Nanomaterials and the Environment: The Chemistry and Materials Perspective

June 28th and 29th, 2011
Arlington, VA

Workshop Report
Appendix D
(Participant Contributions)

http://nsfenv-nano.chem.wisc.edu/
August 26, 2011

This workshop was supported by the National Science Foundation under grant CHE-1138118 to the University of Iowa. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the participants and do not necessarily reflect the views of the National Science Foundation.
Participants were asked to provide input through a three-slide presentation focused on areas related to:

Slide 1 – Research activities relevant to nano/environment of their own research;

Slide 2 – Provide a summary of the most important research challenge(s) at the intersection of nanotechnology and environmental science;

Slide 3 – Identify opportunities for chemists to contribute to molecular-level science at the nano/environment interface. What are the high-impact opportunities?

Power-point slides were solicited from all participants. In this appendix we have included only those slides for which we were able to obtain explicit approval from the participants to release publicly as part of the report.

This document and the entire workshop report can be downloaded from the Nanomaterials and the Environment Workshop website at http://nsfenv-nano.chem.wisc.edu/

Vicki H. Grassian, Workshop Co-Chair
University of Iowa

Robert J. Hamers, Workshop Co-Chair
University of Wisconsin
Research Activities:
To examine the transport behavior, degradation, and effects of metal-based nanomaterials in soil and biota:

1) Characterize interaction between natural organic matter and nanomaterials, and how these interactions influence stability and mobility in the environment.

2) Determine the bioavailability of nanomaterials to soil biota (e.g. earthworm) and plants (food crops), at various environmental conditions.

Research Challenges:
Understand the mechanism of internalization and translocation in plants.

Arabidopsis thaliana

* No obvious internalization
* QDs are visibly aggregated
Figure 2. Different analytical techniques that will be used to provide complementary information to better understand the mechanism of ENM uptake, translocation, biotransformation, and accumulation by fresh food crops.
Reduction of contaminants in aqueous solution by iron metal-core/oxide-shell NPs (D.R. Baer, R. L. Penn, P. G. Tratnyek & team)

- Impact of particle characteristics on reaction rates and reaction pathways
- Particle transformation/aging
- Designing particles to optimization of particle properties (synthesis method, process, and additions)
- Impact of environment (pH, solution composition (e.g. NOM)) on particle aging and reacting properties

Impact of environment on formation, stability and aging of ceria NPs (D. R. Baer, S. Seal, J. Pounds and teams)

- Influence of solution conditions/composition on particle chemical state and time dependent properties

Important challenge(s)

- Understanding and predicting chemical properties and the transformations of NPs in their environment
- Design of particles with predictable properties and environmental fate for environmental remediation
- Nucleation and growth of nanoparticles and films in environmental conditions
- Accurate characterization of NPs in real environments and procedures for ex situ characterization combined with knowledge about their properties (structure-function relationship)
- Influence of pores and nano-features on nucleation, growth and sorption behaviors of surface in the environment
- Surface enrichment/elemental segregation/sorption on NP properties (in ground water and aerosols)
Alternative formulation of challenges

Understanding nano-objects as dynamic entities whose physical and chemical structures, atomic and molecular composition and organization vary with previous history and environmental conditions.

Predictions and understanding the chemical and physical properties and fate of nano-objects as they move through the environment and time.

Developing and applying the tools and analysis protocols to adequately characterize nanostructure objects to enable appropriate characterization (in situ and ex situ) to facilitate structure-function relations and property prediction.

Understanding the physico-chemical processes that occur in nano-pores that influence processes such as sorption, dissolution, nucleation.

Greatest opportunities you see for chemists to contribute to molecular-level science at the nano/environment interface

• Understanding the relationships of surface functionality and environment to properties and behaviors of NPs in the environment
• Predicting the fate and transformations of nanosized materials as they move through the environment
• Developing methods and protocols for appropriate characterization of nanoparticles
Research Activities at the U of R

Overview:
• Linkage of physicochemical properties of nanoparticles to toxicological effects in the pulmonary, cardiovascular, and central nervous systems.
• Biokinetics of nanoparticles as a function of route of administration and particle properties.
• Better understanding of susceptibility (impact of existing inflammation, vulnerability due to underlying disease) as it relates to the effects of ambient and engineered nanoparticles.

