occurrence of cyanobacteria (a.k.a., blue-green algae) which can produce hepatotoxic microcystins (MCs), a group of cyanotoxins that has been reported frequently in freshwater systems around the world. Although various congeners of MCs (MC-LR, MC-LA, MC-RR and MC-YR) have been found in sources of water supply, only the photocatalytic degradation of MC-LR has been extensively studied. However, some of them (e.g. the cyanobacterial toxin MC-YR) are very toxic and there is still high interest for their photocatalytic removal.

Titanium dioxide (titania, TiO_2) as a photocatalyst has been extensively studied for water treatment because of its relatively high photocatalytic activity, low-toxicity, and thermal and chemical stability under environmental conditions. To improve the overall photocatalytic performance and enable practical applications of TiO2 photocatalysis, the immobilization of TiO2 photocatalyst onto various substrates has been proposed, thus avoiding additional separation processes. The structural properties of TiO2 films such as particle size, BET surface area, and roughness are critical parameters for their optimum interaction with the organic contaminants. In addition, the uniformity of nanoparticles is of remarkable importance because the materials properties are generally directly related to particular characteristics such as size and shape. Thus, the combination of monodisperse nanoparticulate titania films with modified TiO_2 layers, such as N, F co-doped TiO_2, S doped TiO_2, or C doped TiO_2, allows them to utilize the visible portion of solar light. Therefore, the layer-by-layer prepared photocatalytic films could provide uniformity of the materials and improve their photocatalytic activity for water contaminants degradation.

In this study, photocatalytic films were prepared using monodisperse TiO2 particles of different particle sizes. In addition, a novel type of TiO_2 films consisting of different TiO2 materials was synthesized, using the layer-by-layer dip coating method. The synthesized films were characterized using transmission electron microscopy, scanning electron microscopy, X-ray diffraction, porosimetry analysis, and atomic force microscopy. Results will be presented on the effect of structural properties of monodisperse TiO_2 films on the degradation of cyanotoxin microcystin-YR under UV irradiation, solar, and visible light irradiation.

SURFACE CHEMISTRY DEPENDENCE ON THE ENVIRONMENTAL FATE AND TRANSPORT OF METALLIC NANOPARTICLES

Ashley E. Hart, Clemson University

Christopher L. Kitchens, Clemson University

Brian Powell, Clemson University

As the number of commercial nanoparticle applications increases, the concern of their environmental consequences becomes more prudent. Many factors contribute to the behavior of nanoparticles in soil, including nanoparticle surface chemistry, elemental composition, size and concentration, as well as the soil properties. Soil inherently contains natural organic matter, (NOM) which contains model compounds such has humic acid, fulvic acid, and desferrioxamine-B. Each of the compounds have a definite affinity for the nanoparticle surface and impact the nanoparticle transport in environmental conditions. In this study, the transport of nanoparticles was monitored using miscible displacement column experiments. Ultrapure silica powder was packed in bench scale columns and nanoparticle suspensions were added in one column volume, followed by nanoparticle free groundwater simulant. The effluent nanoparticle concentration was monitored and the columns were segmented to determine nanoparticle distribution within the column. Silica powder was used to investigate transport properties under ideal conditions. Field lysimeters with sandy loam soil and silver nanoparticles of varying surface chemistry were deployed for 1 year in order to investigate transport in soil systems. Results from this work will determine the role of surface chemistry in nanoparticle fate and transport in systems ranging from ideal to natural conditions.

NANOSILVER SIZE AND SURFACE COATINGS INFLUENCE VASCULAR RESPONSIVENESS FOLLOWING INTRAVENOUS ADMINISTRATION

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Leslie Thompson, Department of Physiology at East Carolina University

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Silver-nanoparticles (AgNP) have unique physicochemical and antimicrobial properties, allowing for numerous biomedical applications; yet their size and surface coatings present potential risks to the vasculature. We hypothesized that instillation of AgNP would alter vascular responsiveness, in both a surface coating-dependent and size-dependent manner. In male Sprague-Dawley rats, 20 nm (SS) or 110 nm (LS) AgNP coated with polyvinylpyrrolidone (PVP) or citrate (Cit) were administered intravenously (1 mg/kg) in the following groups: SSPVP, LSPVP, SSCit, or LSCit. 24 hours later, segments of aorta, coronary and mesenteric arteries were excised and mounted into a wire myograph for cumulative dose-response curve analysis of phenylephrine, serotonin, sodium nitroprusside or acetylcholine. In aorta, SSPVP ($P < 0.0001$) and LSPVP ($P < 0.01$) both promoted increased stress in response to phenylephrine, as compared to vehicle. SSCit ($P < 0.05$) lowered sensitivity to acetylcholine in mesenteric arteries, when compared to vehicle. Lastly, SSPVP ($P < 0.01$), SSCit ($P < 0.001$), and LSCit ($P < 0.01$) promoted enhanced sensitivity to sodium nitroprusside in coronary arteries, when compared to vehicle. These data reveal size-, coating-, and vascular bed-dependent alterations in responsiveness to AgNP, which warrants further research into potential mechanisms of vascular toxicity. This work is supported by NIH-U19ES019525.

TRANSMISSION ELECTRON MICROSCOPY FOR PRIMARY PARTICLE SIZE DISTRIBUTIONS OF NANOMATERIALS: GOLD NANOPARTICLE CASE STUDY.

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Less than 1% of the archival literature reports primary particle size distributions (PPSDs) for nanoparticles. However, primary particle size distributions are often directly linked to the nanomaterial’s performance in commercial products, its environmental and biological fate, and its toxicity. PPSD data has a high growth rate (31% exponential growth) due to its importance for manufacturing, product safety, and EHS issues, suggesting that a technical specification (documentary standard) would be timely and is needed. The authors are working within both the ISO/TC229: Nanotechnology and VAMAS TMA34 Committees to develop guidance on how to capture, measure and analyze transmission electron microscope images to obtain a primary particle size distribution in the nanoscale. We will discuss key elements needed for developing this technical specification: the metrology check list, critical terms and definitions, sample preparation, instrument factors, image capture, and data analysis. We report data from a US Technical Advisory Group Round Robin performed by industrial, government, and academic laboratories using a gold nanoparticle-specific protocol. The

extension, expansion, and generalization of this protocol to other commercially important nanomaterials, such as those on the OECD and EPA lists, are also discussed.

NANOSCALE PERSPECTIVES ON PLASTIC ELECTRONIC MATERIALS AND DEVICES

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Integration of nanoscale objects fabricated from conducting polymers in devices, and control of nanoscale morphology of conducting polymer materials in devices are productive ways of developing efficient plastic optoelectronic devices with precisely controlled properties. In this paper, the importance of molecular architecture of conducting polymers with respect to chain morphology and proprieties will be addressed first. Second, data on conducting polymer nanoparticle devices enabling memory functions via optical programming and electrical erasing will be discussed. These findings open the door for novel approaches to understanding charge-storage mechanisms on the nanometer scale and future applications of composite conjugated polymer nanoparticles in nanoscale memory and photoresponsive devices. Third, recent work on organic photovoltaic (OPV) devices built on Near-Infrared (NIR) photoresponse sensitization of solvent additive processed poly(3-hexylthiophene)/ fullerene solar cells by a low band gap polymer will be highlighted. The combination of a NIR absorbing conducting polymer and processing with solvent additive results in a ternary blended OPV device with controlled active layer morphology, for optimal function across the visible and NIR spectrum in an alternative fashion compared to the more complex tandem solar cells.

SUSTAINABILITY ASSESSMENT OF NANOCOATING MATERIAL: A LIFE CYCLE BASED MULTISCALE APPROACH

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Nanopaint is becoming an attractive coating material with great application potentials in a variety of manufacturing industries duo to its promise of a significant improvement of chemical and mechanical performance or an introduction of novel functionalities. Nevertheless, like many other nanomaterials, nanopaint is under serious questions about its environmental and health risks in different stage of its life cycle, and a consequent hidden cost associated with its production and application for nanocoating manufacturing. Apparently, sustainability assessment in different stages of the nanopaint-nanocoating life cycle becomes critical for successful development and application of this attractive material.In this paper, we introduce a life-cycle-based sustainability assessment methodology for evaluating nanocoating materials from material selection, through its manufacturing and application, to its end-use performance. Different from traditional LCA that emphasizes environmental performance evaluation, this methodology is for describing economic, environmental, and social sustainability performance separately in different life cycle stages. Furthermore, the performance evaluation will include the impact of nanostructures of the materials on nanoparticle emission pathways during material manufacturing and applications. The efficacy of the methodology will be demonstrated through a comprehensive study on nanopaint development for the automotive coating industry.

ROUTES OF CELLULAR UPTAKE OF NANO-SIZED MATERIALS DEPEND ON COMPOSITIONS OF CELL-PENETRATING PEPTIDES

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Betty Revon Liu, National Dong Hwa University

Han-Jung Lee, National Dong Hwa University

Nanomaterials have many proposed applications in basic and medical applications such as cellular receptor trafficking, biomolecule/drug delivery and monitoring, disease/cancer staging and therapeutical planning, and biosensing. Many nanomaterials are slow in cellular entry, thus certain surface modifications or additional carriers are needed to facilitate the process. Cell-penetrating peptides (CPPs) mainly compose of positively charged amino acids and are ideal to carry nanomaterials such as CdSe/ZnS quantum dots (QDs) into cells. We found that routes of uptakes of the noncovalent QD/CPP complex depend on amino acid composition. Nona-arginines (R9) peptides internalize QD via endocytosis while HR9 (CH5R9H5C) peptides use direct membrane penetration. In addition, we found that a plasmid with R9 sequence fused with piggyBac transposase is capable of accomplishing both protein transduction and transposition. We termed this one-plasmid gene delivery system as Transposoduction. As 20 CPPs are under clinical trials for drug delivery, their utility in tandem with nano-sized materials deserves much attention.

NCPI 2.0: RE-INVENTING THE NANOTECHNOLOGY CONSUMER PRODUCTS INVENTORY THROUGH A UNIQUE UNIVERSITY/NGO PARTNERSHIP

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Todd Kuiken, Woodrow Wilson International Center for Scholars, Science and Technology Innovation Program

The Woodrow Wilson International Center for Scholars’ (WWICS) Nanotechnology Consumer Products Inventory (NCPI) provides an important resource for numerous nanotechnology stakeholder groups ranging from consumers to researchers and policy-developers. Despite having nearly 200,000 unique visitors since 2008, and dozens of citations in peer-reviewed publications and grant proposals, a critical limitation of the NCPI has been its reliance on manufacturer claims to justify product listings. In 2011, the Virginia Tech Center for Sustainable Nanotechnology (VT SuN) and the Project on Emerging Nanotechnology (PEN) at WWICS initiated a unique University/NGO partnership to implement several critical modifications to the inventory. These modifications complement manufacturer claims and improve the utility of the NCPI among a growing number of stakeholders who rely on this resource for increasingly diverse and sophisticated uses. Modifications to the NCPI include categorizing products based on science-driven information, integrating Life Cycle Assessment (LCA) input/output databases for

improved analysis and decision-making, creating an open users community to facilitate information sharing, establishing a technical oversight and governance committee, and developing embedded traineeships that leverage the inventory to foster new interdisciplinary research projects at the interfaces between nanoscale science and engineering, consumer product safety, sustainability, and science and technology policy decisions.

LIFE CYCLE ISSUES FOR SCALABLE NANOMANUFACTURING OF CNT-ENABLED PRODUCTS

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Life cycle assessment (LCA) methodology is used to address the ethical, legal, and societal impacts (ELSI) in decision-making as nanomanufacturing scales to commercial production. Resource and emission inventories from three carbon nanotube (CNT) nano-enabled applications are explored as they apply to manufacture, use, and end-of-life (EOL) management, including recycling and disposal. Cost models are under development with inventories collected through collaboration with researchers and industry partners. To assess human exposures to CNT materials, exposure monitoring is underway during manufacturing (machining, grinding) and at end-of-life (recycling, incineration). The viability of recycling strategies for highly loaded polymer based CNT nanocomposites will be determined. Life cycle release, fate and transport, and ecotoxicity model outputs will be combined into an impact assessment characterization factor to be used in standard LCA software. The assumptions embedded in LCA valuation will be examined and adjusted to better incorporate values of sustainability in decision-making. Recommendations for adapting stewardship strategies for nano-enabled products will be developed. This work advocates the responsible development of nanotechnology as central to promoting scalable nanomanufacturing and product commercialization to avoid unintended and unduly harmful consequences. Ultimately, this project will help to foster the sustainable development of nanotechnology.

NANOARCHITECTONIC APPROACHES TO DESIGN GREEN POLYMERS TO ENHANCE EFFECTIVENESS OF NANOPARTICLES IN GROUNDWATER REMEDIATION

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Polymer-based surface modifiers are typically used to overcome the problem of agglomeration of nanoscale zero-valent iron (NZVI) particles in aqueous environment. The authors have recently developed a polysiloxan-based and a soybean oil-based biodegradable amphiphillic graft copolymers (APGCs) to coat the NZVI for application in groundwater remediation. Commercially available polysiloxan, soybean oil, acrylic acid, and polyglycol ethylene are used as the starting materials for the synthesis. Critical micelle concentration is examined to evaluate amphiphilic behavior of the copolymers. The new APGC-coated NZVI particles show improved colloidal stability and effective (~100%) degradation of target compound (trichloroethylene/TCE). Analyses of degradation byproducts

indicate complete degradation of TCE to benign end products. Biodegradation studies have indicated >90% degradation of the APGCs in aqueous environment. The new APGC-coated NZVI particles were found to have shelf-life up to 12 months making them attractive for storage and applications. Sticking (to aquifer materials) characteristics of the new APGC-coated NZVI were determined and found to be ideal for injection into the aquifer for groundwater remediation.

PHOTO-DEGRADATION OF 2,4-DINITROTOULENE BY SILVER DOPED TITANIUM DIOXIDE THIN FILM IN THE PRESENCE OF NATURAL SOLAR LIGHT: KINETICS AND DEGRADATION PATHWAYS

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Developing a low-energy, efficient water treatment technology is a critical need. Titanium dioxide (TiO_2, titania) as a photocatalyst has been widely used for water cleaning, air purification, and soil remediation. Recently, noble metals (Cu, Ag, and Au) have been intensively studied to improve the properties of photocatalysts, such as surface adsorption, electron-hole separation, and light absorption in visible light range. In this study, silver doped TiO_2 (Ag-TiO_2) and undoped TiO_2 nanocrystalline films on glass substrates were prepared by a sol–gel method based on the self-assembly technique with nonionic surfactant to control the nanostructure. High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and BET surface area analysis were employed to characterize particle size, surface morphology, the valence state of the Ag-TiO_2 film, and the surface area. We compared the catalytic activity of Ag-TiO_2 and unmodified TiO_2 thin films towards photo-degradation of 2,4-dinitrotoluene (2,4-DNT) under illumination of natural sunlight. The degradation kinetics of 2,4-DNT followed a first-order rate expression with observed reaction rate

constants (kobs) of 0.087 h-1 and 0.099 h-1 for TiO_2 and Ag-TiO_2 films, respectively. The degradation daughter products of 2,4-DNT were analyzed by high-performance liquid chromatography and gas chromatography–mass spectrometry. Our results suggest that the Ag-TiO_2 and TiO_2 films are suitable catalysts for 2,4-DNT treatment in the presence of natural sunlight.

GREEN SYNTHESIS OF NANOMATERIALS: A NECESSITY FOR SUSTAINABILITY

BARBARA KARN, NSF

This paper will review the state of research in green synthesis of nanomaterials. Highlights in a variety of technical methods will be given. Examples of producing nanomaterials in a 'greener manner' could involve but are not limited to the use of supercritical CO_2, water, or ionic liquids/molten salts to replace volatile organic solvents. Either self-assembly or templating might be used to eliminate waste in manufacturing. Renewables could be utilized as replacements for either nonrenewable and/or toxic starting materials; biological systems themselves may be used for synthesis. Microwave techniques can potentially help to conserve energy, as could both facile thermal and hydrothermal processes. Catalytic and photocatalytic reactions may also increase efficiency and decrease the formation of harmful byproducts. In order for nanotechnology to be sustainable and contribute to sustainability, materials must be made efficiently without production of polluting byproducts, and lowering energy of production, while minimizing critical elements.

GREENER MAGNETIC NANO-ADSORBENTS FOR WATER TREATMENT

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Magnetic permanently confined micelle arrays (Mag-PCMAs) are a novel composite nanomaterial that combines a high adsorbent with a magnetic core, within a mesoporous confining matrix, to address water treatment challenges. MagPCMAs have been shown to remove hydrophobic organic compounds from contaminated water. Here we studied the removal of oxyanions (perchlorate, nitrate, phosphate, and sulfate) found in drinking water sources. These oxyanions are commonly found in many water sources or at the end of wastewater treatment processes and new regulations on nutrients require innovative treatment approaches. We determined the removal efficiency in both competitive and non-competitive environments, as many of these anions are present in these sources. Mag-PCMAs remove 98% perchlorate, 96% phosphate, nearly 100% nitrate and sulfate. We observed little competition for sorption sites among oxyanions at most concentrations. Magnetic core allows fast, effective separation with low energy and no clogging. Mag-PCMAs can be reused several times to remove oxyanions from water.

SYNTHESIS AND PROCESSING OF METALLIC NANOMATERIALS USING CO_2 EXPANDED LIQUIDS AS A GREEN SOLVENT MEDIA

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Advancements in nanotechnology have led to a widespread emergence of different techniques for nanoparticle synthesis and processing. This work investigates the use of CO_2 expanded liquids as a green solvent for metallic nanoparticle synthesis and processing. We have demonstrated the size and shape-selective fractionation of gold and silver nanoparticles using CO_2 as a green anti-solvent. Traditional methods of nanoparticle anti-solvent processing result in copious amounts of organic solvent waste and require time and energy intensive centrifugation techniques. CO_2 is a non-flammable and non-toxic solvent that affords pressure tunable solvent properties. Furthermore, CO_2 is easily recovered by simple depressurization and provides enhanced transport properties, which eliminates the necessity to use centrifugation. The result is a sustainable solvent media for effective and efficient nanoparticle purification and fractionation. We have modeled the dispersibility of nanoparticles in CO_2 expanded liquids using a modified DLVO approach and used small angle neutron scattering to measure the molecular structure of nanoparticle ligands under anti-solvent conditions. Lastly, we have recently demonstrated that the tunable solvent properties of CO_2 expanded liquids can be used to control the size and size distribution of silver nanoparticles synthesized in an AOT reverse micelle system within CO_2 expanded hexane.

NANOTOXICITY STUDIES OF TiO_2 AND CeO_2 WITH IMMUNO-SPIN TRAPPING AND METABOLOMICS

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Kathleen Wallace,

In the immuno-spin trapping method, existing free radicals centered on macromolecules such as DNA are “spin trapped” with an organic molecule, 5,5-dimethyl-1-pyroline N-oxide (DMPO) and then detected via anti-DMPO antibodies in an ELISA format. These studies showed that (a) all eight different TiO_2 and CeO_2 nanomaterials (10-3,000 ug/ml) caused free radical attack on DNA in vitro, but to different extents, (b) some nanomaterials cause these effects at lower exposure concentrations than others, (c) in all but one case there was either an upper asymptote or nonmonotonic dose response curves and (d) a CeO_2 nanomaterial (58nm, cerianite, Alfa Aesar, exposure concentration of 3,000 ug/ml) generated the highest amount of free radical formation. In metabolomics studies using HepG2 cells, many TiO_2 or CeO_2 nanomaterial exposures (3 or 30 ug/ml) resulted in a reduction in glutathione, cysteine-glutathione disulfide, gamma-glutamylglutamate, gamma-glutamylglutamine and gamma-glutamylalanine. Diminished glutathione levels can be indicative of decreased synthesis, increased utilization/degradation, or export from the cell. Asymmetric dimethylarginine (a competitive inhibitor of nitric oxide sythase) was significantly increased in many nanomaterial exposures. Overall, our nanotoxicology studies have shown major differences in the chemical and biological responses between different TiO_2 and CeO_2 nanomaterials. Disclaimer: [This is an abstract or a proposed presentation and does not necessarily reflect EPA policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.]

THE CHEMISTRY OF SUSTAINABLE NANOTECHNOLOGY: IMPACTS OF NANOMATERIAL CHEMISTRY ON THE CHRONIC ENVIRONMENTAL IMPACTS ON AQUATIC SPECIES USING ACUTE GENOMIC AND BEHAVIORAL INFORMATION

Rebecca Klaper, University of Wisconsin-Milwaukee

The surface and core chemistry of nanomaterials play a large role in their interaction with aquatic organisms. Our research works to 1) identify the molecular interaction of nanomaterials with aquatic organisms 2) determine how changing nanomaterial chemistry impacts toxicity 3) provide a potential high-throughput method to evaluate nanomaterials for environmental safety. The ultimate goal is to suggest nanomaterial configurations that are environmentally safe and sustainable. This talk will discuss our work on toxicity with the model aquatic species Daphnia magna where we have shown that carbon and metal oxide nanomaterials differ in their toxicity depending on their core structure and surface chemistry. This presentation will also discuss changes in gene expression induced by exposure to sub-lethal concentrations of nanomaterials as an indicator of molecular-level interactions of nanomaterials with Daphnia magna. Genomic data can also be used as a sensitive indicator of how nanomaterials may be affecting specific physiological systems within Daphnia and how the chemistry of a nanomaterial may change these impacts. The presentation will also discuss the use of behavioral assays as early sensitive indicators of toxicological impacts. The use of molecular interactions and behavior as indicators of higher level or longer-term impacts of exposure will also be discussed.

