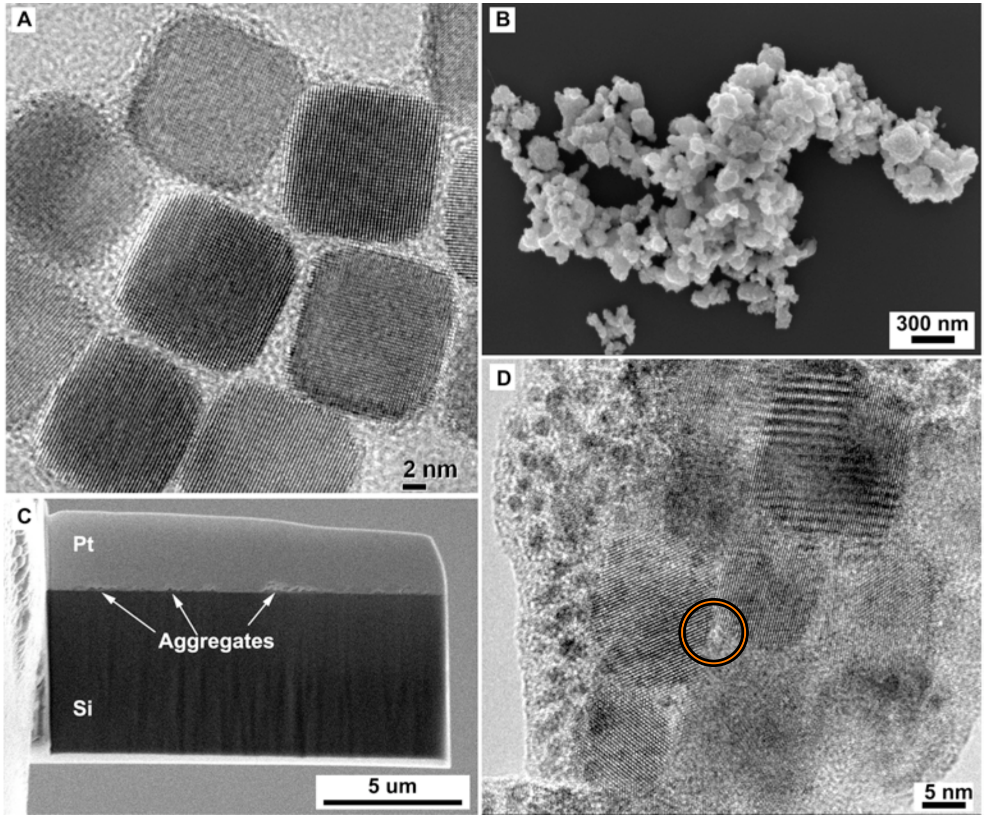
A Rare Look at Nanoparticle Reactivity and Aggregation

Juan Liu (VT), Deborah Aruguete (VT), & Michael Hochella (VT)

Galena, a sulfide mineral, is a common source of lead in the environment. (**A**) shows an electron microscope (EM) image of incredibly small (14 nm) galena crystals. CEINT researchers from Virginia Tech have found that these galena nanocrystals dissolve 10 times faster than larger particles of the same mineral, thus more readily releasing toxic lead into the environment. In nature, these nanocrystals often aggregate (**B**). In the lab, CEINT researchers sandwiched these aggregates between silicon (Si) and platinum (Pt) metals (**C**), then cut out a cross-section with an ion beam to observe the inside (**D**). There, the grains are in such close contact, with only nanometer-sized spaces (ring), that these aggregates dissolves 10 times slower than the individual nanocrystals (**A**), thus slowing the release of toxic lead. Thus, the toxicity of these particles is size and aggregation dependent.



Citation: Liu J., Aruguete, D., and Hochella M.F. Jr. (submitted) Influence of size and aggregation on the non-oxidative dissolution of galena (PbS). Submitted to *Science*.

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CEINT

CEINT Investigator Receives Post-Doc Mentoring Award

Dr. Emily Bernhardt, Assistant Professor
Department of Biology
Duke University

Duke's Office of Postdoctoral Services awarded CEINT investigator Dr. Emily Bernhardt the 2008 Outstanding Postdoc Mentor Award. Dr. Bernhardt has served as mentor for four postdocs who praise her for "going out of her way to help us develop as scientists, challenging us to describe the larger significance of our research, and always emphasizing the importance of making our work relevant to science and society, which increases the chances of our manuscripts getting published in high-profile journals." Dr Bernhardt was also cited for her support of women in science and her commitment to increasing the numbers of minorities in ecology.