More Specifically:
• Development of adequate exposure models (better descriptions of exposure and dose).
• Outcomes (mechanisms of oxidative stress and inflammation).

Important Research Challenges

• How do you characterize nanomaterials in the state in which they accumulate in the environment (air, soil, water)?
• How could the transport of nanomaterials be monitored more carefully in the environment?
• How does one describe exposure and dose (in what compartment? using what metric?)?
• What is the relationship between dose and response outcome and what mechanisms are important?
High-impact Opportunities

• Improvements in collection/sampling methods
• Improvements in analytical tools
• Development of better labeling techniques for nanomaterials to be used in transport studies
• Development of instrumentation that allows the sampling and measurement of several parameters at once in real time or near-real time
• Develop and validate models that describe dose to the target
• Relate target dose to response and response mechanisms

NSF Nanomaterials and the Environment Workshop, June 28-29, 2011
Alison Elder, PhD, University of Rochester
Research Focus

Tori Forbes, University of Iowa

The long-term goal of my research program is to determine the structural characteristics of small (1-5 nm) inorganic nanoparticles and construct a model for contaminant adsorption to the surface of these particles.

1. Synthesis and structural characterization of nanocluster-based model compounds.

2. Perform PDF analysis of small nanocolloid/nanoparticles and amorphous materials to investigate structural similarities to various structurally characterized compounds.

Research Challenges and Opportunities

1. The structural characteristics of small (1-10 nm) nanoparticles: How can we structurally characterize small nanoparticles? What is their relationship to amorphous/colloidal/poorly-crystalline materials? Can we use the structural features of small nanoparticles to gain an understanding of surface structures?

2. The structural characteristics of nanoparticle surfaces: The homogeneous versus heterogeneous nature of nanoparticle surfaces is a key area that needs to be addressed to accurately describe nanoparticle surfaces. Do we see size dependent changes in surface features? Can we structurally characterize the restructuring of the anhydrous nanoparticle surface on exposure to water? How do we accurately describe the adsorption of water on the surface of nanoparticles? How do we accurately characterize a heterogeneous surface?

3. Precipitation and growth of nanoparticles: Are non-classical mechanisms for precipitation important for nanoparticles? Are other systems (oxides, phosphates, silicates) also influenced by the formation of prernucleation clusters? How do structural transformations occur? What are the driving forces behind structural changes?
Research Challenges and Opportunities

4. **Intersections of biology and nanomaterials**: Biological systems can precipitate or alter various mineral phases with amazing nanoscale control. How do biomolecules change/direct structures and surface features? Do biomolecules stabilize prenucleation clusters?

5. **Changes in nanoparticles upon environmental release**: The introduction of engineered nanoparticles in environmental systems brings about interesting questions in regards to how these materials react in a variety of environmental systems. Many of these materials were synthesized under very specific conditions (non-aqueous solvents, embedded within resins, incorporated into fibers) that may degrade in the environment. What is the retention and stability of engineered nanoparticles? Does the presence of capping agents or functionalized nanoparticle surfaces impact transport in environmental systems? Do catalytic nature of certain engineered nanoparticles impact processes in the environment?
Experimental Assessment of Metal Ion Speciation at Environmental Interfaces for New Electrical Double Layer Theories. 


Stereochemistry in Heterogeneous Atmospheric Oxidation Pathways Important in Tropospheric Aerosol Chemistry and Physics. 


Molecular Spectroscopy of Size-Resolved Secondary Organic Aerosol Particles from Tropical and Boreal Forests. 

Image Credit: ACP, in Review (2011)

Molecular Structure of Organic Species on the Surfaces of Engineered Nanoparticles for Predicting their Coupling to the Environment. 