THE EFFECTS OF EXPOSURE TO SILVER NANOPARTICLES RELEASED FROM COMMERCIAL PRODUCTS ON ZEBRAFISH DEVELOPMENT AND GENE EXPRESSION

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Marisol Sepulveda, Purdue University

Cecon Mahapatra, Purdue University

The rapid proliferation of products containing silver nanoparticles (Ag-NPs) in the marketplace has raised concerns over potentially adverse effects resulting from the environmental release of Ag-NPs. Previous studies have focused separately on the release of Ag-NPs from consumer products or the risks associated with Ag-NP exposure. Little has been done investigating the direct effects of exposure to Ag-NPs released from consumer products on early life development and gene expression. For this study Zebrafish, Danio rerio, was chosen as a model organism in order to assess potentially adverse effects as a result of exposure to Ag-NPs released from commercially available athletic socks. Ag-NPs were extracted from socks by soaking in ultrapure water and agitating for twenty-four hours. Samples of the leachate were collected and diluted to environmentally relevant total silver concentrations (less than 2 ppb). In order to assess differences between exposure to silver nanoparticles and ionic silver, several treatment groups were studied including diluted Ag-NP leachate, centrifuged Ag-NP leachate, AgNO3, and citrate coated Ag-NPs. Zebrafish embryos were exposed to the various treatment groups during the gastrula stage and observed for seventy-two hours. Overall mortality, hatching rate, morphology, and expression of the Cyp1a and Nrf2 genes were assessed.

LOW-DOSE COPPER AND ZINC IONS AND NANOPARTICLES AS DISINFECTANTS OF WATER WITH FECAL CONTAMINATION: A CRITICAL EVALUATION

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Alyson Malone, United States Army Medical Service Corps

Mark D. Sobsey, Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill

The disease burden and mortality of vulnerable individuals, particularly the poor, women, children, and rural residents, who suffer from illness as a result of drinking contaminated water, is of a great magnitude. According to the World Health Organisation in 2012, over 2.5 billion people lived without access to improved sanitation, and nearly 800 million didn't receive their water from improved sources. Approximately 1.5 million children die of diarrhea, out of roughly 2.5 billion childhood diarrhea cases, on an annual basis. This research focused on the testing of various combinations of copper and zinc chloride salts, as well as copper and zinc oxide nanoparticles, in three different doses, against three different test organisms, in test waters with and without the presence of dissolved solids gathered from dehydrated lake water. Performance was evaluated by measuring the decrease in culturable (countable) microorganisms over the course of a 6-hour time period. Kinetic models built from the gathered data were used to calculate the amount of time required for each tested disinfectant to reach the W.H.O. performance guidelines of 99% inactivation for bacteria and protozoan parasites and 99.9% inactivation of enteric viruses. Those disinfectant combinations that achieved two of the three suggested guidelines within a time frame appropriate for same-day or over-night application were selected as suitable candidates for capstone testing, and eventual trial in a human health study. Of the original 24 unique experimental combinations tested, four proved to be suitable candidates for capstone testing and eventual trial, two of which were comprised of metal oxide nanoparticles.

DEVELOPMENT OF BIODEGRADABLE ELECTROCHEMICAL SENSORS USING NANOSTRUCTURED POLY(AMIC) ACID MEMBRANES

Peter Kosgei, SUNY Binghamton

Wunmi Sadik, SUNY Binghamton

Nanomaterials are used in medicine and industry for treatment, decontamination among other applications. Most of these nanomaterials find their way into the environment and hence into the human body interfering with biological processes in the body. As our dependence on fossil fuels and factory production rises, so does the pollutants and toxic chemicals dumped in our environment. For this reason, the need for environmental sensors is as important as ever. These devices will be placed in the ecosystem or water supply to gather data on the presence of metal nanoparticles and toxic chemicals. The electrode should ideally follow the principles of green chemistry in that it does not produce excess waste and is environmentally friendly and benign. We hereby present the concept of disappearing electrochemical sensor based on integrated electroactive poly (amic acid) membranes, lignin and Trametes versicolor, a wood-rotting fungi. This biodegradable sensor was fabricated using phase inversion and drop coating techniques. The disappearing sensor was tested for the detection of silver nanoparticles. Cyclic Voltammetry was used to study the electro-activity of the species whereas Scanning Electron Microscope (SEM) provided information on surface morphology of the sensing electrode. This presentation will confirm that indeed the membrane, lignin combination can act as a disappearing sensor for detection of nanoparticles in the environment.

A COMPARATIVE GENOTOXICITY STUDY ACROSS SPECIES OF NANOMATERIALS

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Na Gou, Department of Civil and Environmental Engineering, Northeastern University, Boston, MA

April Gu, Department of Civil and Environmental Engineering, Northeastern University, Boston, MA

Engineered nanomaterials have been reported to induce DNA damage. However, inconsistencies have been observed among studies. In this study, we performed a comparative and mechanistic genotoxicity assessment of four common-used nanomaterials in prokaryotic (E.coli) and eukaryotic cells (yeast and human lung epithelial cell A549) respectively. Biomarkers covering six DNA damage and repair pathways were monitored using RT-qPCR (A549) and infused GFP signal (E.coli and yeast). DNA damage was confirmed with comet test with A549 cells. Mitomycin C was used as positive control. nTiO_2-a induced a wide spectrum of DNA damage, possibly due to oxidative damage. Carbon black led to weaker damage on bases. Fullerene induced severe double strand break in eukaryotic cells only, possibly by photocleavage as electron-poor photosensitizers. Similarly, single wall carbon nanotube also induced double strand break in eukaryotic cells only, but likely due to some unclear mechanism related to membrane damage it may induce. The comparison demonstrated that eukaryotic cell seemed more susceptible, likely due to the differences in the cell structure and uptake mechanism. This study offers a comprehensive in vitro genotoxicity evaluation of tested nanomaterials with across species comparison, for revealing the mechanisms and distinctive details in the DNA damage related to their properties.

FUNCTIONALIZED NANODIAMOND AS A CHARGE TRANSPORTER IN ORGANIC SOLAR CELLS

Xinbo C Lau, New Jersey Institute of Technology

Chintal Desai, New Jersey Institute of Technology

Somenath Mitra, New Jersey Institute of Technology

The organic photovoltaics (OPVs) are excellent alternatives to conventional silicon and thin film solar cells because they attempt to achieve moderate power conversion efficiencies (PCE) at significantly lower cost. Typical OPVs are based on the creation of bulk heterojunctions consisting of blends of an electron-donating semiconducting polymer and an electron-accepting molecule such as fullerene (C60) or its derivative . Improvement in OPVs can be brought about by addressing some of its limitations, namely, improving absorption of a wide range of radiation of the solar spectrum, and enhancing the electron and hole mobilities. We demonstrate for the first time the efficiency improvement of poly(3-hexylthiophene) (P3HT)-fullerene (C60) bulk heterojunction photovoltaic cells by the introduction functionalized nanodaimionds (ND) into the photoactive layer. A novel covalently bonded C60-ND composite was synthesized via a microwave induced functionalization approach. As compared to control devices with only C60, the addition of ND resulted in 71% improvement in short circuit current density Jsc. Such a device design takes advantages of both C60 for electron accepting and ND for efficient electron transport. The results indicate that C60 decorated NDs are promising additives for the performance enhancement of polymer photovoltaic cells.

PLASMA PROTEIN BINDING TO QUANTUM DOTS VARIES DEPENDING ON THEIR SURFACE PROPERTIES

Candice Lavelle, University of Florida

Kevin Kroll, University of Florida

Nancy Denslow, University of Florida

The interaction of nanomaterials with biological systems depends on several factors including their surface characteristics (zeta potential, surface functional groups) and characteristics of the biological system. Using quantum dots (QDs) or near-infrared linked silica nanomaterials modified by different functional groups including carboxy, amino-PEG and PEG, we investigated whether the particles could be internalized through the gut by fathead minnows (Pimephales promelas) following gavage. Most of the QDs passed through the gut and were detectable in the feces 12 h post gavage. The distribution of QDs in blood and internal organs was somewhat different for males and females. We could find QDs in various organs with this order of distribution for males: gut > blood > kidney > liver > spleen > testis and for females: gut > kidney > liver = spleen > ovary. The hydrodynamic radius of the amino PEG QDs increases dramatically in the presence of male plasma that had been treated with ethinylestradiol suggesting that proteins present in this plasma, such as vitellogenin, may bind specifically to amino-Peg QDs. This suggests that nanoparticle protein corona in blood may differ depending on the composition of the blood and the surface characteristics of the nanomaterials.

FATE AND BEHAVIOUR OF NANOPARTICLES IN THE AQUATIC AND TERRESTRIAL ENVIRONMENT

J. R. LEAD, University of South Carolina/ University of Birmingham, UK

Nanoparticles are produced in large and increasing amounts for a range of commercial processes and consumer products, which are almost certainly discharged to the environment, particularly aquatic and terrestrial compartments. Once in the environment, they will undergo microbial, chemical and physical changes such as oxidation, sulfidation, aggregation and dissolution. The timescales and final products of the transformations are considered. These processes will affect NP transport in the various compartments and ultimately their environmental concentration and exposure to environmental biota. The ultimate environmental sinks of NPs will most likely be through diagentic processes leading to burial in deep sediments, dissolution for some NPs and microbial effects. This talk will consider a selection of these transformation and transport processes.

PROBING THE DIFFUSION OF COLLOIDAL NANOPARTICLES TO REVEAL INTERACTIONS WITH COMPLEX ENVIRONMENTS

STEPHAN LINK, Rice University

To exploit colloidal nanoparticles for sustainable energy applications it is important to understand how nanoparticles interact with their solution-phase environment. We have therefore developed correlation spectroscopy approaches based on luminescence and scattering. This in situ characterization approach has the advantage that binding events and aggregation can be monitored in real time without the need to isolate the nanoparticles. However, the difficulty of correlation spectroscopy as applied to nanoparticles lies in the fact that the retrieved hydrodynamic radius is biased towards the brightest and hence largest species. This is an issue because chemically synthesized nanoparticles always show a size distribution and often aggregate. We have overcome this problem by analyzing the frequency and intensity of single transient events and applied this technique to two important systems. 1) We have determined the diffusion of dye-labeled magnetite nanoparticles moving in the presence of an applied magnetic field. Magnetite nanoparticles have been found to be very effective in the energy efficient treatment of water that is contaminated by arsenic. 2) Using the intrinsic scattering and luminescence of plasmonic nanoparticles, we have shown that, depending on the surface chemistry, interactions of Au nanoparticles with a blood serum protein lead to the formation a protein monolayer.

MAKING USE OF THE EDUCATIONAL POTENTIAL OF NANOSCALE ENERGY PRODUCTION AND CONSERVATION

GEORGE LISENSKY, Beloit College

Meeting energy needs in a sustainable manner is a major societal challenge and potential solutions are likely to involve nanomaterials. Education that includes new modes of energy production and efficiency and associated ethical, social and policy issues can be useful for attracting and retaining students, developing a scientifically literate population and workforce, and illustrating the process of science. Talking about the science of high-tech devices stimulates interest. It is also vital for students to see that not everything has already been discovered and that they could contribute to solving important issues. Relevant energy production and conservation demonstrations and laboratory experiments involving semiconductor materials (photovoltaics and Gr?tzel cells, solid state lighting, thermoelectricity, piezoelectricity, and photoelectrochemical cells), energy storage (batteries and supercapacitors), and fuel cells (membranes and hydrogen storage) are being developed, refined and class tested at institutions working with the Materials Research Science and Engineering Center on Nanostructured Interfaces at the University of Wisconsin-Madison (http://mrsec.wisc.edu/nano).

ASIA'S EFFORTS TOWARDS SUSTAINABLE DEVELOPMENT OF NANOTECHNOLOGY

LERWEN LIU, NanoGlobe Pte Ltd

Asian government, scientists, engineers and industrialists have been working aggressively in nanotechnology research and development and commercialization in the last over 10 years. As for today, world class R&D infrastructures are available not only for domestic R&D but also for international collaborations in nanotechnology. Asian countries are actively engaging international partners and building open R&D platforms to accelerate the global development and adoption of nanotechnology in various industries including electronics, chemicals, automotive, energy and others. Asia is becoming the magnets for nanotechnology manufacturing hubs. Recognizing the enormous benefits nanotech is able to contribute to greener manufacturing (use less for more), Asia countries are addressing systematically the Nanosafety issue. Asian countries have been dedicating strong efforts towards education and outreach. In this presentation, Dr Lerwen Liu will cover the following topics to highlight Asia's efforts towards sustainable development of Nanotech:

- ✓ Nanotechnology National Initiatives and Government Investment
- ✓ Benefits of Nanotechnology Recognized by Asians
- ✓ Superior Properties of Nano Carbon Materials and Technologies
- ✓ Asia is Leading the Adoption of Nano Carbon Materials and Technologies with Strong and Progressive Government Support
- ✓ Smart and Responsible Development of Nanotechnology
- ✓ NanoSafety – Case Study: Asia Nano Forum Led by Australia
- ✓ Standardization – Case Study: Nano Carbon Related
- ✓ Education and Outreach – Case Study: Iran

SIMPLE BENCHTOP REACTOR SYSTEM FOR THE HIGH-THROUGHPUT SYNTHESIS OF FUNCTIONALIZE GOLD NANOPARTICLES AND NANORODS

SAMUEL E. LOHSE, University of Illinois Urbana-Champaign

Jonathan Eller, University of Illinois Urbana-Champaign

Catherine J. Murphy, University of Illinois Urbana-Champaign

The controlled synthesis of even the most rudimentary nanomaterials above the milligram scale continuous to be a significant challenge. The synthesis of functionalized nanomaterials in flow reactors provides a viable approach to circumvent some of the shortcomings of traditional batch nanomaterial syntheses, providing improved control over product properties, superior mixing, thermal transport, and a viable high-throughput synthetic approach. Here we demonstrate the construction and operation of a simple capillary flow reactor assembled entirely from commercially available components. This capillary flow reactor facilitates the high-throughput synthesis of a variety of functionalized gold nanoparticles (AuNPs), including the synthesis of gold nanospheres with tightly controlled core diameters and gold nanorods (AuNRs)with controlled aspect ratios between 1.5 and 4.0. We show that within the flow reactor, the absolute dimensions, as well as the aspect ratio of the gold nanorods can be precisely controlled. The high-throughput synthesis approach facilitated by the flow reactor also facilitates the rapid synthesis of monodisperse AuNRs above the gram scale. Furthermore, we show that the reactor can be adapted to enable high-throughput surface functionalization of gold nanorods and concomitant monitoring of AuNP product growth in real time.

NUMERICAL ELECTROKINETIC METHOD TO DETERMINE SURFACE COATING THICKNESS ON NANOPARTICLES IMPROVES PREDICTION OF TRANSPORT BEHAVIOR

STACEY M. LOUIE, Carnegie Mellon University, Department of Civil and Environmental Engineering

Tanapon Phenrat, Naresuan University, Department of Civil Engineering

Gregory V. Lowry, Carnegie Mellon University, Department of Civil and Environmental Engineering

Charged macromolecular coatings such as polymers or natural organic matter can significantly change nanoparticle behavior in the environment by imparting electrosteric effects. Measurement of the coating thickness on nanoparticles is desirable to predict or explain steric forces. However, resolving nanoscale thicknesses of polymeric coatings on polydisperse nanoparticles is difficult using typical sizing methods such as dynamic light scattering or flow field-flow fractionation.We investigate the application of a soft particle electrokinetic model to determine layer properties (thickness, charge density, and permeability) from electrophoretic mobility measurements. This method should be less sensitive to particle polydispersity than other methods. Using statistical analyses, we find that analytical or numerical soft particle models have the least uncertainty in fitted layer thickness for thin layers with low charge, suggesting that it can be useful where other methods cannot resolve thin coating thicknesses on polydisperse nanoparticles. However, confidence in layer thickness estimates of thick, moderately charged coatings is poor. The numerical model is more sensitive and accurate than the analytical model for highly charged coatings because it includes charge polarization whereas the analytical model does not. These more accurate estimates improve predictions of transport behavior. Experimental model validation is also performed to assess the models’ accuracy.

SULFIDATION OF ZINC OXIDE NANOPARTICLES AND THE EFFECT ON RELEASE OF OF Zn ION

Rui Ma, Carnegie Mellon University

Clément Levard, Department of Geological & Environmental Sciences, Stanford University

Gregory V. Lowry, Department of Civil & Environmental Engineering, Carnegie Mellon University

Environmental transformations of nanoparticles (NPs) affect their properties and toxicity potential. Sulfidation is an important transformation affecting the fate of NPs made from class B soft metal cations. Here, the extent and mechansim of sulfidation of ZnO NPs were investigated, and the properties of resulting products were carefully characterized. Synchrotron X-ray absorption spectroscopy and X-ray diffraction analysis reveal that transformation of ZnO to ZnS occurs readily at ambient temperature in the presence of inorganic sulfide. The extent of sulfidation depends on sulfide concentration and close to 100% conversion can be obtained in 5 days given sufficient addition of sulfide. X-ray diffraction and transmission electronic microscopy showed formation of ZnS NPs smaller than 5 nm. Sulfidation of ZnO NPs occurs by dissolution and re-precipitation and is different from that of Ag NPs. The solubility of sulfidized particles was lower than that of the pristine ZnO NPs. Solubility of partially sulfidized materials is controlled by remaining ZnO core and not quenched by ZnS shell formed. Sulfidation also led to aggregation and a decrease of surface charge. These suggest that sulfidation of ZnO NPs will alter behaviors, fate and toxicity of ZnO NPs.

SOFT LAW AND NANOTECHNOLOGY: A FUNCTIONAL PERSPECTIVE

TIMOTHY F. MALLOY, UCLA School of Law

Whether and how to regulate nanotechnology is debated widely. While ad hoc bits of regulation shuffle forward, a comprehensive response eludes us. Some advocate using new governance approaches, seeking to transform regulation from an agency-centric exercise to a collaborative undertaking by actors from multiple segments of society. One central aspect of this new governance is reliance upon “soft law” approaches to regulation. In the area of nanotechnology particularly, numerous commentators have proposed a variety of soft law mechanisms. Yet the concept of soft law is fuzzy in terms of its definition, specific functions and optimal uses. This paper addresses that fuzziness in two ways. First, it provides a definition of soft law informed by the four functions soft law serves: the precursive, normative, directive and complementary functions. Second, it comments upon the usefulness of soft law with respect to each of those functions in the specific context of nanotechnology.

EFFECTS OF NANOPARTICLES ON SYMBIOTIC RELATIONSHIP OF THE COMMON BEAN

Michael Mashock, Marquette University

Krassimira Hristova, Marquette University

Nanomaterials are increasingly incorporated into consumer products which have led to unintentional release into the environment. A common sink for released nanoparticles (NPs) are bacteria rich agricultural fields and thus the ideal model system to study environmental impact of nanomaterials. The main objective of this study is to determine the effects of metal oxide NPs on the relationship of a symbiotic system of *Rhizobium etli* and *Phaseolus vulgaris*. Bacterium, *Rhizobium etli*, induces formation of root nodules of the common bean, *P. vulgaris*, which fix nitrogen for optimal growth and fruit production. Exposing *R. etli* to micro-molar concentrations of ZnO NPs resulted in decreased viability, metabolic activity, and nodule formation. Treating *P. vulgaris* with ZnO NPs resulted in reduced root production and decreased chlorophyll content. We were able to observe significant differences with treatment using ZnO of different NPs diameter and crystal structure. In addition to dissolution of the zinc ions, nanoparticle physical and chemical characteristics contributed significantly in NP toxicity.

Based on these data we propose that the introduction of NPs into the environment significantly affects the function of ecosystems relying on symbiotic relationships.

MOBILITY OF NANOMATERIALS IN THE ENVIRONMENT DURING THEIR LIFE CYCLE

ARMAND MASION, CNRS-CEREGE

Jerome Rose, CNRS-CEREGE

Commercial nanomaterials usually consist of a "core" nano-structure of interest imbedded in a more of less complex matrix. The environmental fate and transport of these materials is then of course different from the pristine nanoparticles they contain. The properties of these materials are very likely to evolve during their regular use, their surface chemistry changing with time. This results at times in very contrasted transport behaviors. A meaningful risk assessment must then be based on an LCA. Ti and Ce based UV filters are used as examples to illustrate how aging influences on the reactivity and mobility of the nanomaterials.