Estimating Global Nano-Titanium Dioxide Production

Mark Wiesner & Christine Robichaud (Duke)

CEINT researchers from Duke and UCLA have produced the best existing estimate of global nano-titanium dioxide production.

The first step in understanding environmental risk is to quantify the amount of the material in question that gets into the environment. When materials are difficult or impossible to measure directly, other methods must be devised to estimate how much is being used and how much is getting into natural systems. Though production figures are closely guarded industrial secrets, CEINT researchers have devised a method for estimating current production based on process limitations and the number of existing facilities. In addition to current estimates, the authors project an upper bound on production over the coming quarter century, under assumptions of rapid and complete adoption of the nano-scale material. This work has been accepted with revisions for publication in the journal, *Environmental Science and Technology.*

❖ Citation: Robichaud, C.O., Uyar, A. E., Darby, M. R., Zucker, L. G., Wiesner, M. R. (In revision.) "Estimates of upper bounds and trends in nano-TiO2 production as a basis for exposure assessment." Environmental Science and Technology.

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Mesocosm Construction
Duke University

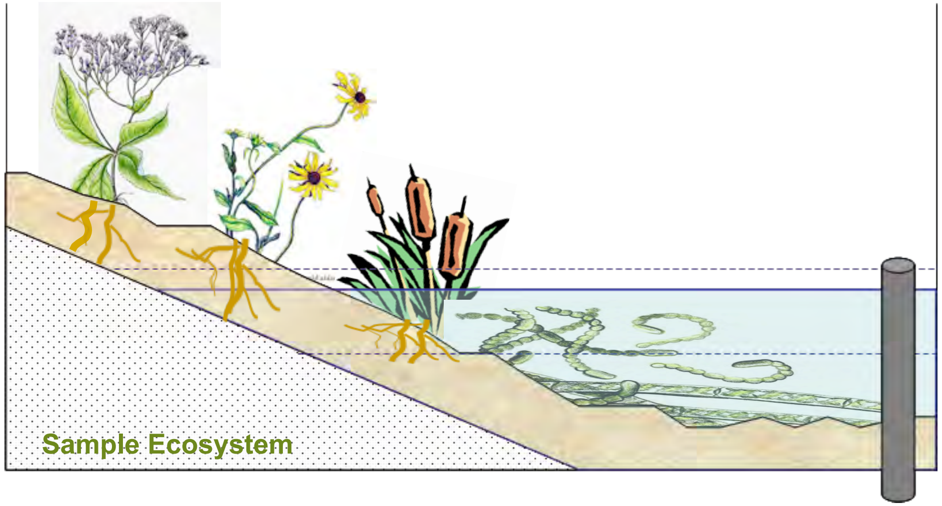
Duke Forest provides collaborative research site for CEINT.

CEINT is in the process of constructing 32 tightly controlled and highly instrumented ecosystems (aka mesocosms) that will be located in the Duke Forest. These mesocosms (3 ft x 12 ft.) will be areas where researchers can add nanoparticles and then study the resulting interactions and effects on plants, fish, bacteria and other elements within these contained systems. The mesocosms will serve as a unifying resource for experiments across all of CEINT's six thrusts. There have been several test mesocosms constructed thus far: one prototype is an excavated system (prototype A) and the alternative is an elevated system (prototype B).


Prototype A


Prototype B

Field site location


Sample Ecosystem

Protocols for Nanomaterial Preparation and Experimentation

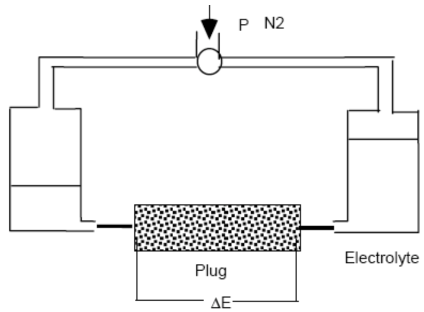
CEINT researchers team up with international collaborators (iCEINT) from over seven French laboratories to develop common protocols that will allow data on nanomaterials in environmental systems to be more readily compared across international studies.