Predicting Metal Ion Coverages, Interaction Energies, and Electrostatics in Interfacial vs. Bulk Environments with Optical Voltammetry. 


Discovery of Molecular Chirality in Aerosol Particles from the Central Amazon Basin in the Climate-Relevant Fine Mode. 

Image Credit: PCCP, Advance Article (2011)

GEIGER: Five Challenges for Nano-Environmental

1) How important is the env'tl endpoint?

2) Why is nano important? Everybody knows it's colloid chemistry, and that has not changed. The molecules matter, not nano.

3) Where to publish? ACS etc? AGU etc? NPG etc? How do we get ACS publications read in the Earth Sciences community? Do they need to?

4) How do we foster international collaborations on projects that most commonly require only one or two months of student support to go abroad to a field site or a special laboratory?

5) How does a lab/field/model study link up to the climate system or cleanup at the legacy sites? Should it?
GEIGER: Opportunities for molecular-level science

1) Let’s ask “what is the chemical origin of the effect that I am seeing?” It’s a great opportunity for basic science.

2) To do this, we need new tools and ask the hard questions. Molecular studies claimed to be of relevance to the environment should be performed using \textit{environmentally relevant samples, conditions, and model systems}. Many of us are do not apply that standard, so the area is wide open.

3) How to link up w/ SEES? Some connections are obvious, some aren’t. (n.b.: NSF established the \textit{Science, Engineering, and Education for Sustainability (SEES) investment area in FY 2010 in order to promote the research and education needed to address the challenges of creating a sustainable human future}.)

4) We need opportunities for cross-cutting student training & a \textit{SEES postdoc program} that funds 10 postdocs a year - use the NOAA postdoc program as a model b/c of its follow-through.
Research Activities

Geochemistry and biogeochemistry of natural nanoparticles
   Bioavailability of ferric iron (oxyhydr)oxide nanoparticles

Reactions of redox-active nanomaterials
   Subnanosecond studies of electron transfer pathways during redox reactions

The structure of disordered nanoparticles
   Interior and surface defects affecting chemistry

Chemistry and colloidal properties of silver nanowires in aqueous media
   Informing mode-of-action research for Daphnia nanotoxicity

Research Meta-Challenge

What to study?
   What materials? The nanotech revolution will not be based on sunscreen
   What context? Do we now have paradigms for environmental impacts of NM to guide research?
   Only through collaboration will basic chemistry research be most relevant to NM impacts

Research Challenges

Redox-active nanomaterials, and NM that perform catalytic roles in environmental or biological systems.
   E.g., CeO₂: Cycling of Ce redox state can catalyze oxidative organic transformations in the environment and buffer oxidative stress in cells.

Elucidating the most important chemical species – often low concentration, difficult to monitor
   E.g., Do NM interact with biological systems through surface chemistry, or the products of dissolution or chemical transformation?

Chemical transformations of nanomaterials in environmental or biological systems
   Many aspects of inorganic NM toxicity are related to metal chemistry but there are severe challenges observing surface and solution metal speciation in complex aqueous media.
Opportunities for High-Impact Science

1: Fundamental studies of nanoparticle properties relevant to many fields, including environment impact but also biotechnology, energy research, etc.

- Experimental & simulation studies of the near-surface chemical environment of NM in complex aqueous media.
  - adsorption of species (‘protein coronas’?) that may invert surface charge and affect transport
  - controls NM aggregation, organismal and cellular uptake
  - can we experimentally visualize the dynamic counterion clouds around NM?
  - can we obtain models of NM-biomolecule interaction, using concepts of aqueous complexation and surface adsorption?

- Atomistic studies of nanoparticle structure.
  - without structure there is no insight into chemistry
  - only one example of a full-nanoparticle structure refinement inc. surface structure and ligand (single crystal diffraction)
  - can we predict nanoparticle structure by molecular simulations of nucleation and growth?