BRIDGING THE GAP BETWEEN THE NANOTECHNOLOGY CONSUMER PRODUCTS INVENTORY AND LIFE CYCLE ASSESSMENT (LCA)

SEAN McGINNIS, Virginia Tech

Matt Hull, Virginia Tech

Todd Kuiken, Woodrow Wilson International Center for Scholars

Many benefits, issues, and constraints for applying Life Cycle Assessment (LCA) to nanotechnology were identified in the 2006 Nanotechnology and Life Cycle Assessment Workshop and summary publication, Nanotechnology and Life Cycle Assessment: A Systems Approach to Nanotechnology and the Environment.The Virginia Tech Center for Sustainable Nanotechnology (VT SuN) and the Project on Emerging Nanotechnology (PEN) are collaborating to address these issues. Three specific activities are underway which will bridge some of the gaps that exist between the current Nanotechnology Consumer Products Inventory (NCPI) and the widespread application of LCA to these products. First, specific NCPI product data is under critical review to better characterize the compositions, dimensions, and concentrations of the constituent nanomaterials. Additionally, ranking schemes are being developed to help stakeholders understand the uncertainties in the nanomaterials' inventory. Second, lab-scale nanomaterial manufacturing processes are being inventoried to provide case studies and process inventory data to share with the LCA and nanotechnology community. Third, the transport, fate, and environmental effects for specific nanomaterials are being studied to improve impact assessment methods. This talk will provide an overview of this research and offer suggestions to this research community for research methodologies and networks to more quickly close these important gaps.

THE INTERACTION OF SILVER AND CERIUM OXIDE NANOPARTICLES WITH ALGAE, DAPHNIA AND SOFT WATER OECD MEDIA AND FULVIC ACID

R. C. MERRIFIELD, University of Birmingham, UK

I. Romer, University of Birmingham, UK

Z. Wang, University of Birmingham, UK

The environmentally relevant behaviour of citrate stabilized silver nanoparticles (AgNP) and two PVP stabilized cerium oxide nanoparticles (Ce(III) and Ce(IV) oxide are reported). Nanoparticle suspensions were diluted into a standard soft water (SW) and soft water with added Suwannee River fulvic acid (SWF). The morphology and chemical composition of the nanoparticles were examined using scanning transmission electron microscopy (STEM) along with electron energy loss spectroscopy (EELs), both with angstrom spatial resolution.The AgNP in SW aggregated and changed shape but no silver oxide layers on AgNPs were observed, while the oxidation state of the ceria NPs altered from originally being predominantly either in the Ce(III) or Ce(IV) oxidation state to being a mixture of both oxidation states, with substantial inter- and intra-particle variability. In SWF, all suspensions were more colloidally stable. Again nosilver oxide layers were observed on the AgNPs. The Ce(IV) appeared to have fewer defects in the structure when compared to the original stock solutions and the oxidation state remained clearly Ce(IV) oxide. In contrast the Ce(III) NPs formed aggregates under STEM observation which were morphologically quite distinct from the particles both as prepared and in SW. The original Ce(III) NPs were converted to a mixed oxidation state.

TYING DISTINCT NANOPARTICLE PROPERTIES TO INTRACELLULAR FATE AND RESPONSE IN ALVEOLAR EPITHELIAL CELLS

COSMIN MIHAI, Pacific Northwest National Laboratory

Dehong Hu, Pacific Northwest National Laboratory

Galya Orr, Pacific Northwest National Laboratory

The physical and chemical properties of engineered nanoparticles (NPs) engage and activate distinct proteins and cellular pathways that, in turn, govern the fate of the NP and its impact on the cell and ultimately on human health. The relationships between particle properties and these complex cellular processes and response are still unclear. Airborne NPs that enter the respiratory tract are likely to be deposited in the alveolar region. To mimic inhaled NP exposure in vivo, we study alveolar cells grown and exposed to aerosolized NPs at the air-liquid interface (ALI). Focusing on ZnO NPs we show fundamental differences in the level and destination of intracellular Zn ions and oxidative stress dynamics between cells exposed at the ALI and cells exposed in submersed cultures. Using super resolution stochastic optical reconstruction microscopy (STORM) we also study the internalization pathways and intracellular fate of amorphous silica NPs – one NP at a time - with 10-20 nanometer resolution. We show that a significant number of particles are found within caveolin- but not clathrin-coated vesicles, indicating a preferential attachment of the NPs to caveolae at the cell surface. A significant number of particles are also found aligned along actin filaments with about 100 nm

proximity, suggesting that the vesicles and their NP cargo are shuttled within the cytoplasm along actin filaments. This work is funded by NIEHS grant 1RC2ES018786-01 (to GO).

ADHERENCE OF SILVER NANOPARTICLES TO CERAMIC WATER FILTERS: THE VALUE OF RAMAN SPECTROSCOPY

ANNE MIKELONIS, University of Texas at Austin

Desmond Lawler, University of Texas at Austin

Bin Chen, LC Tech

Silver nanoparticles (AgNPs) are added as an in situ disinfectant in porous ceramic pot filters used for household drinking water treatment in developing countries and could possibly be introduced into ceramic membranes in the developed world. Unfortunately, the lifespan of these amendments is not well understood. One factor likely to contribute to the disinfection lifespan is the different techniques for manufacturing AgNPs; different stabilizing agents impart varied chemical species and conformations on the particle surface. The goal of this research is to determine how capping agents affect the adherence to and release from ceramic surface. Sample filter disks were produced through dry pressing an Illite clay with sawdust and firing. The disks are coated with AgNPs by different combinations of dip coating, annealing, and saline coupling agents. Raman spectroscopy, a nondestructive technique, was used to monitor the integrity of the silver films over time during water filtration tests. The value and limitations of using Raman will be discussed for silver nanoparticles synthesized with carbon, citrate, and PVP capping agents, and Raman data is complemented with SEM images and bulk silver measurements. The welfare of societies depends upon safe water; better AgNP attachment is important for sustainability.

VERIFICATION OF THE DISCMINI PERSONAL MONITOR FOR EXPOSURE TO NANOPARTICLES IN THE WORKPLACE

JESSICA MILLS, University of Iowa

Jae Hong Park, University of Iowa

Thomas Peters, University of Iowa

We evaluated the robust, lightweight DiSCmini (DM) aerosol monitor for measuring nanoparticle exposures in the workplace. Tests were conducted with monodispersed and polydispersed aerosols composed of sodium chloride and spark-generated metal particles at three steady-state concentration ranges (Low, <103; Medium, 103-104; and High, >104 particles/cm3). Particle number concentration, lung deposited surface area (LDSA) concentration, and mean size measured with the DM were compared to those measured with reference instruments, a scanning mobility particle sizer (SMPS) and a handheld condensation particle counter (CPC). Particle number concentrations measured with the DM were within 21% of those measured by reference instruments for polydispersed particles. Poorer agreement was observed for monodispersed particle tests (±35% for most tests and +200% for 300-nm

NaCl particles). LDSA concentrations measured by the DM were 96% to 155% of those estimated with the SMPS. The geometric mean diameters measured with the DM were ±30% of those measured with the SMPS for monodispersed aerosols and ±25% for polydispersed aerosols, except for one aerosol with substantial concentrations of particles larger than 300 nm. The accuracy of the DM is reasonable for particles smaller than 300 nm but caution should be exercised when particles larger than 300 nm are present.

APPLICATIONS OF SP-ICP-MS: ASSESSING PARTICLE STABILITY IN THE ENVIRONMENT

Denise Mitrano, Colorado School of Mines

Manuel Montano, Colorado School of Mines

James Ranville, Colorado School of Mines

Assessing the environmental fate and effects of engineered nanoparticles (ENPs) relies in part on methods for their detection and quantification. For many inorganic-based ENPs, single particle inductively coupled plasma-mass spectrometry (spICPMS) has recently been shown to be a promising approach. ICPMS provides the low detection limits (ng/L) needed for environmental studies of ENP behavior. Furthermore, the elemental specificity of ICPMS provides a means to detect and quantify ENPs in the presence of interfering particles. Although much of the reported work remains focused on method development, spICPMS applications to environmental systems is growing, and are the subject of this presentation. In dissolution studies of various metal-containing nanoparticles, performed in several natural waters, spICPMS was able to quantify an increase in dissolved metal and the reduction in ENP size. The effects of both surface coating were examined. Future work will no doubt continue to improve this technique and allow further exploration of processes affecting the life cycle of ENPs.

THE EFFECT OF NANOPARTICLE SIZE, SHAPE, COATING AND COMPOSITION ON SKIN TOXICITY

NANCY A. MONTEIRO-RIVIERE, Kansas State University

Alfred O. Inman, Kansas State University

Nanomaterial exposure to skin is a continuing concern after occupational, environmental and consumer product exposure. This study assessed the toxicity of nanoparticle size, shape, coating and composition of ten nanoparticles on human epidermal keratinocytes (HEK) exposed for 24h. Uptake of carboxylated quantum dot 655 (QD) (18nm) into dendritic cells was studied to further assess cutaneous immune response. Nanoparticles studied were dextran-coated SPION 1 (10nm) and SPION 2 (10nm), uncoated SPION (11nm), vitamin C (VC) (5nm) and gluconic acid (6nm) functionalized Fe_3O_4, SiO_2-coated Fe_2O_3 (60nm), VC reduced graphene oxide (2µm), and hollow carbon sphere (176nm), citrate BioPureTMAg (19nm) and silica-coated Ag (40nm). Size was characterized by dynamic light scattering and transmission electron microscopy (TEM). There were numerous particle-dependent changes in viability and inflammatory biomarkers, many of them artifactual at high concentrations. TEM depicted uptake of all NP within HEK cytoplasmic vacuoles. Dendritic cells showed a significant increase in QD uptake compared to HEK. These studies clearly suggest that multiple types of nanoparticles can be taken into and interact with two important cell types which could modulate both skin function and the immune response. Methods used to assess toxicity must be carefully validated for each nanoparticle.

SYNTHESIS AND CHARACTERIZATION OF ZnO AND SiO_2 COATED ZnO NANOPARTICLES FOR BIOLOGICAL APPLICATIONS

Kimberly Marie Murdaugh, Harvard School of Public Health

Joseph D. Brain, Harvard School of Engineering and Applied Sciences

Philip Demokritou, Harvard School of Public Health

ZnO nanoparticles have emerged as a useful vehicle to study biointeractions as they have fluorescence properties that allow real-time tracking with confocal microscopy. However, they are highly soluble in aqueous solutions and the released ions have significant toxic implications. We present a method of using the recently developed, flame spray pyrolysis based, Harvard Versatile Engineered Nanomaterial Generation System (VENGES) to generate ZnO nanoparticles. VENGES platform s was used to synthesize ZnO nanoparticles of various particle sizes, with and without a hermetic coating of amorphous silica (SiO_2).To confirm that ZnO particles were successfully coated with a nanothin layer of SiO_2, highly surface sensitive X-Ray Photoelectron Spectroscopy (XPS) was used. The crystal size was determined by X-ray diffraction, and the nanoparticles were imaged with TEM. In addition, ZnO and ZnO/SiO_2 nanoparticles were dispersed and characterized in DI H_2O and Survanta dispersions. Dynamic light scattering was performed to characterize the hydrodynamic diameter and zeta potential of the solutions. The effect of the SiO2 coating on the UV absorption and fluorescence was also examined. XPS data indicate that the ZnO particles are hermetically coated with SiO_2. XRD analysis indicates that the particles range from approximately 18 nm to 30 nm. Additionally, preliminary evidence suggests that the ZnO and ZnO/SiO_2 nanoparticles have the same absorbance and fluorescence properties; this result is a promising indication that the SiO_2 coatings doesn’t interfere with functional properties of core nanoparticles. Given the fact that amorphous SiO2 is considered a biologically inert material, this concept can also be used to reduce the toxicological effects of ZnO nanoparticles for a wide range of applications. Future animal instillation studies s will be performed to examine the pharmacokinetics and toxicity of the ZnO and ZnO/SiO_2 nanoparticles.

OPPORTUNITIES AND CHALLENGES TOWARD EDUCATION AT THE NANOSCALE

JAMES MURDAY, University of Southern California

The rapid progress in nanoscale science and engineering, paralleled by nano-enabled technologies in the commercial market, is accompanied by both opportunities and challenges to education at all age levels. The ongoing development of the U.S. common core “K-12 Next Generation Science” standards, and the subsequent curricula/teaching aides/teacher training, provides a timely opportunity. At the community college / technical college level there is the challenge to prepare a skilled manufacturing workforce and prepping for four year degrees. Colleges / universities at the bachelors/masters level must not only provide scientists/engineers, but also the business and political leaders who can enable the market entry of nano-enabled technologies. The continued discovery of new nanoscale properties and phenomena depends on PhD level efforts at research Universities. The rate of science and engineering progress (with the nanoscale as a prime example), coupled with longer life spans, compels a need for continuing education. Finally, the acceptance of new, nano-enabled technologies will depend on an informed populace, largely dependent on informal education opportunities. Four recent NSF funded workshops have explored these topics; this presentation will highlight the conclusions and recommendations toward our education goals.

MICROWAVE ASSISTED SYNTHESIS OF GERMANIUM NANOPARTICLES FOR PHOTOVOLTAIC APPLICATIONS

ELAYARAJA MUTHUSWAMY, University of California Davis

Carena P. Church, University of California Santa Cruz

Susan M. Kauzlarich, University of California Davis

Microwave assisted synthesis has gained popularity over the last decade for the preparation of a variety of inorganic nanocrystals primarily due to its clean and energy efficient nature. Our group focuses on the preparation of Group IV semiconducting nanoparticles (Ge, Si) targeting applications in the field of photovoltaics and bio-imaging. In this particular work, we have developed a simple approach for the preparation of crystalline Ge nanoparticles with control on size by microwave assisted heating. Germanium iodides were the precursors and oleylamine was utilized as the reducing agent, binding ligand and solvent in the synthesis. Size control was achieved by primarily controlling the ratio between the Ge iodide precursors (GeI4/GeI2). Heating time, temperature and precursor concentration were also observed to have a limited effect on the size. For comparison, the reduction reactions were also carried out by conventional heating under identical conditions to the microwave synthesis. PXRD measurements indicate that crystalline nanoparticles are obtained at lower temperatures by the microwave route. Currently, efforts are underway to evaluate the photovoltaic properties of the Ge nanoparticles as a function of their size and also to create doped-Ge nanoparticles.

CHANGES IN SILVER NANOPARTICLES EXPOSED TO HUMAN SYNTHETIC STOMACH FLUID: EFFECTS OF PARTICLE SIZE AND SURFACE CHEMISTRY

Samuel Mwilu, EPA

Kim Rogers, EPA

Due to the recent spike in applications utilizing the antibacterial properties of silver nanoparticles (AgNPs), the possibility of human exposure through ingestion has become an increasing concern. The transformation and bioavailability of ingested AgNPs will depend, in part, on the initial particle size and the surface chemistry, properties that will influence their physical and chemical reactivity during transit along the gastrointestinal tract. In this study we investigated the interactions between human synthetic stomach fluid (SSF) and AgNPs of different sizes and with different capping agents. Changes in morphology, size and chemical composition were determined during a 30 min exposure to SSF using Absorbance Spectroscopy, High Resolution Transmission Electron and Scanning Electron Microscopes (TEM/SEM), Dynamic Light Scattering (DLS), and Nanoparticle Tracking Analysis (NTA). AgNPs exposed to SSF were found to aggregate significantly and also released ionic silver which physically associated with the particle aggregates as silver chloride. Generally, the smaller sized AgNPs (< 10 nm) showed higher rates of aggregation and physical transformation than larger particles (75 nm). Polyvinylpyrrolidone (pvp)-stabilized AgNPs prepared in house behaved differently in SSF than particles obtained from a commercial source despite having similar surface coating and size distribution characteristics. These results suggest that size and surface chemistry may play an important role in the transformation of AgNPs in the GI tract.

OIL-WATER SEPARATION BY WRAP-AND-PULL USING SUPERPARAMAGNETIC CARBON NANOTUBES

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Haitao Wang, University of Notre Dame

Kun-Yi Lin, University of Notre Dame

Water contaminated by oil and gas productions poses challenges to the management of America's water resources. We report the design, fabrication, and laboratory evaluation of multi-walled carbon nanotubes decorated with superparamagnetic iron-oxide nanoparticles for oil-water separation. As revealed by confocal fluorescence microscopy, superparamagnetic carbon nanotubes (SCNTs) remove oil droplets through wrap-and-pull, in which SCNTs first disperse at the oil-water interface and then drag oil droplets out of water under an external magnetic field. Measurements of removal efficiency show that wrap-and-pull obeys the kinetics and equilibrium described by the Langmuir model. The separation capacity is a function of the SCNT dose, mixing time, the emulsion volume, and the equilibrium oil concentration. Regressions using experimental data estimate a maximum separation capacity of 1.47(+/-0.05) g-diesel per g-SCNT, a wrapping rate constant of 2.5(+/-0.9) L per g-diesel per min, and a wrap-and-pull equilibrium constant of 3.2(+/-0.1) L per g-diesel. For used MCNTs, we further show that over 80% of the capacity can be restored by a quick ethanol wash. Wrap-and-pull using reusable MCNTs provides an alternative strategy for water treatment in addition to existing ones represented by coagulation, adsorption, filtration, and membrane processes.

NIEHS NANOTECHNOLOGY ENVIRONMENTAL HEALTH AND SAFETY RESEARCH PROGRAM

SRI NADADUR, NIEHS

The increased use of nanoscale materials in diverse industry starting from cosmetics, therapeutics, and electronics to environmental remedy presents opportunities for intentional and accidental exposures to engineered nanomaterials (ENMs) with unknown health consequences. The novel nanomaterial-biological interactions observed in initial toxicology studies led to a clear recognition that gaining a fundamental knowledge of the specific physical or chemical properties of ENMs that dictate interaction

with biological systems is critical. The ease with which thousands of variants of ENMs can be generated with diverse physical and chemical properties necessitate the need for multidisciplinary collaborative approaches to gain comprehensive understanding. Towards this, the NIEHS has initiated consortia-based multidisciplinary teams of investigators work together towards a common goal- how diverse physical and chemical properties of ENMs dictate their biological interactions. These coordinated efforts aims to integrate data from in vitro and in vivo studies to develop computational predictive modeling to elucidate biological response. Current efforts of the consortia are generating data across multiple laboratories using relevant in vitro and in vivo model systems, systems biology approaches and toxicokinetics modeling. Results generated across these common efforts will feed into predictive models for assessing health effects associated with ENMs physical and chemical properties. This presentation will review current understanding and identify critical research gaps and needs to strategically address Nanotechnology Environmental Health and Safety research.

FATE OF FULLERENE NANOPARTICLES (NC60) IN THE ENVIRONMENT: POTENTIAL RELEASE OF FULLERENES FROM BIOSOLIDS

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Rai Kookana, CSIRO Land and Water

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In the recent years, the fate of nanoparticles (NPs) in wastewater treatment plants has been of increasing interest. Indeed, among different stages involved in wastewater treatment, NPs have often been reported to be present in sludge materials. Application of biosolids (treated sludge) as soil amendments/fertilizers, hence, presents another important route for NPs to be remobilized and enter the environment. This study examines the release of fullerenes (C60) from biosolids spiked with different forms of fullerene NPs (nC60) across a wide range of Australian soils. Results showed that different levels of C60 could be released from different biosolid-soil systems, suggesting that soil properties influence C60 mobilization. The form of nC60 used, on the other hand, had negligible effect on the levels of C60 released. Aging nC60 in these systems only slightly increased C60 release; after 8w of aging, majority of the biosolid-soil systems only released approximately 3% of the initial nC60 spike. The application of biosolids to soil favored the retention of C60 rather than release. Though the exact release mechanism in these systems is still unclear, it is apparent that both pH and natural organic matter played a part in controlling the binding and release behavior of fullerenes in soils.

SAFE IMPLEMENTATION OF NANOTECHNOLOGY TOWARDS A SUSTAINABLE FUTURE

Andre Nel, UCLA

In order to live and be sustained on Earth, every human being needs adequate food, water, energy, shelter, clothing, healthcare, and employment. Not only do we need the resources and successful economic development to achieve these goals, but also need to do so by limiting the impact of human activities on Earth’s ecosystems and the global environment. Nanotechnology holds great promise for sustainable development and has emerged as an important platform technology to address global sustainability challenges such as food, water and energy supplies, habitat, transportation, mineral resources, green manufacturing, clean environment, climate change, and biodiversity. I will illustrate a few of the key advances that have been made in the development of more efficient renewable energy generation and storage technologies, improved water treatment and desalination membranes, detection and monitoring systems for crop growth and safe food supply, more efficient environmental remediation technologies, monitoring of pollutants and CO_2 sequestration, as well as major advances in healthcare delivery. I will also comment about the key role of education in sustainable development of nanotechnology and the necessity to train an interdisciplinary workforce that includes scientists, engineers, entrepreneurs, policymakers, and regulators. Sustainable development of nanotechnology is also critically dependent on societal awareness and the development of practical communication, management and entrepreneurial skills. Although nanotechnology holds great promise for solving global sustainability challenges, there is growing awareness that some engineered nanomaterials could introduce novel environmental and health hazards. Thus, we have to make sure that any potential adverse effects on humans and the environment are effectively assessed and addressed as an integral component of the safe and sustainable implementation of nanotechnology. This requires fundamental knowledge generation about the interaction of nanoscale properties and nanoscale functions with a wide range of biological interfaces. Events at the nano/bio interface constitute a new science that requires new investigative approaches and a 21st-century philosophy that considers the rapid growth of nanotechnology and the necessity to develop rapid and high throughput decision-making tools that address potential safety problems in advance rather than relegating them to a post-hoc cleanup exercise. I will cover some of the interdisciplinary scientific developments and knowledge generation the UC CEIN and the UCLA Center for Nano Biology and Predictive Toxicology to illustrate the implementation of high throughput discovery approaches towards safe and sustainable development of nanotechnology.