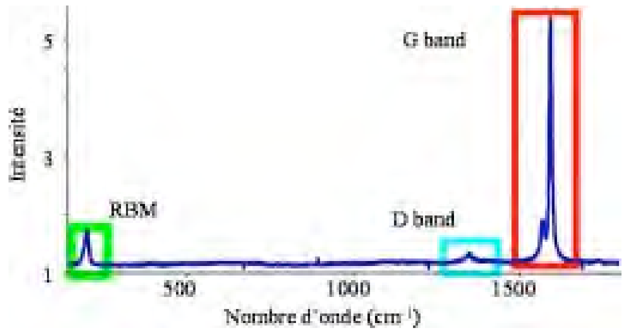
Protocols are being developed for common use across CEINT laboratories that will facilitate the exchange and interpretation of data between labs and minimize duplication of efforts. Protocol development has included two international meetings with iCEINT collaborators in the US and in France.

The protocols describe procedures and measurements to be performed that span the preparation of nanoparticle dispersions, procedures for physicochemical characteristics such as size and charge, and the manner in which they are introduced into cell cultures and microcosms. To date, nine protocols have been proposed.

These procedures will be first adopted and tested by CEINT/iCEINT researchers and then published on the CEINT website for comment and use by the larger scientific community.

iCEINT
International Consortium for the Environmental Implication of Nano Technology





Typical Raman spectra of carbon nanotubes

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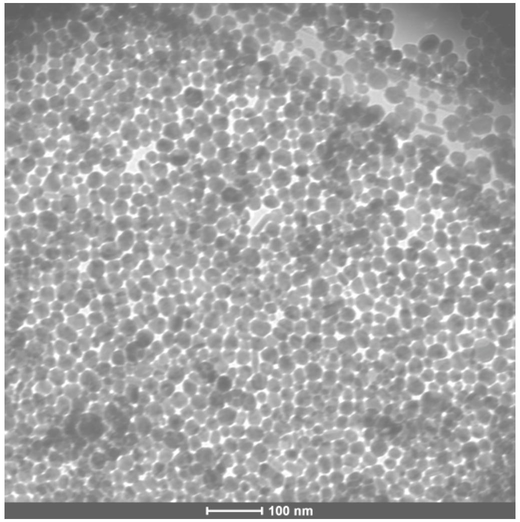
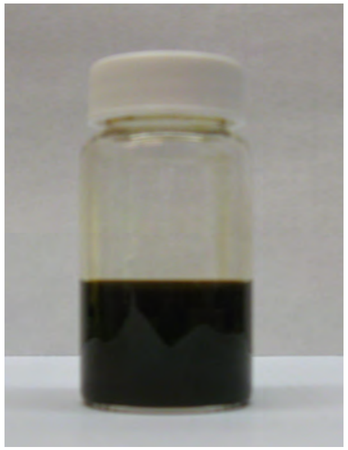
CEINT

Synthesis of Silver Nanoparticles Using Environmentally Friendly Dispersant

Yingwen Cheng and Jie Liu
Department of Chemistry, Duke University

Evaluation of toxic properties of silver nanoparticles (Ag NPs) is of great importance since they are widely used in products such as food-storage containers and detergents. One prerequisite of such evaluation is getting Ag NPs coated with environmental-friendly capping agents to avoid any side effects associated with chemicals present in the Ag NPs dispersion. To meet such criteria, we prepared Ag NPs using water as environmental benign solvent and gum arabic (also used in beverages) as a dispersant for the nanoparticles. The Ag nanoparticles suspended in water with GA demonstrated long term stability and the size of silver nanoparticles synthesized using GA as dispersant is uniform. This work is important to provide the CEINT team with large quantity of silver nanoparticles coated with non-toxic chemicals to rule out the concern that dispersants used for silver nanoparticles might be toxic.





TEM image and Photo of silver nanoparticles shown on the right.

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Tobacco Plants Take Up Gold(Au) Nanoparticles

Jason Unrine, Lee Newman, & Paul Bertsch (University of Kentucky)

Researchers in the laboratory of Dr. Paul Bertsch (CEINT Co-Investigator at the University of Kentucky) have found that *Nicotiana xanthi* (tobacco) take up 3.5 nm gold (Au) citrate spheres from hydroponic growth medium. Plant growth does not appear to be impacted by the nanoparticle exposure (Figure A) but Syncrotron X-ray mapping and microXANES analysis of the Au (Lα fluorescence) demonstrate that tobacco plants translocate the Au nanoparticles from roots to leaf tissues (Figure B). Recently initiated experiments are examining the potential for trophic transfer of Au nanoparticles between tobacco and its herbivore pest - the tobacco hornworm (Figure C). Although this study was not designed to show effects, one is able to see clear signs of marginal necrosis on the plants that were exposed to gold nanoparticles.