2: Studies that discover/predict mechanisms for severe nanomaterial impact, requiring collaboration with toxicologists, environmental scientists, etc. Potential for regulatory input.

Nanomaterials often combine several distinctive transport and chemical properties that together can cause significant impact. E.g., ZnO nanoparticles are highly toxic: Small size can lead to organism and cellular uptake, followed by complete dissolution and Zn\textsuperscript{2+}(aq) release. Is this pathway more broadly relevant? What are other examples of specific impact?

- What chemical properties of NM may lead to long-term bioaccumulation and persistent toxicity?
  - Do highly reactive nanomaterials (e.g., zero valent iron) or relatively inert (e.g., TiO\textsubscript{2}) actually exert most profound environmental impact?
SLIDE 1: Research Activities Relevant to nano/environment

Vicki H. Grassian, Workshop Co-Chair, University of Iowa

1. Fate and transformation of metal and metal oxide nanomaterials including TiO₂, ZnO, Ag and Cu in aqueous environments.
   – State of nanoparticles: the roles of size and surface chemistry in dissolution and aggregation.

2. Size-dependent properties of iron oxyhydroxy minerals in aqueous environments.
   – Importance of size in iron bioavailability, role of atom exchange in Fe cycling (in collaboration with Michelle Scherer, Civil and Environmental Engineering).
   (see Rubasinghege et al. PNAS 2010, 107, 6628-6633)

3. Atmospheric chemistry of metal oxide nanoparticles with trace atmospheric gases including SO₂, HNO₃ and O₃ as a function of relative humidity and solar light.

4. Inhalation toxicity of metal and metal oxide nanomaterials (in collaboration with Peter Thorne and Patrick O'Shaughnessy, Environmental and Occupational Health).

SLIDE 2: Summarize the most important research challenge(s) that you see at the intersection of nanotechnology and environmental science.

Vicki H. Grassian, Workshop Co-Chair, University of Iowa

1. In the applications of nanomaterials, it has been shown that there are size dependent properties that do not simply scale as size (simple scaling would include e.g. changes in surface area and volume). These properties include electronic properties (quantum dots) and catalytic activity as well as selectivity (gold catalysis). Additionally, catalysis of nanomaterials of specific surface planes show enhanced activity (see Lee et al. Nature of Materials 2009, 8, 132-138).

   Research Challenge: Are these non-scaling, size-dependent and surface-specific structural properties important in environmental processes?

2. Measuring detailed surface and bulk structure and composition under environmentally relevant conditions (in air, water and soil).

   Research Challenge: What is the most promising approaches for further development, what is the best approach for technique development?
SLIDE 3: Identify what you see as the greatest opportunities you see for chemists to contribute to molecular-level science at the nano/environment interface. What do you see as the high-impact opportunities?

*Vicki H. Grassian, Workshop Co-Chair, University of Iowa*

Chemists, with their ability to synthesize monodispersed nanomaterials as well as their ability to provide unique state-of-the-art experimental and theoretical methods to understanding these materials, should be using this arsenal to measure “environmentally relevant” properties as a function of size and shape. Surface specificity of these properties need to be understood given the large surface to volume ratio of nanomaterials and the unique properties of nanomaterial surfaces. There are great opportunities for chemists to contribute to:

1. Careful size and shape dependent studies of engineered nanomaterials and other nanoscale particles important to the environment (e.g. redox properties – see Ivanova and Zamborini. J. Am. Chem. Soc., 2010, 132, 70–72 and melting – see Pan et al ACS Nano 2011 ASAP article DOI: 10.1021/nn200252w).
2. Characterizing nanomaterials and their surfaces beyond standard methods to gain additional insights into structure, reactivity and unique behavior (see – Geiger Ann. Rev. Phys. Chem. 2009, 60, 61-83)
3. Furthering our understanding in important ways - under what conditions does the core of the particle matter and under what conditions does the surface matter in environmental processes.
4. Designing integrated experimental approaches that combine state-of-the art measurements taken from surface science and chemistry, solid state and materials chemistry, colloid and aerosol chemistry along with studies of molecular mechanisms of toxicity and biological interactions is needed to understand implications of nanomaterials. This suggests an interdisciplinary team approach for these types of studies.
5. Furthering the use and development of techniques to measure nanomaterials in complex media.
6. Determining how surface functionality impacts the stability of nanomaterials and delineating the details of the surface adsorption process (such as the mode of adsorption, reversibility of adsorption and possible displacement reactions that can occur).
7. Identifying various reaction mechanisms that nanoparticles can undergo in the environment so as to better understand transformations that are most likely to occur.
Research Activities relevant to nano/environment