NANOSCALE SILVER MEDIATED DNA DAMAGE UNDER CELL-FREE CONDITIONS

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Bryce J. Marquis, NIST

Shyam Nathan, Brigham and Womens Hospital

Silver nanoparticles (AgNPs) are widely used in commercial products due to their nominal antibacterial, antimicrobial and antifungal properties. The currently accepted paradigm is that AgNPs slowly release Ag^+ ions and the free Ag^+ ions are the species mainly responsible for the antibacterial and other toxicological effects from AgNPs. We have focused our studies on the fundamental interaction of AgNPs and Ag^+ ions with nuclear DNA. We utilized stable isotope-dilution gas chromatography/tandem mass spectrometry (GC/MS/MS) to quantitatively detect and measure AgNP and Ag^+ ion induced damage to DNA. Using calf-thymus DNA and AgNPs of different sizes (10, 20, 30, 60, 100 nm) in phosphate buffered solutions, we demonstrate for the first time, that AgNPs can induce the formation of oxidatively modified DNA lesions such as 2,4-diamino-5-formamidopyrimidine (FapyAde) and 2,6-diamino-4-

hydroxy-5-formamidopyrimidine (FapyGua). Both FapyAde and FapyGua are mutagenic lesions. In contrast, using $AgNO_3$ as a source of Ag^+ ions, we further show that Ag^+ ions generate 8-hydroxyguanine (8-OH-Gua), a well established biomarker of oxidative stress, without inducing significant accumulations of FapyAde and FapyGua. The induction of reactive oxygen species does not appear to mediate the formation of the lesions. Surprisingly, increasing NP diameter does increase the accumulation of lesions.

TITANIUM DIOXIDE NANOPARTICLE (TiO_2 NP) GENERATION OF DNA BASE DAMAGE UNDER CONTROLLED ILLUMINATION

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TiO_2 NPs are found in numerous commercial products. It is well known that photoactivated TiO_2 NPs can generate •OH in aerated aqueous solutions and O_2•? in non aqueous media. Hydroxyl radicals can interact with and damage various biological molecules, such as DNA, at diffusion limited rates resulting in the formation of oxidatively induced DNA damage. Many in vitro studies have shown, using the comet assay, that photoactivated TiO_2 NPs induce oxidative damage to DNA. Surprisingly, recent comet assay data show that non-photoactivated TiO_2 NPs (NPs kept in the dark) can also induce significant DNA damage. We utilized gas chromatography/tandem mass spectrometry to quantitatively characterize the levels and types of oxidatively generated lesions in DNA exposed to 25 nm TiO_2 NPs under controlled illumination conditions. We demonstrate that TiO_2 NPs incubated with DNA in the dark do not lead to the formation of lesions when tested over 24 h (1 to 100 µg/mL TiO_2). However, when samples are exposed to UVA illumination at 370 nm (energy dose of ? 10 kJ/m2 for 30 min), there is a significant (p values < 0.0001) formation of mutagenic lesions at 10 µg/mL TiO_2 NP. These preliminary findings suggest that commercial P25 TiO_2 NPs do not have an inherent capacity to oxidatively damage DNA bases in the absence of sufficient photoactivation.

USE OF SUSTAINABLE NANOTECHNOLOGY EXAMPLES IN THE COLLEGE CLASSROOM: A RICH EDUCATIONAL OPPORTUNITY

DEB NEWBERRY, Dakota County Technical College, Nano-Link Regional Center for Nanotechnology Education

Benefits and risks are both significant as nanoscale materials are applied and interact with the environment - whether intentional and unintentional. This interaction between nanoscience and the environment is an area rich in educational opportunities. This paper will discuss how 3 nano/environment examples are used in college level courses to discuss and teach technology, societal aspects, EHS, design of experiments, FMECA process, critical thinking and cost considerations of production, control and risk mitigation.

SUSTAINABLE CELLULOSE NANOMATERIALS STANDARDS DEVELOPMENT

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In the past several years, companies and organizations in the Americas, Asia and Europe have become increasingly interested in sustainable cellulose nanomaterials research and its commercialization. As some cellulose nanomaterials-based products near the commercialization stage, the necessity to developing international standards to harmonize research, remove international trade barriers and inform policy makers and regulators have become essential. Efforts to date in informing SDO's and coordinating opinions from various organizations with interest in cellulose nanomaterials have resulted in the completion of a Roadmap for the Development of International Standards for Nanocellulose. TAPPI will house the roadmap document and engage in the effort to coordinate nanocellulose international standards development with its volunteer force. This presentation will briefly discuss current activities in sustainable cellulose nanomaterials international standards development, the roadmap, the players and the significance of developing international standards in cellulose nanomaterials to a future bioeconomy.

ZINTL PHASE SOLUTION SYNTHESIS OF SILICON NANOPARTICLES FOR PHOTOVOLTAIC APPLICATIONS

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Bulk silicon, a non-toxic, environmentally benign material, is the most widely used material for photovoltaic (PV) devices. However, quantum dot materials are anticipated to become a significant contributor to PV related device development. Quantum confinement effects, which allow for control over a semiconductor's band gap, as well as increased efficiencies by multiple exciton generation (MEG) are promising advantages of PV devices made from nanoscale materials. We have developed a solution based synthesis using the Zintl phase sodium silicide, Na_4Si_4, to synthesize silicon nanoparticles that can be dispersed in both polar and non-polar solvents. Efforts are underway towards producing silicon nanoparticle thin films by means of spin coating for measuring PV properties. Furthermore, we are evaluating the Zintl phase $K_{12}Si_{17}$ as a new precursor for a potentially enhanced yield of silicon nanoparticles. In the future, we will synthesize and evaluate the properties of boron doped, phosphorus doped, as well as boron phosphorus co-doped silicon nanoparticles.

INVESTIGATING THE EFFECTS OF CARBON NANOTUBES ON STRUCTURE AND FUNCTION OF METHANOGENIC MICROBIAL COMMUNITIES

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In order to examine the impact of nanotubes on methanogenic communities, wastewater treatment digester sludge was used as the inoculum for anaerobic microcosms. We monitored gas formation for approximately eight months as an indicator of community function. Sodium 2-bromoethane sulfonate (BES) inhibits methanogenesis and was used as a toxicity reference (1.04 x 106 mg/kg). Treatments and concentrations (mg nanotube carbon/kg biomass (dry weight)) were as follows: SWNT-CO(NH2): 12,780 mg/kg, MWNT: 47,840 mg/kg, MWNT-COOH: 45,970 mg/kg, and SWNT-COOH from two different manufacturers (A): 15,240 mg/kg and 1,588 mg/kg and (B): 45,060 mg/kg and 44,680 mg/kg. SWNT-COOH (A) had residual nickel (Ni) and yttrium (Y), which were hypothesized to contribute to effects seen in previous experiments. A mixture of Ni and Y was prepared for a set of reference microcosms in order to assess the effect of these metals. Ni/Y-treated microcosms over time received approximately three -fold concentrations of Ni and Y as were measured in SWNT-COOH (A) and showed altered function. Microcosms treated with 15,240 mg/kg SWNT-COOH (A) and fed glucose/methanol/ethanol (GME) showed increased gas formation (6.6%) compared with untreated reference samples. Metals in aqueous phase and biosolids will be measured by ICP-MS. Community structure is being analyzed by PCR-DGGE.

CATALYTIC REDUCTION OF HEXAVALENT CHROMIUM USING FLEXIBLE NANOSTRUCTURED POLY(-AMIC) ACID

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O. A. Sadik, SUNY Binghamton

Conducting polymers can be tuned by manipulating the delocalized π electron system for chemical and electrocatalytic applications. We hereby describe the reduction of Cr(VI) to Cr(III) by flexible nanostructured conducting poly(-amic) acid (PAA). Sodium borohydride was used as a reducing agent to prepare different sizes (3-20 nm) of palladium nanoparticles (PdNPs). The effects of experimental parameters such as particle size, temperature, and concentration on the kinetics and efficiency of reduction process were investigated. Results show that in PAA solution, Cr(VI) was efficiently reduced by 85.9% within a concentration range of 1.0 x10-1 - 1.0 _ 102 mM. In the presence of PdNPs and heat (40 oC), the reduction efficiency increased to 96.6% and 99.9% respectively. The method was validated using both colorimetric and Electron Paramagnetic Resonance techniques, confirming the formation of Cr(III) as the product of catalytic reduction. Additional characterization conducted using transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) confirmed that there was no significant change in Pd particle size and distributions after dispersion in PAA whereas its phase and oxidation state remained unchanged. Electrochemical characterization showed the reversible and recyclable features of PAA thus confirming its dual role as catalyst stabilizer and reducing agent.

TUNABLE NANOSTRUCTURED MATERIALS FOR CATALYTIC REDUCTION OF HEXAVALENT CHROMIUM

Veronica Okello, SUNY Binghamton

Prof. O. A. Sadik, SUNY Binghamton

Nanoscale materials offer new possibilities for the development of novel remediation and environmental monitoring technologies. Different nanoscale materials have been exploited for preventing environmental degradation and pollutant transformation. However, the rapid self-aggregation of nanoparticles or their association with suspended solids or sediments where they could bioaccumulate supports the need for sustainable material to improve mobility, allows faster site cleanups and reduces remediation cost. The ideal sustainable material must be able to coordinate different functionalities and exhibit the potential for reusability. We hereby describe novel environmental applications of nanostructured poly (amic acid)-palladium (nPAA) materials. nPAA was used as both reductant and stabilizer during the in-situ chemical reduction of Chromium (VI) to Chromium (III). These materials can be tuned by manipulating the delocalized π- electron system. Results showed that Cr (VI) species were rapidly reduced within the concentration range of 1.0 - 10-1 x 102 mM with efficiency of 99.9% at 40ºC in water samples and 90% at 40oC in soil samples respectively. The reversible switching between oxidized and reduced forms of the nPAA by electrochemical doping/undoping provides a means for repetitive and reusable reduction of Cr(VI) in complex media.

IMPACT OF SURFACE FUNCTIONALIZATION ON BACTERIAL CYTOTOXICITY OF SINGLE-WALLED CARBON NANOTUBES

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Julie B. Zimmerman, Yale University Department of Chemical & Environmental Engineering

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The surface functionalization of single-walled carbon nanotubes (SWNTs) is being explored to achieve enhanced performance in the intended application. At the same time, several functionalized SWNTs (fSWNTs), compared to SWNTs, have been shown to exhibit decreased cytotoxicity. Therefore, this emerging class of SWNTs offers the potential for enhanced performance while simultaneously reducing their potential adverse human health and environmental impacts. Here, the percent cell viability loss of *Escherichia coli* K12 resulting from the interaction with nine fSWNTs is presented. The functional groups range in molecular size, chemical composition, and physicochemical properties. While physiochemical characteristics of the fSWNTs did not correlate, either singularly or in combination, with the observed trend in cell viability, results from light scattering techniques suggest that there is a correlation between percent cell viability loss and the fSWNT dispersed aggregate state. Specifically, when the aggregate size polydispersity and the aggregate compactness are taken together, it is observed that highly compact fSWNT aggregates with a narrowly distributed aggregate size range result in reduced cytotoxicity. The results presented here suggest that surface functionalization has an indirect effect on the bacterial cytotoxicity of SWNTs through the impact on aggregation state, both dispersity and morphology.

INFLUENCE OF THE AMOUNT AND TYPE OF SURFACE OXYGEN ON MULTI-WALLED CARBON NANOTUBE (MWNT) CYTOTOXICITY

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Lisa Pfefferle, Yale University Department of Chemical & Environmental Engineering

This study explores the impact of varying amounts of surface oxygen, the type of oxygen functional group (carbonyl carboxy versus hydroxy), and surface charge on MWNT cytotoxicity. In addition to standard material characterization, the dispersed sample aggregate size distribution and morphology is characterized by light scattering to elucidate the potential correlation between these properties and the observed trend in cytotoxicity. Two independent cytotoxicity assays are utilized to investigate multiple contributing factors to cytotoxicity including physical damage of the bacterial cell wall and chemical disruption of the cellular redox environment. Loss of cell membrane integrity is evaluated by exposing *Escherichia coli* K12 to a filtered deposit layer of each MWNT sample. After incubation with the deposited sample, the cells are enumerated using fluorescence microscopy to determine viable and non-viable cells. The oxidation potential of each sample is determined by monitoring the oxidation of glutathione (GSH), an abundant biomolecule in gram-negative bacteria that is essential to the maintenance of a healthy redox environment. It is hypothesized that surface oxygen will indirectly impact the loss of cell viability by influencing the dispersed aggregate state and that increased surface oxygen content will lead to increased oxidation potential.

GATE-TO-GATE LIFE CYCLE ASSESSMENT OF GOLD NANOPARTICLE SYNTHESIS PROCESS

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The rapid growth of promising nanotechologies has raised concerns over their environmental and health impacts. Most studies in the literature have focused on the acute toxicity of engineered nanomaterials. However, a quantitative estimation of the energy, environmental and socio-economic footprint of these emerging nanotechnologies is sorely lacking. Life cycle assessment (LCA), which provides a framework for quantifying the environmental footprint of a product, can be used to fill this lacuna. This is especially important in the context of noble metals (e.g., gold, silver, platinum), which are present in limited quantities and involve energy intensive extraction and synthesis processes. To date, most nano-based LCAs have been conducted for carbon nanotubes, titanium dioxide and silver nanoparticles. No comprehensive LCAs for gold nanoparticles (AuNPs) exist at present. Information on mass and energy balance for the processes for synthesizing AuNPs from bulk gold is especially missing. This information is crucial to accurately estimate the environmental impact of downstream AuNP-based products (e.g., nano-based detectors, nanomedicines, cosmetics etc.). To address this issue, we conducted a

laboratory-scale, gate-to-gate LCA of the AuNPs, using SimaPro to create the life cycle inventory (LCI) and for data analysis. We present some preliminary findings in this poster.

ATTACHMENT OF MODULARLY FUNCTIONALIZED TiO_2 NANOPARTICLES TO MODEL ENVIRONMENTAL SURFACES

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Attachment of engineered nanoparticles to soil particle surfaces is expected to influence their transport and fate in the environment and influence their bioavailability to organisms. Titanium dioxide nanoparticles (TiO_2 NPs) rank among the most widely used nanomaterials and have the potential to be released into the environment. The objective of this study was to determine the influence of solution chemistry on the deposition of engineered TiO_2 NPS to either humic acid-coated and metal oxide surfaces. To achieve this objective we synthesized TiO_2 NPs with mean diameters of 5.1 nm. Using a novel citric acid derivative, organic ligands were anchored to TiO_2 nanoparticles using azide-terminated polyethylene glycol molecules presenting different head groups to solution. TiO_2 NP attachment to model environmental surfaces (e.g., Fe_3O_4, Al_2O_3, humic acid) was studied as a function of solution chemistry using quartz crystal microbalance with dissipation monitoring (QCM-D) and optical waveguide lightmode spectroscopy (OWLS). Final adsorbed masses, attachment efficiencies, and water content (determined through parallel QCM-D and OWLS experiments) were determined. The rates and extents of attachment were strongly affected by solution pH and ionic strength consistent with electrostatics dominating interactions between the nanoparticles and the surfaces.

SYNERGISTIC EFFECTS BETWEEN SOLAR LIGHT-ACTIVATED NF-TiO_2 AND VARIOUS OXIDANTS FOR THE DESTRUCTION OF ATRAZINE AND AMITROLE IN WATER

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Lisa Guay, University of Arizona, Tucson

Concerns regarding pesticides have been reinforced by a 2012 article in Environmental Science and Technology [1] that linked the effects of certain pesticides on honeybees with effects responsible for severe honeybee population drops around the world. Thus, the destruction of pesticides that can persist for years in the environment is important. Advanced oxidation technologies, such as titanium dioxide photocatalysis, can provide a sustainable alternative for the degradation of pesticides in water. Recently engineered at the nanoscale, nitrogen- and fluorine-codoped titanium dioxide (NF-TiO_2) allows for activation by visible light, increasing utilization of solar light by the photocatalyst. Titanium dioxide photocatalysis used in a treatment facility as unit process could, with relative ease, be combined with the addition of chemical oxidants. Examples of oxidants of interest for water treatment include potassium peroxymonosulfate, (PMS as Oxone®), sodium persulfate, and hydrogen peroxide. Through thermal and/or light irradiation, these oxidants generate extremely reactive radicals. For example, sodium persulfate generates sulfate radicals, and hydrogen peroxide can generate hydroxyl radicals. Given enough time, both radicals will oxidize most organic matter to carbon dioxide, water, and minerals. This work examines the ability of NF-TiO_2 combined with these oxidants to synergistically destroy, under simulated solar light, two widely used pesticides: atrazine and amitrole. Studying these two pesticides allows us to also observe how their structures affect the destruction of these compounds by NF-TiO_2 illuminated by simulated solar light, in the presence of each of these oxidants.

GREEN PROCESS FOR THE REMOVAL OF HEAVY METALS FROM AQUEOUS SYSTEMS

Cory Perkins, Oklahoma State University

Allen Apblett, Oklahoma State University

Heavy metals have been used extensively throughout the history of man through a variety of different practices. More specifically, lead has been extensively used in applications ranging from plumbing, car batteries, and as a gasoline additive, among others. Unfortunately, the toxicity of lead has been well documented, affecting almost every organ in the body with the nervous system being the primary target. Typically lead poisoning results from the ingestion of lead through contaminated water and foodstuffs, allowing the toxin to be rapidly absorbed in the blood stream. There is a strong need for processes for heavy metal remediation of natural water and drinking water systems. Calcium tungstate has proven to be an attractive candidate for remediation of heavy metals due to its high selectivity and capacity for sorption of heavy metals. Equally beneficial is the ability for the sorbant to be separated and regenerated for reuse; with the isolation of the heavy metals allowing for proper disposal or reuse. For a more convenient reaction process, nanometric calcium tungstate can be supported on high surface area support pellets for more rapid uptake and recovery processes.

SUSTAINABLE OCCUPATIONAL HEALTH AND SAFETY FOR THE NANOTECHNOLOGY INDUSTRY

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Candace Tsai, University of Massachusetts at Lowell

Occupational health and safety is a critical aspect of sustainability for the nanotechnology industry. Unique exposures may result when raw nanomaterials are produced or handled and when objects that contain nanomaterials are manipulated in production of commercial products. Exposures in the workplace are often many times higher than those that occur via environmental release or that may be experienced by consumers of products that contain nanomaterials. Professionals trained in the field of industrial hygiene hold the responsibility to assess and mitigate exposures to nanomaterials in the workplace. This job is challenging due to limited health-based occupational exposure limits, exposure equipment that has been designed for more traditional exposures, and control methods that are generally untested for their effectiveness to control nanoparticle exposures. We will provide the general status of the state-of-the-art in the primary activities central to the practice of industrial hygiene (anticipation, recognition, evaluation, and control) in the context of workplaces where nanomaterials are present. The speakers in this session will then present their work relevant to this practice in categories of general industrial hygiene practice, exposure assessment, and control. These efforts will contribute to sustainability by mitigating unanticipated adverse health effects and diseases from nanomaterial exposures.

TOOLS AND APPROACHES FOR THE ASSESSMENT OF NANOMATERIAL-INDUCED OXIDATIVE DNA DAMAGE

Elijah J. Petersen, NIST

Bryant C. Nelson, NIST

Miral Dizdaroglu, NIST

In recent years, there has been substantial research interest in nanotechnology as a result of the unique or enhanced properties that many nano-scale particles exhibit. With the maturation of this field and a greater understanding of the properties of these particles, there is increasing interest in the use of nanoparticles in consumer products. While research on the properties of nanoparticles for such applications will continue to increase, one of the limitations to the widespread application of nanoparticles is their potential human and environmental health effects.Hyphenated mass spectrometry techniques have been employed as one of the primary analytical tools for investigating the effects of ionizing radiation, chemical/biological carcinogens, and oxygen-derived free radicals on the induction and subsequent repair of oxidatively induced DNA damage in living systems. The National Institute of Standards and Technology has established a comprehensive research program focused on identifying mechanisms of DNA damage caused by commercially relevant engineered nanoparticles using these techniques for the quantification of oxidatively induced DNA damage. We present an overview of our recent findings from studies on metal (gold, silver) and metal oxide (ultrafine superparamagnetic iron oxide, titanium dioxide) nanoparticles using isotope dilution liquid chromatography/tandem mass spectrometry and gas chromatography/tandem mass spectrometry.