During these experiments it was also discovered that 18 nm Au sphere were not taken up by the tobacco plants although they were found to accumulate at the root surfaces. Currently Bertsch's group is performing a similar study with three intermediate sizes of nanoparticles.

Figure A

Figure B

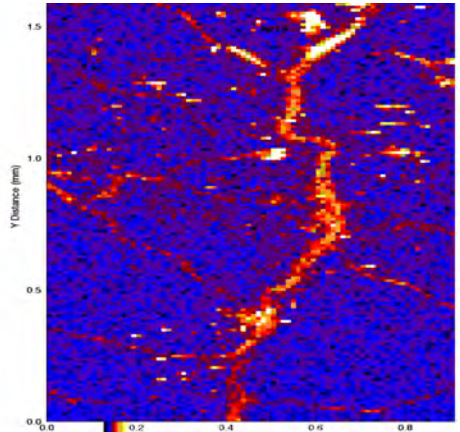


Figure C

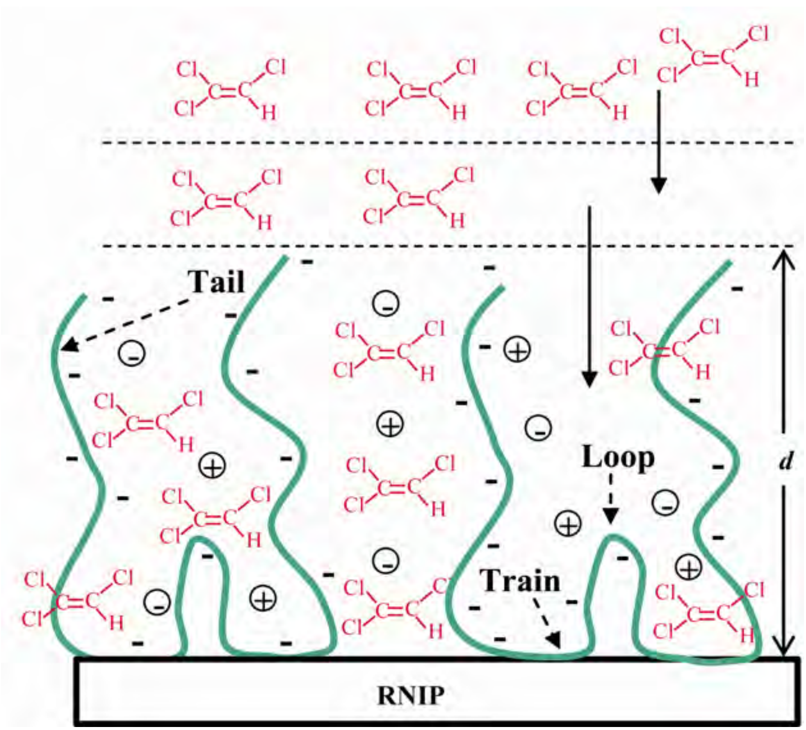
Understanding the Effect of Adsorbed Organic Macromolecules on Nanoparticle Reactivity

Tanapon Phenrat, Robert Tilton, Greg Lowry (CMU)

CEINT researchers from CMU provide a mechanistic understanding of how adsorbed polyelectrolyte (a designed particle surface coating) affects nanoparticle reactivity with environmental contaminants.

Most nanomaterials are manufactured with a surface coating for functionality, or will acquire a coating (e.g., natural organic matter) in the environment. These coatings affect their mobility and reactivity. Understanding the effect of such coatings on nanoparticle reactivity is essential for understanding the environmental and ecological risk of nanoparticles.

CEINT researchers proposed a mechanistic model describing the effect of surface coatings on Fe^0 nanoparticle reactivity with organic contaminants. Reactive site blocking by adsorbed polymer and a decrease in the availability of contaminant at the nanoparticle surface both decrease reactivity. This model should also apply to adsorbed natural organic matter. This work has been recently published in the journal, *Environmental Science and Technology.*



❖ Citation: Tanapon Phenrat, Yueqiang Liu, Robert D. Tilton and Gregory V. Lowry. Adsorbed Polyelectrolyte Coatings Decrease Fe^0 Nanoparticle Reactivity with TCE in Water: Conceptual Model and Mechanisms. Environ. Sci. Technol., 2009, 43 (5), pp 1507–1514

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