Robert Hamers, workshop co-chair, University of Wisconsin

How do the size, shape, and surface functional groups of nanoparticles impact bioavailability/toxicity?

Synthesis of nanoparticles with controlled sizes and shapes (nanocarbon, metal oxides) and well-defined surface ligands


Characterization of how surface ligands impact bioavailability, toxicity


Characterization of environmentally-induced changes in nanoparticle chemistry and structure


Direct toxicity vs. indirect toxicity (e.g., photochemical generation of ROS species)

(Primarily in collaboration with Joel Pedersen, Richard Peterson, Warren Heideman)

Near future (hopefully!)

Molecular-level origins of toxicity, sublethal/transgenerational effects

- How do peptides/proteins interact with nanoparticles?
- How do nanoparticles impact protein conformation?
- Are there identifiable biomarkers of nanoparticle exposure?
- Can one predict specific protein sequences that are most likely to bind to nanoparticles?

Top Research Challenges:

1. Nanomaterials bring new mechanisms of bioavailability and transport into living organisms. To understand the environmental impact of nanomaterials we need to understand how biological molecules and biological systems respond to nanomaterials. Even at low concentrations nanomaterials may induce long-term impact by affecting gene expression, cell signaling, protein folding. To understand the full impact of nanomaterials we need to fully understand how nanoparticles interact with the many complex molecules within living organisms and how both nanoparticle and biomolecules are affected by the presence of the other.

*Research challenge: How can we rapidly identify the most important nanoparticle-biomolecule interactions in complex nano-bio systems?*

2. Nanoparticle toxicity may be strongly affected by environmental degradation/alteration processes. We have very little understanding of these processes.

*Research challenge: How can be develop, implement, and validate laboratory-based methods that will be effective predictors of how the environment impacts nanomaterials and how nanomaterials impact the environment? Need a systems-based approach.*

Hamers 1/2
Opportunities for chemists? High-impact opportunities

Extend techniques of molecular biology (e.g., phage display, etc.) to rapidly identify and characterize nanoparticle-biomolecule interactions as a first-line screening method for potential toxicity.

Develop multi-scale computational methods able to characterize nanoparticles interacting with biomolecules in aqueous environment, with laboratory-based validation.

Develop, implement, and validate laboratory-based assays that mimic environmental conditions characteristic of specific locals (soils, water, littoral, oxic, anoxic...) to assess influence of environment on nanoparticles.

Identify how size, shape, and surface chemistry of nanoparticles impact bioavailability (fat-soluble, water-soluble, etc.) and concentration effects within food chain.

Identify how to make nanoparticles with specific properties of interest (e.g., absorptive, catalytic, etc.) but with reduced potential for adverse impact by manipulating the surfaces and/or bulk structure/composition.

Develop new instrumentation able to fully characterize the chemical composition and structure of nanoparticles in complex environments.

Develop nanoparticle-based catalysts able to initiate specific chemical reactions to reduce overall use of energy (esp. fossil-fuel), avoiding environmental damage associated with existing approaches.
IRG2-3 (Holden): Mechanisms (bacterial); Outcomes (populations, communities, ecosystem)
Important Challenges

• Discern “NP effects” and their origins at cellular level (i.e. distinct from, or in concert with, specific ion effects)
• Understand roles of surface vs. core chemistry in cellular effects / responses.
• Understand dynamic nature of surface chemistry, particularly as it related to cellular effects / responses.
• Understand biological response as a factor in uptake and effects.
• Mathematically operationalize effects / responses at population level, and project for wide NP spectrum.
• Build capacity to recognize paradigms and avoid erroneous conclusions; strategically select research path to achieve.