STOICHIOMETRIC CONTROL OF LIGHT ABSORPTION BY COPPER-SULFIDE-BASED NANOPARTICLES

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Semiconductor particles that consist of abundant elements can help reduce the cost and environmental impact of solar photoconversion devices while maintaining useful energy conversion efficiencies. Copper sulfides and mixed metal copper sulfides are particularly attractive due to their near-optimal light absorbing properties, ability to enhance charge transfer in sulfide-electrolyte DSSCs, and mature recycling technology. To advance this technology, we have explored the stability of Cu_2S particles, developed new syntheses of a variety of copper sulfide-based nanoparticles of different polytypes, and developed techniques for controlling stoichiometry. Here we will demonstrate that alteration in dodecanethiol/oleic acid ratio in the reaction media systematically alters solid-state phase, morphology, and band structure of Cu_2-xS particles. Furthermore, using this new synthetic scheme we generated a series of copper iron sulfide nanoparticles in which the NIR absorbance is controlled by the Cu:Fe stoichiometry. Such rational control over light-absorption has implications for the energy conversion efficiencies of photovoltaic devices using these materials.

A NOVEL METHOD FOR BACTERIA INACTIVATION USING ENGINEERED WATER NANOSTRUCTURES

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James McDevvitt, Harvard University

Philip Demokritou, Harvard University

Herein a novel nanotechnology based method for microbial disinfection that utilizes the formation of unique Engineered Water Nanostructures (EWNS) generated via the electrospraying of water is presented. Electropsray is a method widely, used to generate aerosols. The objectives of this work are twofold: 1) showcase the proof of concept that these EWNS can be potentially used for the inactivation of pathogens from both surfaces and in the air; 2) Characterize the physico-chemical and morphological properties of EWNS and understand their formation and transport mechamisms. Bacteria Inactivation on surfaces: The inactivation of bacteria on surfaces by the EWNS was assessed both quantitatively and qualitatively. Different types of bacteria were used in order to cover a wide range of potential applications including Serratia Marcescens (gram-negative), Staphylococcus Aureus (gram-positive) and Bacillus Atrophaeus (spore forming). For the Serratia Marcescens the results showed that there is more than a 2-log10 reduction in 90 minutess of exposure. Similarly, the results for Staphylococcus Aureus showed nearly an 1-log10 reduction for same dose. The spore forming bacteria although exposed to the EWNS for 24 hours were not affected. Air disinfection: Serratia Marcescens was aerosolized in an environmental chamber and mixed with a controlled concentration EWNS aerosol. The potential of the EWNS to inactivate bacteria in the air was evaluated using a culture system approach under steady state and decay scenarios. The bioaerosol experimets showed the ability of EWNS to deactivate in a dose dependent matter, the suspended in the air Serratia Marcescens bacteria, by achieving 50% reduction at steady state and complete removal at 45 min under the decay scenario. EWNS synthesis and properties: The synthesis process and the properties of the generated EWNS, including size distribution, charge and reactive oxygen species were assessed. The size and particle charge were measure using atomic force microscopy (AFM) and an electrometer, respectively. Our results show that the EWNS have a size of approximately 25 nm, which is stable over time (hours), and carry an average charge of 10 electrons per particle. EPR was utilized to characterize the present of chemical species and showed that the EWNS are loaded with primarily with OH• radicals and secondary with O2•.

Particle to particle and particle to cell interactions in physiologic fluids using Atomic Force Microscopy (AFM)

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The formation of protein corona has emerged as a key mechanism in the particle-cell and particle-particle interactions in physiological fluids. While the particle corona formation was studied using proteomics and another analytical techniques, there is a lack of data in terms of atomic forces at the molecular level and their link to bio-interactions. In this novel bottom-up approach we investigate the interactions between particles and between particles and cells in physiological fluids, utilizing the state of the art Atomic Force Microscopy (AFM). Industry relevant ENMs (SiO_2, F_2O_3 and CeO_2) were synthesized with the Harvard VENGES flame spray pyrolysis platform and were deposited on pristine Si substrate in the flame. The same ENMS were collected and characterized off-line regarding their size, crystal structure and surface area using state of the art analytical methods. The collected ENMs were also used to modify AFM tips by attaching them on the tip from an ethanol or water suspension under an inverted microscope and the use of micromanipulators. The surfaces and the tips were characterized with SEM before and after each experiment to ensure that the particles did not detach during the experiment. The interaction (adhesion) force between the surface and the tip (particle-particle interaction) was measured in various media (air, water, RPMI and RPMI with FBS) as a function of the particle material and size. Iron oxide particles were found to experience less adhesion between them compared to ceria, in water, while both of them experience the same adhesion in physiological fluid (RPMI and FBS). The measured adhesion is in accordance with the DLVO theory and was verified with the DLS particle size.

Acute inhalation study of realistic nano scale CeO_2 using the Harvard VENGES toxicological platform

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Ceria nanoparticles are increasingly used for a number of industrial and commercial applications including catalysis, chemical mechanical polishing, UV-shielding, and nanocomposites. As the number of consumers and factory workers exposed to CeO_2 nanoparticles increases, the need for a comprehensive toxicological characterization is pressing. While most in-vitro models predict minimal toxicity for nanosized CeO_2, preliminary in-vivo animal models using instillation of CeO2 nanoparticles point to fibrogenicity and inflamation. However, to date, most toxicological evidence is limited to in-vitro studies, intratracheal instillation studies which however, do not represent realistic nanoscale exposure scenarios. Here, we present the first ever whole-body systematic animal inhalation study of nano-CeO_2. In addition, the use of a nanothin amorphous SiO_2 coating as means of mitigating CeO_2 toxicity was evaluated as a safer formulation concept. CeO_2 (uncoated and SiO_2-coated) nanoparticles were synthesized using the Harvard Versatile Engineered Nanomaterial Generating System (VENGES), which enables the synthesis and coating of industrially relevant nanoparticles in the aerosol phase with precise control over primary particle size, aggregation, and aerosol concentration. The generated aerosol was diluted and introduced into a customized exposure chamber, that is fully automated and maintain very stable exposure conditions. The generated CeO_2 particles (SiO_2 coated and uncoated) were characterized (1) in-situ with respect to aerosol size distribution and number concentration (SMPS), aggregate morphology (TEM, SEM) and (2) ex-situ with respect to crystallinity and chemical composition (XRD, XPS, EDX), surface area (BET), and morphology (TEM, SEM). Exposure atmospheres in the chamber were monitored in real time and characterized with respect to particle number concentration as a function of size (CPC, SMPS), mass concentration (Gravimetric Filter Measurements), aerosol mass size distribution (MOUDI), temperature, humidity, CO, CO_2, (Q-Track) and NO_x concentrations. Sprague Dawley rats (n=12/group) were exposed to either coated or uncoated CeO_2 (2.7 mg/m^3, 2 h/day, 4 days). Exposed animals, along with particle free- controls, were sacrificed at either 1 or 84 days post exposure. Pathophysiological analysis was performed and inflammatory and cytotoxic biomarkers were measured in the bronchoalveolar lung lavage (BAL) of the animals. Preliminary results showed that CeO2 is associated with lung inflammation and cytotoxicity as demonstrated by elevated PMN and LDH levels in the BAL fluid. In addition, SiO2 coatings revealed a significant reduction of toxicity, a clear indication of the effectiveness of this safe by design concept.

DIRECT AND INDIRECT TOXIC EFFECTS OF ENGINEERED NANOPARTICLES: ROLE OF EXOPOLYMERIC SUBSTANCES IN PROTECTING PHYTOPLANKTON

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In order to define the overall risk posed by engineered nanoparticles (ENPs) to aquatic ecosystems, their biological effects on the base of the food web must be evaluated. We present results from studies conducted with a variety of ENPs (AgNPs, ZnO, QDs) and marine phytoplankton (Phaeodactylum tertiolecta, Phaeocystis globosa, Dunalliela tertiolecta, *Thalassiosira pseudonana* and *T. weissflogii*) which illustrate both their direct and indirect effects. We show that while the surface properties of ENPs govern their aggregation behavior, and ionic strength controls their dissolution, exopolymeric substances (EPS) determine the potential of ENPs to be toxic. EPS produced by phytoplankton do not reduce the solubility ENPs but rather decrease their stability. Further, we show that the degradation rate of ENPs is correlated to the protein composition of EPS (defined by the ratio of protein/carbohydrate). The production of EPS reduces the impact of ENPs and/or their ions on cellular activities of phytoplankton. Complicating our current understanding of these interactions is the availability of a greater variety of surface coatings for ENPs. Our studies highlight the need for further research, particularly focused on determining the role of EPS on the fate and transport of ENPs in the aquatic environment.

A BIOPHYSICAL STUDY OF PROTEIN-NANOPARTICLE FORMATION

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Ran Chen, Clemson University

Pu Chun Ke, Clemson University

This study intends to delineate the mechanisms of protein-nanoparticle interaction. Upon entering the bloodstream, nanoparticles readily interact with plasma proteins to form a surface coating of protein “corona”. The diversities of protein structure and nanoparticle physicochemistry are shown to impact the affinity and dynamics of the nanoparticle-protein corona. The first aim of the project was to identify and quantify the physical interactions that guide the formation of the complex. In this study we used proteins such as ubiquitin, bovine-serum albumin (BSA) and fibrinogen, along with silver nanoparticles and carbon-based single-walled nanotubes (SWNTs), multiwalled nanotubes (MWNT) and fullerol $C_{6}0(OH)_{20}$. Based on our measurements of the zeta-potential, thermodynamics, UV-Vis absorption, and fluorescence quenching we were able to identify the driving forces that dictate the formation of protein corona on these common nanostructures. The final aim of the project is to describe the fate of nanoparticle-protein corona in eukaryotic cells, through fluorescence imagining and computer modeling.

SUSTAINABLE NANOTECHNOLOGY EDUCATION THROUGH INTEGRATION OF CROSS-TRAINING FOR COLLEGE STUDENTS

Narayanan Rajendran, Kentucky State University

Nanobial additives, the biologically influencing nanoparticles, have bioaccumulation potential to induce allergic and respiratory responses. The poor toxicological data on engineered nanomaterials and lack of provenance of nanobial additives make it more daunting task to detect early and analyze their potential impact on health and environment. Despite the success, as the global nano sector has been inventing and using novel nanobial additives on a regular basis, its consequences on health and ecosystems may raise a query on its sustainability. Though the bioaccumulation of nanobial additives is traceable, the challenge is the manpower to study their cellular responses associated with in vivo binding, and how the complex ribosomal and non-ribosomal cellular machineries are being affected or altered. It is expected that 2 million specially-trained people is needed by 2015, hence an interdisciplinary cross-training in nanoscience and nanobial health and safety is highly recommended. More colleges should offer degree programs in nanoscience or electives in nanobial health and safety education. It provides students a regulatory updates, and elicits current and future concerns about possible hazardous exposure, fate, transports, and bioaccumulations of nanobial additives. Public and private sectors should come forward to help universities beyond the initiation phase to ensure nanotechnology education through an integration of cross-training approach for future sustainability.

DIRECT TO DISCOVERY (D2D): AN INNOVATIVE DIGITAL APPROACH TO EXTENDING UNIVERSITY-BASED NANOSCIENCE INTO K-12 CLASSROOMS IN THE US AND ABROAD

W. JUD READY, Georgia Tech

Jessica Pater, Georgia Tech Research Institute

Grer Book, Georgia Tech

This work details an innovative application of high-speed networking technology and high-definition videoconferencing to offer educational enrichment to a high school chemistry course in Barrow County, Georgia as well as the equivalent grade level in Sydney, Australia and Killina, Ireland. The course was collaboratively designed, developed, and delivered jointly by the high school teachers and Georgia Tech researchers. Preliminary impacts, both quantitative and qualitative, will be presented, along with an outline of the educational needs, the pedagogical foundation, the guiding principles for design and development, and lessons learned. If adequate technology is available at the meeting site, we will demonstrate the capability by videoconferencing back to the Georgia Tech labs or remote national or international classrooms. In the course, students learned about carbon nanotubes, what they are, why they matter, and how they're grown. They learned about how different 'recipes' for growing carbon nanotubes produce differing results and will ultimately be able to remotely develop and run recipes. After the CNTs are grown, the samples are sent to the scanning electron microscope (SEM) at GT where the students are able to view the results from their classroom. The high fidelity of the SEM images and the video images allows students to see the same if not better quality image as the SEM operator sees on a monitor. This Chemistry course is part of a larger effort called Direct-to-Discovery, or D2D. D2D provides K-12 classrooms with engaging role models for science and technology careers and up-to-date professional development for K-12 STEM teachers. Engaging curricular enrichments that inspire STEM learning are provided, and the collaborative development model ensures that content will be aligned with relevant standards. The model has been used to establish international collaborations between K-12 classrooms in multiple nations, and plans for the future include applications in other STEM courses (such as an Astronomy that is currently under development) as well.

APPLICATIONS OF SPICPMS: DETECTING RELEASE OF CNTS FROM POLYMERS

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One challenge in assessing the life cycle of engineered nanoparticles (ENPs) lies in the difficulty in quantifying the release of these materials from products. Even detection of ENPs can be made difficult by low ENP concentrations, polydispersity arising from aggregation/partial dissolution, and the presence of other components released from the matrix. For many inorganic-based ENPs, single particle inductively coupled plasma-mass spectrometry (spICPMS) has recently been shown to be a promising approach for their detection and quantitation. In particular, the elemental specificity of ICPMS provides a means to detect and quantify ENPs in complex matrices. In order to examine the potential for introduction of ENPs into the environment, we examined the release of carbon nanotubes (CNTs) from laboratory-prepared polymer matrices. This was accomplished using spICPMS to detect metallic impurities in the CNTs. Data collected for yttrium showed a clear increase in CNT with increased leaching time. Similarly, increased loading of CNTs into the polymers resulted in an increase in CNT leached into solution. Although the results are largely qualitative, spICPMS provided a method of CNT detection that was applicable at much lower concentrations than other established techniques. Future work with spICPMS will allow exploration of the processes affecting the life cycle of ENPs.

MEGA-NANO FORUMS AND OPTIMAL REGULATION FOR THE SAFE DEVELOPMENT OF NANOTECHNOLOGY

RICHARD REIBSTEIN, Massachusetts Office of Technical Assistance

Irresponsible business or research practices, poorly designed products, or use of nano-containing items without knowledge could cause exposures that could generate an interest in curtailing nanotechnologies. It is in the interest of nano proponents as it is in the interest of workers, neighbors and environmental protection to have effective rules that prevent releases and exposures. Businesses and researchers have concerns about overregulation; however, a lack of sufficient control enhances the risk of accidents that could create a political momentum for overregulation. It is more likely that the right balance of an approach that accomplishes prevention without discouraging technological advancement or safe commercial application will be found if businesses, government, and others are cooperatively engaged in the effort. Businesses and researchers can become effective at contributing to the development of rules that achieve the optimal balance between over- and under-regulation if they work together to actively stay current on new nano-safety information, share preventive design ideas and constructively engage with others. MEGA-Nano Forums are a proposed mechanism for businesses to interact concerning best practices, which would form the basis for the design of optimal regulation.

THE IMPACT OF CeO_2 NANOPARTICLES ON RICE ROOTS: THE RELATIONSHIP BETWEEN ENZYME ACTIVITY, CELL MEMBRANE DAMAGE AND LIPID CONTENT

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Reports on the effects of cerium oxide nanoparticles (CeO_2-NPs) on rice are lacking, despite the fact that rice is one of the most widely grown food crops in the world. In this study, rice seeds were germinated for 10 days in CeO_2-NPs suspension at 62.5, 125, 250 and 500 mg/L concentrations. The Ce content, stress levels, enzymatic antioxidant responses [ascorbate peroxidase (APOX), dehydroascorbate reductase (DHAR) and glutathione reductase (GR)], and FT-IR of xylem in roots were analyzed. Results showed that Ce in roots increased with increased NP concentrations, but no visible signs of toxicity were observed. Relative to the control, the H_2O_2 generation significantly increased at the 500 mg/L treatment while enhanced lipid peroxidation and electrolyte leakage were observed in 125 mg/L CeO_2-NPs only. The CeO_2-NP treatments altered the enzymatic antioxidant activities, but consistently downregulated activities were observed at 125 mg/L CeO_2-NPs. The FT-IR analysis revealed that CeO_2-NPs modified the macromolecular contents of roots wherein higher lipid, protein and carbohydrate contents were observed at the control and 125 mg/L treatments. These findings demonstrate that the enhanced cell membrane damage at 125 mg/L CeO_2-NPs was due to inefficient removal of H_2O_2 and high lipid contents.

CHARACTERIZATION OF NANOMATERIALS RELEVANT TO BIOMOLECULAR INTERACTIONS

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Realistic nanomaterial risk assessments require an approach to characterization using descriptors and properties relevant to biomolecular properties that govern nanomaterial interactions with living tissues. The biological surface adsorption index (BSAI) developed by our group (Nature Nanotech 5:671-5, 2010) is a novel approach to characterize surface adsorption energy of nanomaterials that is the primary force behind nanoparticle aggregation, protein corona formation, and other complex interactions of nanomaterials within biological systems. BSAI nanodescriptors are intrinsic properties of nanomaterials useful for quantitative structure-activity relationship (QSAR) model development. Five nanodescriptors represent the surface adsorption forces (hydrophobicity, hydrogen bond, polarity/polarizability, and lone-pair electrons) describing the nanoparticle-biomolecule interaction. When this five-dimensional nanointeraction fingerprint is reduced to two dimensions, 16 diverse nanomaterials could be classified into distinct clusters according to their surface adsorption properties. Such an index allows diverse nanomaterials to be described based on the nature of their potential surface interactions, functioning in many regards as a multi-dimensional partition coefficient. This research provides a promising approach to quantitatively characterize the surface adsorption forces of nanomaterials in biological environments, which could open computational avenues as well as practical screening approaches in predictive nanomedicine development, risk assessment, and safety evaluation of nanomaterials.

DYNAMICS OF SWNT DISTRIBUTION AND AGGREGATE STRUCTURE DURING AQUATIC EXPOSURES

Tara Sabo-Attwood, University of Florida

Joseph Bisesi, University of Florida

Navid Saleh, University of South Carolina

Carbon nanomaterials present unique challenges in toxicological assessments as methods to detect, quantify and characterize these materials in biological organisms are limited. To address these issues we utilize near infrared fluorescence (NIRF), a highly sensitive and selective technique, for accurate quantification and visualization of these nanomaterials in vivo. Using fathead minnows as model organisms, we reveal the capability to monitor the distribution of single-walled carbon nanotubes (SWNTs) with real-time repeated measurements in live animals. Minnows exposed orally by gavage or feed show that SWNTs are primarily retained in the GI tract as determined by NIRF imaging of whole fish and subsequent quantification performed on homogenized tissues. Although no acute toxicity was observed, retention of SWNTs in the GI tract may cause dietary-related alterations with more long term health consequences. To gain a better understanding of SWNT behavior, dynamic changes in their aggregate morphology in simulated intestinal fluid was measured with static light scattering (SLS). These predicted structures likely influence their ability to interface with biological molecules which is currently being testing through proteomic approaches. Overall, these studies highlight the use of NIRF imaging and SLS as powerful tools for assessing in vivo distribution and characterization of SWNTs.

NOVEL SENSORS, INSTRUMENTS, AND MONITORING TOOLS FOR ACHIEVING SUSTAINABLE NANOTECHNOLOGY

WUNMI SADIK, SUNY Binghamton

Nanotechnology is creating new discoveries in areas such as medicine, automotive, energy, agriculture, remediation, consumer products and the entertainment industry. Central to the core of sustainable nanotechnology is the need to develop characterization parameters, metrological tools, novel instrumentation, and protocols that can provide information on the interactions of engineered nanomaterials with biological and environmental systems. Conventional methods for assessing these parameters focus on the size distribution and effects. They are however unsuitable for the detection and quantification in complex matrices. The goal of this session is to identify the research drivers, and the challenges of developing new tools as nanotechnology transitions from the research laboratories to consumer products. It will help researchers identify research goals for the needed data and new ideas, and enable policy makers to define a pathway forward using these data. It will also provide beneficial information for corporations engaging or seeking to engage in the manufacturing of nanomaterials and nanotechnology products. In this session, I will review the need to develop new instruments, approaches, and/or further refinement of existing tools for characterizing nanomaterials. I will present current research in our laboratory focusing on novel sensors for nanostructured silver, Fe_2O_3, fullerenes, TiO_2 and ceria.