Opportunities for Chemists

• Characterization and function
  – Reactivity and relationship to characteristics (surface, core)
  – Stability (against dissolution, agglomeration) under environmentally-relevant conditions
• Directed synthesis of NMs for specific hypothesis testing:
  – NP effect vs. solute effect; test w/ biologists
  – Electronic interactions (band gap modification)
• Research collaboratively w/ biologists
  – Design experiments to test hypotheses using materials from directed synthesis.
  – Simultaneously quantify biological and NM transformations
  – Build theoretical basis for cellular effects; build QSAR-level understanding.
Research Activities

Toxicity Assessment Before and After Chemical Functionalization

Ga Concentration Following Soaking of GaN Wafers in 1.5 mL Aqueous Solutions for 7 Days

<table>
<thead>
<tr>
<th>Solution</th>
<th>Gallium Concentration (ppb) by ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>3.68 +/- 0.54</td>
</tr>
<tr>
<td>10% H₂O₂ in saline</td>
<td>3.52 +/- 1.65</td>
</tr>
<tr>
<td>pH 5 Acetic Acid</td>
<td>24.84 +/- 3.01</td>
</tr>
<tr>
<td>pH 9 Tris Base</td>
<td>45.19 +/- 31.41</td>
</tr>
</tbody>
</table>

Ga concentration in drinking water is ~5 ppb\(^6\).


Challenge(s)

- Correlate stability under different environmental conditions with bio-recognition properties
- Understand the role of chemical stability of nanoscopic materials in vitro and in vivo

PC12 Cells on GaN nanowires
Wires grown by Prof. M. Manfra (Purdue University)
Opportunities

Development of new analytical methods and/or techniques to correlate stability, toxicity, and chemical reactivity with bio-recognition properties.

General approach used by many...

PBS solution
Rinse
Receptor PEG Ligand Tagged BSA Tagged 2nd Ab
PBS solution
Rinse
Fluorescence Microscopy

Albena Ivanisevic

NC STATE UNIVERSITY
Research Challenges in Atmospheric Nanoparticle Chemistry

**Significance:**
- New particle formation influences global climate change by producing cloud condensation nuclei (CCN).
- Inhalation is a key mode of exposure to airborne toxic nanomaterials.

**Important research questions:**
- What is the chemical mechanism for "stable cluster" formation (~1 nm)?
- How do clusters (~1 nm) grow into nanoparticles (~3 nm)?
- Is cluster formation and growth different for ions and neutrals?
- How do nanoparticles grow into the CCN size range (1 nm → 10 nm → 100 nm)?
- What are the sources of primary nanoparticles and how do they grow into the CCN size range?
- What are the chemical and morphological factors that determine whether a particle in the 50-100 nm size range grows by uptake of water?
- How do nanoparticles deposited in the respiratory tract cross biological barriers?
- What are the relative roles of chemical composition and morphology in determining inhaled nanoparticle toxicity?

Figure reproduced from: "Analytical Atmospheric Chemistry", T. Hoffmann et al., Anal. Chem. (2006) article ASAP.