MECHANISTIC HETERO-AGGREGATION OF GOLD NANOPARTICLES FOR A WIDE RANGE OF SOLUTION CHEMISTRIES

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Aggregation of nanomaterials can be highly influenced by secondary particulate entities in aqueous environment. Heteroaggregation of gold nanospheres (AuNS) in presence of highly-stable, nonionic surfactant (NIS) modified single-walled carbon nanotube (NIS-SWNT), is systematically studied utilizing dynamic light scattering (DLS). The use of NIS-SWNTs is based on the premise of co-existence of nanomaterials, while the choice of NIS is based on the organic matter presence in natural environment. NaCl and $CaCl_2$ concentrations, spanning the entire range of reaction limited (RLCA) and diffusion limited (DLCA) regimes, are used. NIS-SWNTs are found to be uninfluenced by the electrolyte chemistry; whereas, AuNS aggregation rates showed regime dependent responses. At RLCA regime, AuNS aggregation was hindered by NIS-SWNTs, compared to its homoaggregation behavior. In the contrary, an enhanced heteroaggregation of AuNS was observed for DLCA regime. The mechanism of such interaction is hypothesized to be physical hindrance to aggregation with NIS-SWNTs at RLCA conditions; while the tubes served as additional surfaces for interaction in the DLCA regimes. Such mechanisms are probed with TEM. Such first-of-kind findings present mechanistic evaluation of AuNS heteroaggregation for a wide range of electrolyte conditions and thus can have profound significance for reliable prediction of AuNS fate.

CeO_2 AND TiO_2 NANOPARTICLES: DIVERGENT CATALYTIC BEHAVIOR DRIVES IMMUNOMODULATION AND TH1/TH2 RESPONSE POLARIZATION

Brian Schanen, UCF

Examination of catalytic nanoparticle-induced human immunomodulation has been scarcely explored. We investigated in parallel the effects of two catalytic nanoparticles, TiO_2 (oxidant) and CeO_2 (antioxidant), towards innate and adaptive immunity. We focused on the effect of these nanoparticles on human dendritic cells and TH cells as a strategy towards defining their impact to cellular immunity. We report that TiO_2 nanoparticles potentiate DC maturation, inducing the secretion of IL-12p70 and IL-1B, while treatment with CeO_2 nanoparticles induced the secretion of the anti-inflammatory cytokine, IL-10. TiO_2 nanoparticles induced T cell proliferation in comparison to CeO_2. A strong differential in TH polarization was observed using an allogeneic T cells assay, stimulated with DC treated with either nanoparticle. Specifically, TiO_2 nanoparticles provoked a TH1 dominate response, whereas CeO_2 nanoparticles directed a TH2 biased response program. Combined, identifying the physicochemical features underlying the capacity for nanomaterials to be immunomodulatory can provide researchers direction for developing materials for inciting or avoiding particular immune functions.

NANOSCALE SCIENCE AND ENGINEERING IN AGRICULTURE AND FOOD SYSTEMS: AT A CROSSROADS

NORMAN R. SCOTT, Cornell University

Nanotechnology, as an enabling technology, has the potential to revolutionize agriculture and food systems in the United States and World. Examples of potential applications include disease diagnosis and treatment delivery systems, new tools for molecular and cellular breeding, identity preservation of animal history from birth to a consumer's table, assessing the safety of food products, major impact on animal and human nutrition scenarios ranging from diet to nutrient uptake and utilization, development and modification of new food products, modification of animal waste as expelled from the animal, pathogen detection, and many more. Thus, building blocks do exist and are expected to be integrated into systems over the next couple of decades on a commercial basis. While it is reasonable to presume that nanobiotechnology industries and unique developments will have major implications on agriculture and food systems, this optimistic view must be informed and balanced with uncertainties to reach its potentially exciting future.In this presentation, I will address:A brief introduction of the process leading to development of research funding within the USDA/NIFA for nanoscale science and engineering in agriculture and food systems,How the research supported by NIFA has developed over the past almost decade and a projection for the future,Examples of research successes from supported projects by NIFA,What are lessons learned to date and suggestions for the future, and A vision for the program at 2020.

THE INTERDISCIPLINARY NATURE OF NANOSCIENCE AND TECHNOLOGY EDUCATION

SUDIPTA SEAL, University of Central Florida

Nanoscience and technology represent the most rapidly developing areas in scientific discovery and innovation. Nanotechnology may be defined as the understanding of unique observation at the atomic levels, leading to the design, construction and utilization of functional nanostructures, again with at least one dimension measured in nanometers. At the nanoscale, the majority of the traditional scientific disciplines converge, and this convergence is a defining feature and one of the greatest interdisciplinary strength of nanoscale science and technology. Due to its interdisciplinary nature, presents educators with a considerable challenge in developing appropriate and effective teaching methodologies and ask the very important question about its sustainability. Extensive knowledge and knowhow exist in each of the constituent disciplines, and each has its own specialized jargon and technical language. Thus there is a need to effectively communicate to students and the public of the fundamental essence of nanoscience and technology and its applications, in which quantum effects will become increasingly important in various engineering areas including molecular electronics, photonics, biomedical devices, and a wide range of consumer products. This talk will present a brief overview of nanoeducation practiced in schools, colleges and Universities.

USE OF LASER SCANNING CYTOMETER TO INVESTIGATE THE INFLUENCES OF NANOPARTICLE SIZE AND SHAPE ON THE TRANSPORT IN POROUS MEDIA

Megan Seymour, University of Nebraska-Lincoln

Ryan May, Mechanical Sales, Inc.

Yusong Li, University of Nebraska-Lincoln

Mechanistic understanding of transport and retention of nanoparticles in porous media is essential both for environmental applications of nanotechnology and assessing the potential environmental impacts of engineered nanomaterials. Traditional column experiments can provide breakthrough curves or retention profiles, which reflect averaged behavior of particles in the column. Modern visualization techniques are able to observe in pore spaces with high resolution, which, however, are typically qualitative in nature. In this work, we present our recent work on using Laser Scanning Cytometery (LSC) to quantify the spatial distribution of nanoparticles in a porous medium domain at centimetre scale.Fluorescent polystyrene nanospheres with diameters of 510 nm, 210nm and 57 nm were chosen as model nanoparticles, which were later stretched into rod-shape nanoparticles to investigate the effects of shape on the transport. Deposition of nanoparticles onto model environmental surfaces was studied using a Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). Retention of nanoparticles in a microfluidic flow cell packed with glass beads were scanned by LSC. Spatial distributions of retained nanoparticles in a domain of 12 mm long and 5 mm wide were analyzed corresponding to detailed porous medium configuration and flow fluid simulations.

EVALUATING THE STATE OF NANOTECHNOLOGY EDUCATION IN LIBERAL ARTS COLLEGES ACROSS THE US

VISHAL SHAH, Dowling College

Lucas Loffredo, Vanderbilt University

Luke Latario, Grove City College

Training and exposing undergraduate students in various aspects of nanotechnology is critical for the sustainable growth and for improving the public understanding of the field. Major universities across the US have been at the forefront of providing specialized courses and degree programs in various areas of nanotechnology. The goal of the current study was to determine if nanotechnology education has penetrated the liberal arts colleges across the US. An exhaustive list of 497 liberal arts colleges from 45 different states was compiled, and course descriptions (generally from the school's undergraduate catalog) were searched for courses regarding nanotechnology, nanoscale processes, nanochemistry, and/or nanoscience. Only 13.7% of liberal arts colleges had a course referencing nanotechnology in any way, and just 4.6% had a STEM course devoted exclusively to nanotechnology topics. The anemic nature of nanotechnology education at liberal arts colleges has the potential to severely disadvantage the STEM graduates of these schools and create a knowledge gap of "haves" and "have-nots". We will present some of the major reasons for the lack of penetration of nanotechnology education in the liberal arts colleges.

INFLUENCE OF PROTEIN CORONA ON NANOSILVER TOXICITY IN EPITHELIAL AND ENDOTHELIAL CELLS

JONATHAN SHANNAHAN, East Carolina University

Josh Pitzer, East Carolina University

Jared Brown, East Carolina University

Nanoparticles (NP) can absorb a variety of serum proteins forming a protein corona (PC). The PC can affect cellular interactions, and clearance impacting NP toxicity. Nanosilver particles (AgNP) formulated in PVP or citrate buffer were incubated with human serum albumin, bovine serum albumin, high density lipoprotein, or water (control). Rat lung epithelial cells (RLE) and rat aortic endothelial cells (RAEC) were exposed to increasing concentrations of AgNPs (0, 6.25, 12.5, 25, or 50 μg/ml) with or without PC for 3h and 6h. In general, AgNPs with all versions of the PC demonstrated dose-dependent cytotoxicity at both time-points and in both cell types. The addition of the PC to PVP-coated AgNPs exacerbated cytotoxicity at 3h and 6h in RAEC at the highest concentrations (25 and 50 μg/ml) while enhancing the cytotoxicity of citrate-coated particles at only 3h. Furthermore, exposure of RAEC to 50 μg/ml of all AgNPs in the presence of a scavenger receptor class B antagonist prevented cytotoxicity at 3h. In conclusion, we observed an increase in cytotoxicity resulting from the addition of the PC to AgNP, which may be dependent on scavenger receptor activation.

FATE OF ENGINEERED NANOMATERIALS IN CONSTRUCTED WETLAND TREATMENT SYSTEMS

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Paul Westerhoff, ASU

Pierre Herckes, ASU

Constructed wetlands are considered natural alternatives to remove contaminants from wastewater treatment plant (WWTP) effluent. Organic pollutants have received significant attention because of the perceived risks towards human and ecosystems. Considerable interest is now directed to the fate of engineered nanomaterials (ENMs).For example, TiO_2 nanomaterials are found in WWTP influents and effluents. One of the major features of the wetlands are plants that can provide functions to various treatment processes. Sorption to these plant surfaces decreases the concentration of contaminants as water passes through wetlands. This presentation investigates sorption of a number of ENMs on wetland cattails (Typha.). Batch isotherm techniques were used to investigate the extent of sorption and desorption of aqueous fullerenes (aq-nC60) and three types of silver NMs- (i) carboxy coated (CAR-Ag), (ii) PVP coated (PVP-Ag) and (iii) Gum Arabic coated (GA-Ag) in separate experiments. ENMs were introduced in simulated wetland microcosms operated at different hydraulic loading rates. Using the loading rate and assuming plug flow, rate constants for ENMs were obtained. Among the selected ENMs, aq-nC60 showed higher sorption affinity and consequently better removal in the wetland

microcosms. The findings from this study suggest that constructed wetlands can effectively remove ENMs present in the WWTP effluent.

SUSTAINABILITY STANDARD METRICS FOR NANOMATERIALS AND NANOTECHNOLOGIES: STATE OF PLAY

JO ANNE SHATKIN, CLF Ventures

Sustainability science and nanotechnology share the characteristic of being relatively new areas of investigation. They also represent fields where multiple standardization efforts are developing independently, creating confusion in the marketplace, and among governmental and non-governmental organizations, even simply on definitions. In order to facilitate the sustainable development of nanotechnology, there is a need to measure the sustainability of nanoscale materials and products of nanotechnology, in a consistent and meaningful way. With dozens, if not hundreds, of different metrics to measure the sustainability of materials, products or companies, there exists a wealth of options to choose from, and a need to refine the core concepts as they are applied across the many sectors where nanotechnologies are used. This presentation will discuss the state of standards development for sustainability measurements and metrics and evaluate existing alternatives and needs for developing these measurements for nanoscale materials and nanotechnologies.

INCORPORATING LIFE CYCLE THINKING INTO RISK ASSESSMENT FOR NANOSCALE MATERIALS: CASE STUDY OF NANOCELLULOSE

JO ANNE SHATKIN, CLF Ventures, Inc.

Theodore Wegner, U.S. Forest Products Laboratory

World Neih, U.S. Forest Service

Responsible and sustainable technology development requires proactive consideration of potential impacts across the life cycle of materials. The need for data a priori to application development creates challenges for a structure designed to test individual substances in pure form. For novel nanoscale materials, limitations in the availability and reliability of data create challenges for measuring and assessing their potential risks to health and the environment in real world applications, particularly because of the dynamic nature of these materials in the environment. This talk describes a methodology for assessing potential health and environmental risks of novel materials, and presents a case study demonstrating the framework. This talk describes NANO LCRA, an iterative, tiered approach to risk assessment of nanomaterials, incorporating life cycle systems thinking into the risk analysis paradigm to inform data gaps, with increasing data requirements as products approach commercialization. Potential risks are framed across the product life cycle, utilizing a structured approach to identify critical uncertainties and priority data needs at each stage. A case study of NANO LCRA with crystalline nanocellulose demonstrates the approach and identifies research needs to address current uncertainties in health and environmental risks, and overall product performance.

TOWARDS SOLAR FUEL GENERATION WITH A CARBON NITRIDE PHOTOCATALYST

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Frank E. Osterloh, Deptartmetn of Chemistry, University of California, Davis

Graphitic carbon nitride (g-C_3N_4) is a visible light driven photocatalyst for water reduction - a pathway to hydrogen fuel from solar energy. The material is interesting because it does not require precious elements and can be made from abundant precursors (xxx, xxx) through simple heating (xxx deg C). Problems of g-C_3N_4 are low activity and photocorrosion in the absence of sacrificial agents. This study tries to solve these problems through a three pronged strategy involving nanoscaling, addition of water reduction cocatalysts, and interfacing with a suitable photoanode material for water oxidation. Toward these goals, results on the synthesis of nanoscale and Ni-modified g-C3N4 are presented. The materials were characterized with transmission electron microscopy and UV vis spectroscopy. The effect of the modifications on phototalytic activity was measured during irradiation tests in the presence of methanol as sacrificial electron donor. Surface photovoltage spectroscopy (SPV) was employed to analyze charge separation of electron and holes at the material-cocatalyst interface. The implications of these findings on the development of sustainable catalysts for solar energy to fuel conversion will be discussed.

ANTIMICROBIAL PROPERTIES OF FULLERENE DERIVATIVES AS A FUNCTION OF STRUCTURE AND AGGREGATION STATE

SAMUEL SNOW, Georgia Institute of Technology

KyoungEun Park, Georgia Institute of Technology

Jaehong Kim, Georgia Institute of Technology

As fullerene technologies continue to expand, there is an increasing need for understanding the relationships between the physical and chemical structure and the biological and photochemical activity of functionalized fullerene nanomaterials. To initiate the process of establishing quantitative structure-activity relationships (QSAR), three series of mono-, bis- and tris- adducted fullerene materials were selected and studied. Dispersion of the derivatives in the aqueous phase via sonication resulted in stable colloidal aggregates. Physicochemical properties of these derivatives and their aggregated forms have recently been characterized. Antimicrobial activity, from both innate and photosensitizing properties, of the materials was measured using *E. coli* and MS2 bacteriophage virus. Minimum Inhibitory Concentration experiments and Inhibition Zone tests were performed for *E. coli* to evaluate the innate antimicrobial properties of the fullerene aggregates. Inactivation kinetics were measured for *E. coli* and MS2 bacteriophage to assess the phototoxicity of the fullerenes under UVA, fluorescent, and natural sunlight. Toxicity mechanisms were probed using a standard Bradford assay, lipid perioxidation quantification, a cell permeability assay, specific oxidant scavengers as well as several surface analysis techniques including transmission electron microscopy and x-ray photoelectron spectroscopy.

MULTIFUNCTIONAL PLASMONIC NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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Plasmonic nanoparticles play an important role in biomedical applications today as they can serve as superior optically-stable bioimaging agents, be employed in biosensor devices for the early diagnosis of diseases, and exhibit promising results for their employment in vivo as therapeutic agents. For several bioapplications, however, nanoparticles that express more than one functionality are often advantageous. This has led to the synthesis of multifunctional plasmonic nanoparticles that combine the attractive plasmonic properties with other functionalities like magnetism, photoluminescence, dispersibility in aqueous solutions and resistance to degradation. Here, biocompatible, SiO_2-coated, Janus-like multifunctional plasmonic nanoparticles are prepared by one-step, scalable flame aerosol technology. A nanothin SiO2 shell around these multifunctional nanoparticles leaves intact their morphology, magnetic and plasmonic properties but minimizes their toxicity. Furthermore, this silica shell hinders flocculation and allows for easy dispersion of such nanoparticles in aqueous and biological buffer (PBS) solutions without any extra functionalization step. Their performance as bioimaging agensts was explored by selectively binding them with live tagged Raji and HeLa cells enabling their detection under dark-filed illumination. Finally, their potential in photothermal treatment of cancer cells is investigated.

EVALUATION OF PROPERTIES AND PERFORMANCE OF NANOSCOPIC MATERIALS IN VANADIUM BORIDE-AIR BATTERIES

JESSICA STUART, The George Washington University

Stuart Licht, The George Washington University

Chris Rhodes, Lynntech Inc.

In recent years, there has been an escalating need for a high capacity battery that can meet the demands of emerging technologies. A nanoscopic vanadium diboride air battery is presented, utilizing an eleven electron per molecule oxidation with an intrinsic gravimetric capacity of 4060 Ah kg-1, notably greater than that of the Li-ion or other comparable electrochemical energy sources. In this study, cell performance is evaluated though the electrochemical characterization of the VB2-air battery to develop a system that is capable of producing high capacities and voltages during rapid discharge rates. The nanoscopic VB2 material was characterized using transmission electron microscopy to determine particle size and morphology. Nitrogen physisorption experiments were performed to determine surface area and pore size. Electrical conductivity measurements were performed using a two-electrode powder conductivity configuration. Additionally, impedance testing was conducted before and after discharging of cells to evaluate reaction kinetics and internal resistance. Nanoscopic synthesized VB2 is shown to exhibit higher electrical conductivity hence lower resistance, lower impedance, and maximized surface area when compared to macroscopic commercial material. Furthermore, improvement in both the anodic capacities as well as the voltage plateaus at various discharge rates were observed.

MOLECULAR MECHANISMS OF NANOTOXICITY IN MOUSE EMBRYONIC STEM CELLS

Christopher Stucke, University of Dayton

Muneaki Hikital, Western University of Health Science

Yiling Hong, Western University of Health Science

Nanotechnology has enormous potential for biomedical and other applications. To better understand how nanoparticles' composition, shape, charge, surface chemistry, and particle size relate to the integration of a material into a living organism, we use embryonic stem cells as model to study the impact of several types of nanoparticles on a stem cell's fate. Our studies indicated that carbon nanotubes and nanosilver particles induced a DNA damage response, stem cell factors cleavage, and cell death in mouse embryonic stem cells. The molecular mechanisms of toxicity were the production of free radicals in the cells and changes in the surface conductivity of the cell. This study will further explore the relationship between NP characteristics and physiological responses and develop methods to evaluate the health and safety of nanoparticle applications.

ELECTROCHEMICAL METHODS TO PROBE AND MONITOR NANOMATERIALS

IAN IVAR SUNI, Clarkson University

Concerns about the environmental health and safety of nanomaterials must be addressed in order for nanotechnology to become widely accepted. Nanomaterials sustainability is enhanced by the capability to rapidly determine the size, shape, and composition of nanomaterials in the environment in which they are produced or consumed. This allows the development of portable sensors for early warning systems, regulatory monitoring of potentially harmful nanomaterials, and even improved process control during nanomaterials fabrication. Electrochemical methods have important advantages for portable sensor applications, including rapid response, high sensitivity, speciation capability, ease of miniaturization, and low cost. Unlike optical methods, noise levels can be extremely low at room temperature, and measurements can be made on turbid samples. Common electrochemical methods include amperometry, potentiometry, capacitance, and impedance measurements. One area of recent interest is multielectrode sensors, which provide multiplexed measurements of numerous analytes, and allow for reference measurements to calibrate for the presence of interfering species, changes in temperature, or changes in sample viscosity. Multielectrode sensors are increasingly economical due to the commercial availability of microelectrode arrays.

SUSTAINABLE NANOTECHNOLOGY AND THE UN MILLENNIUM GOALS

CLAYTON TEAGUE, Consultant

Achieving the UN Millennium Development Goals (MDGs) offers many opportunities for innovations in sustainability and nanotechnology to contribute toward making the world a far better place for everyone in the world. The eight MDGs are: 1) eradicate extreme poverty and hunger; 2) achieve universal primary education; 3) promote gender equality and empower women; 4) reduce child mortality; 5) improve maternal health; 6) combat HIV/AIDS, malaria and other diseases; 7) ensure environmental sustainability; 8) develop a global partnership for development. Countries of the UN have agreed to a large number (21) of challenging targets toward reaching these goals as spelled out at: http://www.un.org/millenniumgoals/bkgd.shtml. This talk will explore the ways in which development of standards for - and better means of characterizing - the products of sustainable nanotechnology can aid achievement of the UN MDGs.

OXIDATION OF C60 AEROSOL BY OZONE

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the atmosphere during production, use, and disposal. There, they will be subject to physical and chemical transformations which could modify their fate, transport, and toxicity within the environment. The objective of this research is to determine the products and rates of reaction of aerosolized C60 with atmospherically relevant concentrations of ozone. Batch reactions between atmospherically relevant ozone levels (45 and 120 ppb) and C60 aerosol were carried out in a Teflon chamber. Following exposure to ozone, aerosols were collected and analyzed by high performance liquid chromatography (HPLC), infrared spectroscopy (RAIRS), and transmission electron microscopy (TEM). Results indicate that the reaction proceeded within minutes and appeared to be complete in less than 1 h. Reaction products included several oxygen-containing fullerene species and may also have included an oxygen-linked C60 polymer. The reaction products were not appreciably soluble in water. These results suggest that at atmospherically relevant ozone levels, C60 is rapidly oxidized and that this process may affect its fate and transport in the environment. Other carbonaceous nanomaterials such as carbon nanotubes may be subject to similar transformations.

CYTOTOXICITY OF NANO-TiO_2 TO BACTERIA: INFLUENCE OF PHYSICOCHEMICAL PROPERTIES AND ENVIRONMENTAL FACTORS

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We have studied the potential environmental impacts of nano-TiO_2, with the specific aims to (1) assess their cytotoxicity to bacteria under environmentally relevant conditions and (2) link the physicochemical properties of different materials to cytotoxicity. The toxicity of nine nano-TiO_2 materials characterized by different phases, morphologies and photoactivities to a model bacterium *E. coli* were assessed in Lake Michigan water. Except for two pure-phase rutile samples, all anatase-based materials displayed significant short-term cytotoxicity under simulated solar illumination despite aggregation to particle sizes greater than the nanoscale range. Only slight or negligible toxicity was observed in the dark. Cytotoxicological trends generally followed the photocatalytic activity of nano-TiO_2, with the exception of nanotubes exhibiting comparable photooxidative activity to Degussa P25 but being much less toxic. The size of TiO_2 aggregates did not correlate to the extent of cytotoxicity, but their morphology may play an important role. Two environmental factors, irradiation wavelength and natural organic matter content, were found to be critical in influencing nano-TiO_2 toxicity: UVA irradiation exerted the largest effect on the phototoxicity of nano-TiO_2, and Suwannee River fulvic acid was able to stabilize nano-TiO_2 but reduced its cytotoxicity to bacteria likely due to shading and radical scavenging effects.

AS-PRODUCED AND FUNCTIONALIZED SINGLE-WALL CARBON NANOTUBES (SWNTS) IMPLICATIONS TO SOIL MICROORGANISMS

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To better understand the potential environmental impacts of single walled carbon nanotubes soils with either low or high organic matter contents as well as pure cultures of *E. coli* are challenged with either raw As Purchased (AP-SWNTs) or SWNTs functionalized with either polyethyleneglycol (PEG-SWNT) or m-polyaminobenzene sulfonic acid (PABS-SWNT). To mimic chronic exposure, the soil systems were challenged weekly for six weeks; microbial activities and community structures for both the prokaryote and eukaryote community were evaluated. Results show that repeated applications of AP-SWNTs can affect microbial community structures and induce minor changes in soil metabolic activity in a low organic matter soil. Toxicity of the three types of nanotubes was also assessed in liquid cultures of a bioluminescent *E. coli* strain O157:H7, where AP-SWNTs suppressed metabolic activity of *E. coli* while the functionalized SWNTs had no effect. We suggest that while metals associated with the AP-SWNT were notable, the levels of metals released from or associated with, the raw forms of the tubes did not play a major role in the effects seen in soil or the pure culture. We suggest that sorption to soil organic matter or biomacromolecules in microbial communities plays a controlling role in the environmental responses to these nanomaterials.

OCCUPATIONAL HEALTH & SAFETY

CANDACE TSAI

Airborne nanoparticles released during the production of nanomaterials such as carbon nanotube were of particular concerned. Our research investigates potential environmental emission from various production processes. The study of investigating environmental emission during synthesis of single-walled and multi-walled carbon nanotubes will be presented. In this study, released particles from CNT furnace were measured and characterized. This study reported the field measurements during the development of carbon nanotube production.Particle number concentrations for diameters from 5 nm to 20 µm were measured using the Fast Mobility Particle Sizer and the Aerodynamic Particle Sizer; the particles released from the furnace were found to be less than 500 nm in diameter. The morphology and elemental composition of the released nanoparticles were characterized by scanning and transmission electron microscopy and energy dispersive spectroscopy. Different operating conditions of multi-walled carbon nanotubes (MWCNT) production were studied to evaluate their effects on the number and morphology of aerosol particles, and the number of particles released. Carbon nanotube filaments and carbon particles in clusters were found among the released aerosol particles during production of multi-walled carbon nanotubes.

CARDIAC ISCHEMIC/REPERFUSION INJURY RESPONSE TO INSTILLED AND INTRAVENOUS C60 FULLERENE ADMINISTRATION

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C60 fullerenes are nano-sized particles with widespread use in commercial and biomedical industries. This study evaluated cardiac ischemia injury following acute pulmonary instillation of C60. Male and Female Sprague Dawley rats were I.T. instilled or I.V. injected with (0.28mg/kg) C60 in 1.4% PVP or PVP alone. Pulmonary inflammation and cardiac ischemic/reperfusion injury were assessed 1 day post-administration. Pulmonary response revealed a modest elevation in the protein concentration and cell differential showing elevated neutrophils, eosinophils and lymphocytes in the C60 exposed groups. Seurm cytokine analysis showed increases in IL-6 and MCP-1 with loss of TNF- ? following either route of C60 administration. C60 exposure resulted in expansion of myocardial infarction (46% as compared to 26% PVP). Female rats infarctions were 8 % smaller then the males as were infarcts following I.V. administration. Our study indicates that C60 fullerenes administration increased susceptibility of cardiac tissue to ischemic/reperfusion injury with minimal pulmonary inflammatory responses. Even though these effects were observed at relatively high doses they may pose a significant risk to the cardiovascular system under stress. This work is supported by NIH R01 ES016246 (CJW) and U19 ES019525 (JMB/AL/TF/SS/CJW).

GREENER PATHWAYS TO NANOMATERIALS AND THEIR SUSTAINABLE APPLICATIONS

RAJENDER S. VARMA, US EPA

Sustainable synthetic efforts involving alternate energy input, and greener reaction medium will be summarized wherein vitamins B1, B2, C, and tea and wine polyphenols, which function both as reducing and capping agents, provide simple, one-pot, green synthetic methods to bulk quantities of nanomaterials. Shape-controlled synthesis of noble nanostructures via MW-assisted spontaneous reduction of noble metal salts using sugars will be presented including a general methodology for the cross-linking reaction of poly (vinyl alcohol) (PVA) with metallic systems; bimetallic systems, and SWNT, MWNT, and C-60. The strategy is extended to the formation of biodegradable carboxymethylcellulose (CMC) composite films with noble nanometals; such metal decoration and alignment of carbon nanotubes in CMC is possible using MW approach which also enables the shape-controlled bulk synthesis of Ag and Fe nanorods in poly (ethylene glycol). MW hydrothermal process delivers magnetic nanoferrites and micro-pine structured catalysts are obtainable in water from readily available metal salts. Sustainable route to nanoparticles using polyphenols from winery waste or agricultural residues, their applications in catalysis, toxicity and environmental remediation will be highlighted.

THE VALUE OF NANOTOXICITY TESTING TO SUSTAINABILITY

BELLINA VERONESI, EPA

Sustainable technology promises to replace conventional synthesis and disposal of nanomaterials in the future. It is critical, however, that “green” nanomaterials which are designed to be more environmentally friendly, also retain the critical properties inherent to their pristine state and ideally exhibit a reduced toxicity to biological systems. Many issues remain unresolved in evaluating sustainable nanomaterials. Do “doping” or surface modification of the pristine parent nanomaterial invalidate the predictive value of the nanoparticle’s physicochemistry? Does surface coating with benign materials modified the transport of nanoparticles through biological barriers or their eventual toxicity to target cells? Do sustainable modifications alter particle organ deposition? Answering these and other critical questions will require a strategic assembly of biological test models, endpoints and exposure methods to be useful in the evaluation of “green” nanomaterials for biological effect.

MONITORING NANOPARTICLE INTERACTIONS AT BIOLOGICAL INTERFACES WITH NONLINEAR OPTICS

STEPHANIE WALTER, Northwestern University

Franz Geiger, Northwestern University

This work seeks to understand the fundamental chemistry of nanoparticles at biological interfaces, such that knowledge gained at the molecular level can be applied to design environmentally and biologically sustainable nanomaterials. Nonlinear optical spectroscopies, including sum frequency (SFG) and second harmonic generation (SHG), are employed to study the interactions of nanoparticles with lipid membranes, specifically probing the molecular vibrations, electronic transitions, charge densities, and interfacial potentials at these solid-liquid interfaces in situ. Tracking how nanoparticles influence pure and mixed lipid bilayers will provide key insights necessary to understand, predict, and control molecular interactions between nanomaterials and living systems.

GENERATION OF TOXIC DEGRADATION PRODUCTS BY SONICATION OF PLURONIC® DISPERSANTS: IMPLICATIONS FOR NANOTOXICITY TESTING

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Poloxamers (trade name Pluronic®) are triblock copolymer surfactants that contain polyethylene glycol and polypropylene glycol. Poloxamers are widely used as dispersants for nanotoxicity studies where sonication is employed to prepare nanoparticle suspensions. It is known that poloxamers are susceptible to sonolytic degradation; however, the possibility that poloxamer degradation products are toxic to mammalian cells has not been well studied. We report that poloxamers sonicated in the presence or absence of multi-walled carbon nanotubes in water can became highly toxic to cultured cells. Toxicity correlates with the sonolytic degradation of the poloxamers. A search on Google Scholar using the four terms “carbon”, “nanotubes”, “toxicity”, and “pluronic” returned over 1400 articles (patents and legal documents excluded), an estimate of how widely used these polymers are in nanotoxicity studies with carbon nanotubes. Whereas some reports in the literature did not use conditions likely to degrade poloxamers, a sampling of the articles revealed many where nanoparticles were sonicated under conditions that are likely to have produced suspensions containing toxic poloxamer degradation products. These results suggest that caution should be used in interpreting the results of nanotoxicity studies where the sonolytic degradation of dispersants has not been eliminated as a potential source of toxic material.

RISK ASSESSMENT FOR NANOPARTICLES DURING LITHIUM-ION BATTERY PRE-RECYCLING PROCESSES

XUE WANG, Rochester Institute of Technology

Gabrielle Gaustad, Rochester Institute of Technology

Lithium-ion batteries (LIBs) have been widely used in consumer electronics (e.g. cellular phones, laptop computers, digital cameras, etc.) and anticipated use in electric vehicles will likely accelerate consumption over the next several years. Nanomaterials are also being integrated into these batteries at an increasing scale, specifically, nano-iron phosphate in cathodes (already commercialized), single-wall carbon nanotubes in anodes, and silicon nanowires in anodes. Environmental and health risks associated with the end-of-life (EOL) processing of these LIBs containing nano-particles has not been well studied yet. This work focuses on providing an initial characterization of nano-particulate risk for several pre-recycling processes including shredding and sorting. Batteries of several cathode chemistries and the same form factor were industrially shredded and sorted by particle size. Presence, size, concentration, and composition of nano-particles were determined using electron microscopy, x-ray fluoresce, and spectroscopy. Results indicate the potential for release and exposure during these recycling activities.

This initial work will help to fill life cycle inventory data gaps for airborne nanoparticle emission that would affect both human health and safety impact assessment as well as ecotoxicity.

INTRAVENOUSLY DELIVERED GRAPHENE NANOSHEETS AND MULTI-WALLED CARBON NANOTUBES INDUCE SITE SPECIFIC TH2 INFLAMMATORY RESPONSES VIA THE IL-33/ST2 AXIS

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Carbon based nanomaterials, such as graphene nanosheets (GNS) and multi-walled carbon nanotubes (MWCNT) have been proposed for nanomedical applications such as biomedical devices and carriers for drug delivery. However, our understanding of systemic toxicity of these carbon-based nanomaterials is limited. We hypothesized that intravenous administration of GNS and MWCNT would result in contrasting systemic inflammatory responses due to physicochemical differences between these two nanomaterials. In the lungs of C57BL/6 mice, GNS actuated a Th2 immune response 1 day following i.v. administration which consisted of neutrophil influx and significant increases in IL-5, IL-13, IL-33 and its soluble receptor ST2 (sST2) in the bronchoavolar lavage fluid. In contrast to inflammatory responses in the lung, MWCNT elicited a significant increase in expression of cytokines including IL-4 and IL-33 which were associated with an increase in CD4+ and CD8+ T cells in the spleens of C57BL/6 mice following i.v. injection. These adverse immune responses were absent in ST2-/- mice suggesting a critical role for IL-33 in the allergic responses to nanomaterials. In conclusion, the use of GNS and MWCNT as nano-carriers for drug delivery may result in Th2 immune responses mediated through the IL-33/ST2 axis which could promote adverse allergic reactions.

ZEBRAFISH XENOGRAFT MODEL OF GLIOBLASTOMA TO INVESTIGATE STRUCTURE ACTIVITY RELATIONSHIPS OF ZINC OXIDE NANOPARTICLES WITH ANTICANCER PROPERTIES

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Zinc oxide nanoparticles (ZnO-NPs) demonstrate preferential cytotoxicity toward tumor cells in culture. We developed a NP screening paradigm by xenotransplanting human glioblastoma cells into the cranium of zebrafish to assess the physicochemical properties of ZnO-NPs that enhance cytotoxicity to cancer cells. The goal is to identify ZnO-NPs that inhibit cancer cell proliferation. We investigated the role of charge, size, Fe as a ROS catalyst and route of exposure (waterborne vs. micro-injection) on the toxicity of ZnO-NPs in embryonic zebrafish. Generally, the ZnO-NPs did not induce significant adverse effects below 10 $\mu g \bullet ml^{-1}$. Charge influenced the biological response with highly positive NPs inducing less response than nearly neutral NPs, depending on route of exposure. Reducing the ZnO-NP size was associated with more malformations. Increasing the Fe content amongst similarly sized and positively charged ZnO-NPs induced greater adverse response in zebrafish via waterborne exposure. An optimized ZnO-NP was synthesized (mean diameter=8.35 nm; zeta potential=+43.6 mV) and preliminary results demonstrate that it inhibited glioblastoma cell proliferation at 0.1 mM. Our screening paradigm holds promise for identifying physicochemical traits which enhance the anti-cancer properties of ZnO-NPs while supporting safe NP design. Research support: NSF 134468, NIEHS P30ES000210, ES016896, T32ES07060, and Air Force Research Laboratory #FA8650-05-1-5041.

ANTICIPATORY LIFE CYCLE ASSESSMENT OF NANO-ENABLED LITHIUM ION BATTERIES

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There is a critical need for life cycle assessment (LCA) during the formative stages of technology development, so that the systemic environmental consequences of new technologies may be identified and mitigated early in product development cycles. For example, several studies have called for the application of LCA to nanotechnology. However, LCA typically relies on detailed inventory and performance data collected from existing industries at commercial scales. In the case of nanotechnology, collecting manufacturing and use-phase LCA inventory data is problematic, both because nanotechnologies are proprietary and because the energy and material flows studied at the laboratory-scale will likely change as the technology matures. This necessitates the development of anticipatory LCA methods that can be used to explore potential environmental impacts of technologies and industries before they exist at scale. Anticipatory LCA can be viewed as a quantitative scenario development tool used in situations of high uncertainty (e.g., nano-enabled energy technologies) to inform research, investment, and policy decisions. This requires a combination of laboratory-scale inventory measurements and technological performance modeling. The results suggest that anticipatory LCA may uncover new research directions that will reduce life-cycle burdens, such as improving synthesis reactions yields, recovering metal catalysts from liquid waste streams, and recycling inert gases.

UNINTENTIONAL EXPOSURE TO NANOPARTICLES VIA AN INDUSTRIAL SILICON PROCESSING ACCIDENT

ORION WENRICH, University of Maryland, College Park

Ariel Stein, National Oceanic and Atmospheric Administration

Sheryl Ehrman, University of Maryland, College Park

As the nanotechnology industry has grown so have the concerns regarding nanoparticle exposure. Nanoparticles may also form and be released as unwanted byproducts of industrial accidents. While research has been performed regarding health and ecological effects of nanoparticle exposure, there has been surprisingly little research using regional transport modeling software to develop and study exposure event scenarios. Chlorosilanes are used in the Siemens process for silicon purification. Silicic acid and silica nanoparticles are an unwanted side effect of chlorosilane processing into solar grade silicon. Given the global increase in start-up companies in the silicon and solar industries, we investigate the regional effect that a silicon processing accident might have using Hysplit and ALOHA software. Results from ALOHA indicate an AEGL-1 toxic air hazard up to 3.9 km away for a release of trichlorosilane alone, from a plant that produces 1,600 metric tons annually of solar grade silicon. For a plant that produces ten times as much the AEGL-1 hazard level could extend up to 10 kilometers from the plant when the source amount is scaled up accordingly. Additional results incorporating chemical reactivity will be discussed.

FULLERENE-ENHANCED ACCUMULATION OF P,P’-DDE IN AGRICULTURAL CROPS

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Roberto De La Torre Roche, Connecticut Agricultural Experiment Station

Baoshan Xing, University of Massachusetts

The effect of C60 fullerene exposure on the accumulation of p,p’-DDE by zucchini, soybean, and tomato was determined. The plants were grown in 125-mL jars of vermiculite amended with 0 or 40 mg of fullerenes and over 21 days, were watered with p,p’-DDE containing solutions (100 ng/mL of p,p’-DDE with 0 or 100 mg/L humic acid). Total shoot p,p’-DDE levels in non-fullerene exposed tomato, soybean and zucchini were 26.9, 131, and 675 ng, respectively; total root DDE content for the three plants was 402, 5970, and 5830 ng, respectively. Fullerenes increased the shoot p,p’-DDE content of zucchini by 29%; contaminant levels in soybean shoots were decreased by 48% but tomato shoot content was unaffected. The root and total plant p,p’-DDE content of all three species were significantly increased by fullerene exposure; enhanced contaminant uptake ranged from 30-65%. Humic acid significantly decreased the p,p’-DDE uptake in all treatments. Fullerenes were detected in the roots of all plants but were not initially detected in plant shoots. In a follow up study designed to maximize biomass, half the stems contained fullerenes (60.5- 4,490 ng/g). These findings show that the carbon-based nanomaterials may significantly alter the availability of co-contaminants in agricultural systems.

NANOMATERIAL INTERACTIONS WITH AGRICULTURAL CROP SPECIES

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Roberto De La Torre Roche, Connecticut Agricultural Experiment Station

Baoshan Xing, University of Massachusetts

Although nanomaterials (NM) use has increased dramatically, the risks posed to humans and the environment have been investigated only recently. The interaction between NM and agricultural plants is an area of particular concern. Current investigations are focused on a screening study evaluating the acute toxicity of 12 nanoparticles (including bulk/ion controls) to 12 agricultural crops under hydroponic and soil conditions. Results to date show numerous instances of particle size-specific phytotoxicity, as well as concentration-dependent and species-specific response to NM exposure. In a mechanistic study, the toxicity and accumulation of CuO nanoparticles (NPs) in corn was evaluated. Cu in the NP form exhibited significantly greater phytoxicity than equivalent bulk and ion treatments. CuO NPs were present in xylem sap as determined transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). In split-root experiments, high resolution TEM observation further showed that CuO NPs were translocated from shoots back to roots via phloem. Our data clearly demonstrates differential toxicity, accumulation, and fate of several nanomaterials relative to respective bulk particles and ions. The implications of these findings for accurately determining the fate and transport of nanomaterials in agricultural systems, as well as for exposure and risk posed to humans, will be discussed.

TEACHING ETHICS THROUGH ROLE PLAYING IN A NANOTECHNOLOGY CLASS FOR FIRST YEAR COLLEGE STUDENTS

KURT WINKELMANN, Florida Institute of Technology

This presentation describes an interactive method for first-year college students to learn about ethical issues related to nanotechnology. Modeled after the PBS show, “Nanotechnology: The Power of Small”, this activity asks students to play the roles of fictional characters who debate how nanotechnology might improve or impair their own lives and their community. Students are given background information about a fictional but realistic scenario that involves their characters, along with a character’s description and point of view. Each student researches his or her position to provide facts that support the character’s opinion. Playing their character roles, students debate the issues during class. Following this, each student writes a reflection paper in which the student describes his or her own view of the issue and how the activity may or may not have changed that view. A pilot-study of this activity occurred during the spring 2012 semester with success. Debate topics included the use of nanotechnology for (1) improving consumers’ experience by providing their shopping preferences and tendencies to retailers, (2) monitoring the public by the police to improve safety at the expense of public privacy, and (3) providing high-tech jobs with questionable impact on the environment.

CARBON NANOTUBE, NANOSILVER AND NANOCLAY PROTEIN CORONA COMPOSITION IN CELL CULTURE MEDIA

FRANK A. WITZMANN, Indiana University

Jared M. Brown, East Carolina University

Jonathan H. Shannahan, East Carolina University

The formation of protein corona has emerged as a key mechanism in the particle-cell and particle-particle interactions in physiological fluids. While the particle corona formation was studied using proteomics and another analytical technique, there is a lack of data in terms of atomic forces at the molecular level and their link to bio-interactions. In this novel bottom-up approach we investigate the interactions between particles and between particles and cells in physiological fluids, utilizing the state of the art Atomic Force Microscopy (AFM). Industry relevant ENMs (SiO_2, F_2O_3 and CeO_2) were synthesized with the Harvard VENGES flame spray pyrolysis platform and were deposited on pristine Si substrate in the flame. The same ENMS were collected and characterized off-line regarding their size, crystal structure and surface area using state of the art analytical methods. The collected ENMs were also used to modify AFM tips by attaching them on the tip from an ethanol or water suspension under an inverted microscope and the use of micromanipulators. The surfaces and the tips were characterized with SEM before and after each experiment to ensure that the particles did not detach during the experiment. The interaction (adhesion) force between the surface and the tip (particle-particle interaction) was measured in various media (air, water, RPMI and RPMI with FBS) as a function of the particle material and size. Iron oxide particles were found to experience less adhesion between them compared to ceria, in water, while both of them experience the same adhesion in physiological fluid (RPMI and FBS). The measured adhesion is in accordance with the DLVO theory and was verified with the DLS particle size. In addition, the atomic level forces between the particle functionalized tip and lung epithelial cells (A549) adhered on a slide glass and immersed in physiological media were measured.

NANOCOMPOSITE MATERIALS: INDUSTRIAL APPLICATIONS AND CORRESPONDING MODELS OF NANOFILLER RELEASE

WENDEL WOHLLEBEN, BASF, Material Physics and Experimental Toxicology

Nanocomposite materials are a focus of BASF in nanotechnology, since they are key to sustainable systems that enhance the energy efficiency during production and use. Such materials may be considered a low risk application of nanotechnology, if the rate of release of nanostructured fragments is vanishing throughout the life cycle of the products - or low as compared to the risk profile of the specific nanostructure.

We experimentally address limiting cases of nanofiller release from composites, such as tubular protrusions of CNTs from brittle matrices after mechanical energy input. The matrix material determines the in-vivo inflammation potential in the respiratory system, not the embedded or protruding nanofillers. We perform quantitative fractionation of the debris to detect any released nanofillers. Along the axis of chemical degradation, especially photochemical degradation and hydrolysis of the matrix is a consumer- and environment- relevant scenario. Degradation of the matrix clearly occurs, but it takes worst case combinations of weathering plus wear to release e.g. CNTs from their entangled network.

Synergy of chemical degradation and mechanical energy input is identified as the priority scenario of release. Lab simulation indicates low rates of release, but still requires real-world validation.

SOLAR-LIGHT INDUCED PLASMONIC ENERGY TRANSFER FROM METAL TO SEMICONDUCTOR

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Solar energy is a clean and abundant energy source that can be converted to electricity in photovoltaic devices, chemical energy by photocatalysts, and thermal energy using solar concentrators. The recent and rapid development of surface plasmon resonances (SPR) has offered a new opportunity to overcome the limited efficiency of photocatalysts and photovoltaic devices. SPR improves the solar-energy-conversion efficiency by (i) extending light absorption to longer wavelengths, (ii) increasing light scattering, and (iii) inducing charge separation by transferring the plasmonic energy to the semiconductor. We have synthesized metal/oxide composite nanostructures to investigate the plasmonic enhancement of photocatalysis. We have investigated how the SPR induces the charge separation.

DETECTION OF HEAVY METALS BY QUANTUM DOT BASED FLUORESCENT BIOSENSOR VIA NANOMETAL SURFACE ENERGY TRANSFER

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An ultra-sensitive and highly selective nanosensor, which is based on the nanometal surface energy transfer (NSET) in the quantum dots/DNA/Au nanoaprticle ensemble, has been successfully developed for Mercury(II) detection in water. In this sensor, complementary oligonucleotide strands are linked to quantum dots (QD) and gold nanoparticles, respectively. When specific heavy metal ions (such as Hg^{2+}) are present in the aqueous solution that contains the oligonucleotide-conjugated QDs and Au nanoparticles, the heavy metal ions selectively bind to the oligonucleotides, which drives the formation of DNA helixes. As a result, a quantum dot and the gold nanoparticles are brought into a close proximity, leading to the NSET from the QD to the Au nanoparticles. Consequently, the fluorescence emission of the QD is quenched by the Au nanoparticles. The target ion selectivity can be achieved by selected DNA sequences. This sensor has showed a limit of detection of 0.4 ppb in the buffer solution. The excellent selectivity toward Hg^{2+} has been demonstrated in an aqueous solution in the presence of the other environmental metal ions.

NANOPARTICLE ELECTROSPRAY FACILITATES THE BREAK OF COAT-IMPOSED SEED DORMANCY

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This study demonstrates a novel technique to promote plant seed germination through the electrospray of trace amounts of nanoparticles (NPs). With an electric field and space charge effect, sprayed nano-

droplets (TiO_2 NPs) carrying with high electrical charges can be accelerated and used to penetrate lettuce (Lactuca sativa) seed coats. After a brief treatment of lettuce seeds with the NP electrospray, germination percentage of the lettuce seeds was significantly improved ($P < 0.05$). Such enhancement was pronounced if seeds were recalcitrant to germinate. For example, the germination of lettuce seeds under stress conditions (i.e., acidic environment) was improved by fivefold after the treatment. In shelf life studies, the lettuce seeds continued to have improved germination one month after the NP treatment. TEM and SEM-EDX images suggest that the ultra-fine TiO2 NPs striking the seed coat create “nano-holes” in the seed coat, resulting in the breaking of coat-imposed seed dormancy. This technique is also effective for the germination of several recalcitrant weed seeds, thus having the potential for various applications in agriculture and horticulture.

CARBON NANOTUBES AS WATER POLLUTANTS: AQUEOUS DISPERSIBILITY AS A FUNCTION OF SIZE AND ASPECT RATIO

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As CNTs find their way into industrial and consumer products, they may be inadvertently released into the environment during their production, use and disposal. While there exists the possibility for raw, unrefined, and hydrophobic CNTs to settle out of aqueous media into solid phases such as river sediments, water dispersible forms may persist in water resources increasing the risk to public health. Therefore there is a need to develop a comprehensive understanding of the fate and transport of the dispersible CNTs in aqueous media. This paper presents the effect of size and aspect ratio on the colloidal behavior of aqueous dispersions of carboxylated multiwall carbon nanotubes (c-MWCNTs). The presence of carboxylic groups on the nanotube surface provided electrostatic stabilization in water, and the aggregation behavior of the colloidal system was observed to be dependent on the aspect ratio. It was observed that the MWCNTs with short length, large diameter and low aspect ratio were less prone to aggregation. All the c-MWCNTs were highly stable in pure water and showed excellent long term stability in the presence of the Na electrolytes. Our results suggest that these highly dispersible c-MWCNTs can be relatively stable in typical aquatic environments.

NANOPARTICLE BINDING TO HOMOGENOUS AND HETEROGENOUS MODEL CELL MEMBRANES

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Nanoparticles can bind to, disrupt, and translocate across cell membranes through physical interactions. Trends in nanoparticle-membrane activity general follow those for nanotoxicology; activity increases with decreasing nanoparticle size and increasing cationic charge. To gain a more mechanistic understanding of nanoparticle binding and membrane response, previous studies have used model membranes composed of physiologically-relevant lipids. While insightful, these studies have been primarily performed with homogenous membranes (often supported on substrates), and information on the effects of binding on membrane phase behavior and structure is limited. Using lipid bilayer vesicles (unsupported) and lipid monolayers, we examine physical nanoparticle interactions with homogenous and heterogenous membranes, and the impact of these interactions on local and global membrane structure. This presentation will focus on commercially and environmentally relevant inorganic nanoparticles (Ag, Au, Fe_2O_3) with anionic and cationic surface coatings. Preliminary results based on calorimetry, microscopy, and spectroscopy have revealed a complex landscape of physicochemical factors that govern nanoparticle binding (weak verses strong; endothermic verses exothermic) and resulting changes in membrane structure (stabilization verses destabilization). Ultimately, the ability to quantify, mitigate, or exploit nanoparticle-membrane interactions will have broad implications in the fields of nanotoxicology and nanomedicine.

RGD MODIFIED FERRITIN NANOCAGES FOR IMAGING AND DRUG DELIVERY

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Ferritin is a major iron storage protein found in human and most living organisms. Each ferritin is comprised of 24 subunits, which self-assemble to form a cage-like nanostructure. Ferritin is an interesting nanoplatform because: 1) Despite the rigidness under physiological conditions, recent studies have shown that the FRT nanoarchitecture could be broken down in an acidic environment and restored when the pH returns to neutral. 2) The outer surface of FRT can be chemically or genetically modified. Functional units, such as targeting peptides, can be easily imparted onto the FRT surface. 3) The ferritin cavity can be encapsulated with transition metals or small molecules. We previously constructed RGD-modified ferritin nanoparticles and through careful imaging studies, confirmed their good tumor selectivity. Very recently, we found that doxorubicin could be encapsulated into RGD-ferritin nanoparticles with high efficiency (up to 70 wt%). Further in vitro and in vivo studies confirmed the potential of RGD-ferritin nanoparticles as efficient drug delivery carriers for tumor therapy.

A TWO-STAGE EXPERIMENTAL DESIGN FOR DOSE-RESPONSE MODELING IN TOXICOLOGY

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Quantifying the dose-response relationship of a substance is one of the most fundamental steps in risk assessment. To obtain such functional relationships, paired dose-response data need to be collected through biological experiments which are usually of very restricted size. How to utilize the limited resources (i.e., how to select the experimental doses and allocate animals) to achieve the best possible model? This is the experimental design question that this work intends to address. Optimum design for dose-response modeling is challenging due to the special features of toxicity data, which include nonnormality, variance heterogeneity, possibly nonlinearity of the dose-response curve, and data scarcity. In this work, a two-stage design procedure particularly suitable to toxicity data is developed. The two-stage procedure allows for a learning process: information derived from the first stage experiments is used to guide the second-stage experiments. The design aims at minimizing the uncertainty of the estimated model parameters as well as the uncertainty on the benchmark dose inferred from the estimated model. These estimation uncertainties are evaluated via bootstrapping, a computationally intensive resampling method, as opposed to conventional statistical inference methods which are subject to the various assumptions that may well not apply to toxicity data.

BACTERIA DECONTAMINATION USING SUSTAINABLE NANOSTRUCTURED POLY(AMIC) ACID MEMBRANES

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The ubiquitous nature of microorganisms and their relatively fast growth rates make microbial contamination unavoidable through air, water, human body and food system. Besides, the size of microorganisms is in the range of nanometers to micrometers, which enhances the impact of pathogenic contamination of the bacteria. In addition to preventing the microbial contamination by simply blocking their entry into a zone, sustainable materials can exhibit inhibitory action on microorganisms by decreasing their viability and/or growth rates; thus decreasing the risk of contamination. We hereby describe a new approach for inhibiting bacterial contamination using nanostructured poly (amic acid)-based (nPAA) materials. nPAA contains amino and carboxyl groups, which can undergo chemical modification. At the same time, these groups can interact with proteins available at the outer surface of microorganisms resulting in the disintegration of their cellular membrane. Besides being water resistant, the ease of fabrication makes nPAA a suitable membrane having different pore sizes for a variety of sustainable applications. In this study, we will report the decontamination and filtering of *E.coli* in different media using modified and un-modified polyamic acid membranes.

BIODISTRIBUTION, BIOPERSISTENCE AND TOXICITY OF SYSTEMICALLY-INTRODUCED NANOCERIA IN THE RAT

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Nanoscale ceria (cerium oxide) is redox reactive with industrial (diesel fuel additive and chemico-mechanical polishing agent) and medical (antioxidant therapeutic) applications. Our objective was to determine the nanoceria physico-chemical properties that influence its distribution, biopersistence, and toxicity after intravenous dosing of the rat. Citrate-coated 5, 15, 30 and 55 nm cubic/polyhedral ceria and a ceria nanorod (synthesized and characterized in-house) were intravenously infused into rats that were terminated 1 h to 90 d later. Cerium was quantified in urine and feces; blood, plasma and blood cells (as the blood clot); brain; and peripheral tissues. Oxidative stress markers, light and electron microscopy-based histology, and nanoceria valence as prepared and in situ, were also determined. Less than 1% of 30 nm ceria was eliminated in feces and urine within 2 weeks of dosing. Each nanoceria sample was quantitatively retained, for example up to 90 days for 30 nm ceria but little entered brain parenchyma. Nanoceria bioretention was associated with pro-oxidant effects and liver and spleen histopathology, including granulomas. Nanoceria valence did not significantly change after one month in situ. Nanoceria biopersistence, associated with toxicity, is consistent with the concern that slow clearance of insoluble nanomaterials may be result in adverse responses.

IMPROVING THE PERFORMANCE OF NANOCRYSTAL DEVICES THROUGH THE ENCAPSULATION OF SEMICONDUCTOR NANOCRYSTALS INTO HETEROEPITAXIAL INORGANIC MATRICES

MIKHAIL ZAMKOV, Bowling Green State University

We will present a novel methodology for depositing colloidal semiconductor nanocrystals into all-inorganic solid films with implications both to nanocrystal solar cells and nanocrystal light-emitting devices. The reported strategy utilizes a simple scheme for incorporating PbS or CdSe semiconductor nanocrystals into matrices of a wide-band gap CdS semiconductor for stable and efficient operation of solution-processed devices. The two key benefits of this approach include: (i) all-inorganic architecture promoting superior thermal and chemical stability, and - (ii) a unique film morphology, which offers the possibility of tuning the film properties between conducting (for applications in solar cells) and light-emitting (LEDs, lasers) simply by changing the interparticle distance in the matrix. This approach is universal and can be extended to a large number of nanocrystal/matrix combinations.

EFFECT OF MANUFACTURING VARIABLES AND INFLUENT WATER CONDITIONS ON BACTERIAL REDUCTION EFFECTIVENESS OF POINT-OF-USE CERAMIC WATER FILTERS

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The World Health Organization has estimated that about 884 million people on earth do not have access to improved safe water. As drinking water can be contaminated by pathogenic bacteria, it is crucial to apply point-of-use water treatment device to treat the unsafe water and make it potable. Point-of-use ceramic water filter is one of the popular water treatment devices. It is a simple device of low cost and can be produced locally.This study aims to determine the effect of the manufacturing variables and influent water conditions on the performance of ceramic disks cut from point-of-use ceramic water filters. The results of this study suggested that (1) during 10 days evaluation, the bacterial reduction performances of ceramic disks decreased with increasing time; (2) bacterial reduction performances of ceramic disks increased with increasing concentration of silver applied (log reduction values: 2.88-5.64); (3) bacterial reduction performances of ceramic disks were affected by the origins of the clay in the following order:Indonesian>Tanzanian>Nicaraguan; (4) bacterial reduction performance using influent water chemistry conditions did not show significant difference. The significance of this work lies in that

it could lower the cost of the point-of-use ceramic water filters manufacturing process by optimizing the manufacturing variables.

RELATIONSHIP BETWEEN PROTEIN ADSORPTION AND NANOTOXICITY

WENWAN ZHONG, University of California, Riverside

Lei Ren, University of California, Riverside

Jonathan Ashby, University of California, Riverside

Our research effort is dedicated on exploring the relationship between protein adsorption and nanotoxicity. We are studying protein adsorption on two nanomaterials, single-walled carbon nanotubes (SWCNTs) and iron oxide nanoparticles (NPs), using LC-MS/MS to identify the protein corona formed on nanomaterials when incubated with biological matrices. Carboxylate SWCNTs were incubated with mitochondria extract and several inner membrane enzymes including ATP synthase and NADH dehydrogenase, were found to be adsorbed on the SWCNTs. However, if SWCNTs were coated with BSA, only ATP synthase still remained adsorbed. The BSA-coated SWCNTs induced lower cytotoxicity and lower ROS level if incubated with cells. These results point out that adsorption of these enzymes could be directly related to cytotoxicity of SWCNTs. Adsorption may have altered the activity of the enzymes and increase ROS production, which leads to cytotoxicity. On the other hand, we developed a method to discriminate proteins that were transiently or stably adsorbed on iron oxide NPs, and have applied it to study the hard-core or transient layer of protein corona formed when the NPs were present in human serum. The biological significance of such distinct binding behaviors of the corona proteins is under exploration.

SENSING WITH CATION EXCHANGE IN NANOCRYSTALS AND NANOCLUSTERS

WENWAN ZHONG, University of California, Riverside

Jingjing Yao, University of California, Riverside

A large variety of fluorescent nanomaterials have been prepared and shown great success in molecular detection. However, production of highly fluorescent nanomaterials in an environmental friendly manner and with bio-safe elements could be challenging. My group has developed a signaling scheme by gently releasing thousands of cations encapsulated in one nanocrystal by cation exchange reaction, and igniting the free cations with a metal-responsive dye to produce high fluorescent signal for detection. Since our scheme does not rely on the intrinsic fluorescence property of the nanocrystals (NCs), we can flexibly change the composition and structure of NCs for higher amplification efficiency. We have applied cation exchange in nanocrystals for signal amplification (CXAmp) to produce high fluorescence with CdSe or ZnSe NCs, and clusters of ZnS NCs, all synthesized in water, a green and environmentally friendly approach. Detection of small RNA and protein molecules at fmol or fM levels has been achieved. Moreover, our recent effort has successfully combined CXAmp with rolling circle amplification (RCA) to achieve cascade signal amplification, and allow detection of small RNA species present at amol level. Our CXAmp scheme has great application potential in disease diagnosis and prevention owing to its high amplification efficiency and robustness.

WOUND HEALING OF HUMAN CELLS FROM THE CORNEA IS IMPACTED BY NANOPARTICLES

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The eye surface can be a major site of environmental exposure and resulting irritation. However, there is a lack of understanding of the effects of engineered nanoparticles (ENPs) on the eye. We wanted to explore whether ENPs can impede the wound healing of the ocular surface. We developed a novel wound healing assay utilizing cells from the human cornea. We tested a panel of well characterized, industrially relevant ENPs, including several commercially available ENPs and metals and metal oxides generated using our recently developed Versatile Engineered Nanomaterial Generation System (VENGES). TiO_2 and SiO_2 ENPs did not affect wound healing at doses up to 100 μag/ml. By contrast, copper oxide, zinc oxide, and silver ENPs substantially impede wound healing in a dose-dependent manner. These studies provide a novel in-vitro model system for evaluating the impact of nanoparticles on the ocular surface. They also show the importance of studying the impact of ENPs on recovery from injury.

PAPER BASED DISPOSABLE TESTING KITS FOR IN VITRO GENOTOXICITY ASSAY UPON NANOMATERIAL EXPOSURE

Xuena Zhu, Florida International University

CHEN-ZHONG LI, Florida International University

Oxidative stress is one of the most discussed mechanisms regarding the negative effects of nanomaterials. Studies have shown that some metal oxide nanoparticles can cause reactive oxygen species generation that leads to oxidative stress and DNA damage in the body.8-hydroxy-2'-deoxyguanosine is one of the predominant forms of oxidative DNA damage, and therefore has been widely used as a biomarker for oxidative stress. Current risk assessments primarily rely on the analysis of the toxic contents. Despite the urgent need to develop analytical tools capable of routinely assessing toxic exposures at the points of need, few practical methods have been developed. We present here a competitive immunochromatographic paper strip capable of detecting DNA damage biomarker, which can be used for in vitro genotoxicity assessment of metal oxide nanoparticles. The strip will provide a point of care testing method for rapid risk assessment of nanomaterials with high sensitivity, specificity, speed of performance and the advantages of simplicity.

INHIBITION OF LUNG SURFACTANT BY NANOPARTICLES - MORE THAN CYTOTOXICITY?

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Nanotoxicology has been commonly studied by three means: epidemiologic studies in humans, inhalation/instillation studies in animals, and cytotoxicity studies using cell culture models. Despite the numerous nanotoxicological knowledge obtained from these studies, little is known how nanoparticles interact with the biological system at the molecular level. It has been reported that some non-cytotoxic nanoparticles can still cause adverse health effects if inhaled. Here we studied a potentially alternative source of nanotoxicity, i.e., inhibition of the lung surfactant system. Lung surfactant is synthesized by alveolar type II epithelial cells and coats the entire respiratory tract as a thin film. This surfactant film plays a crucial role in maintaining the normal respiratory mechanics by reducing the alveolar surface tension. Any inhaled nanoparticles must first interact with this lung surfactant film. We found that hydroxyapatite nanoparticles at a low concentration, although benign to human bronchial epithelial cells, inhibited an in vitro model of the natural lung surfactant. Using combined experimental characterizations and molecular dynamics simulations, we found that the molecular mechanism of surfactant inhibition is most likely due to adsorption of a surfactant specific protein onto the particle surfaces. This study provides novel insight into the toxicological study of nanomaterials.