Johnston 1/2
### Opportunities for Chemists in Atmospheric Nanoparticle Chemistry

**Opportunities for Chemists:**

**Instrumentation**
- In-situ chemical characterization of nanoparticles at low concentrations (1000 cm⁻³)
- On-line chemical characterization of nanoparticles in the 1-10 nm size range
- Adapt so-called “inlet ionization” MS methods (developed for biomolecular assemblies) to environmental nanoparticles
- Methods for characterizing neutral clusters and nanoparticles
- Methods for determining morphology

**Computational Chemistry**
- Accurate and precise thermochemical calculations for large neutral clusters

**Important research questions:**
- What is the chemical mechanism for “stable cluster” formation (~1 nm)?
- How do clusters (~1 nm) grow into nanoparticles (~3 nm)?
- Is cluster formation and growth different for ions and neutrals?
- How do nanoparticles grow into the CCN size range (3 nm → 10 nm → 100 nm)?
- What are the sources of primary nanoparticles and how do they grow into the CCN size range?
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- How do nanoparticles deposited in the respiratory tract cross biological barriers?
- What are the relative roles of chemical composition and morphology in determining inhaled nanoparticle toxicity?
Environmental NanoChemistry Laboratory (The Jun Group)

Research topics

- Chemical kinetics, thermodynamics, and mechanisms of environmental interfacial reactions at nanoscale.
- Nucleation, growth, and aggregation of oxide nanoparticle formation with/without impurity metals and/or organic compounds.
- Structures and reactivities of nanoscale oxide films and environmental nanoparticles, and their environmental impacts.
- Water reuse and water quality: Heavy metal or other hazardous contaminant adsorption and incorporation to iron or manganese (hydr)oxides nanoparticles.
- Biomineralization and bio-inspired chemistry: Development of nanoparticles for remediating contaminated water and soils.
- Nanoscale control for CO₂ sequestration to mitigate climate changes.

Interdisciplinary Approaches:

**Synchrotron-Based Techniques** at national synchrotron facilities (X-ray scattering, spectroscopy, and diffraction)

**Various Surface Chemistry Techniques**, such as AFM, HR-TEM, SEM-EDX, and XPS with **Aqueous Chemistry** (ICP-MS, DLS, and IC) with **Reactive Transport Modeling**.

PI: Young-Shin Jun (ysjun@seas.wustl.edu)

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Probing the Chemical Evolution of Nanoparticles *In Situ* at Environmental Interfaces: Examples from the Jun research group

**Simultaneous SAXS/GISAXS**

SAXS yields shape, size and inter-particle distance of small clusters in solution.

GISAXS yields the same parameters at the mineral-water interfaces.

**Nanoparticle nucleation and growth on quartz**

Drying effect on the iron oxide nanoparticles

Dehydration can promote facet formation of nanoparticles

Nucleation and growth in confined nanopores

Competition between the hindrance of nucleation due to interfacial energy between nuclei or the reduction of the activation energy of nucleation due to surface contribution.
Probing the Chemical Evolution of Nanoparticles *In Situ* at Environmental Interfaces: *Examples from the Jun research group*

Under extreme environments such as high pressures and temperatures, how can we measure non-equilibrium intermediate mineral phases and visualize their morphological changes?

Example: CO$_2$ sequestration (left), nuclear waste disposal, seawater encroachment, and aquifer recharge.

Can we develop sensitive probes to detect *in situ* the concentration and pH gradients at nanoscale interfaces?

**Grand challenges and opportunities in molecular-level science at the nano/environment interface:**

- How can we determine the structures of the precursors of amorphous (intermediate) phase formations? How will different structural complexities affect the reactivity?
- How can we successfully observe the real-time evolution of nanoparticle distributions and topology at an active interface without dehydration?
- How do confined nanopore spaces affect nanoparticles’ nucleation and growth under diverse environmental conditions?
- How can we track simultaneous dissolution and precipitation reactions of minerals in water? Metal concentrations and pH gradients from the mineral surfaces continuously generate complexity in experimental environments: how can we elucidate these complexities and their effects on chemical reactions? Can we develop sensitive probes to detect *in situ* the concentration and pH gradients at nanoscale interfaces? How can we monitor the reaction with sufficient temporal resolution and efficiency to permit observations of electron transfer?
- Under extreme environments such as high pressures and temperatures, how can we measure non-equilibrium intermediate mineral phases and visualize their morphological changes?

Young-Shin Jun (ysjun@seas.wustl.edu)
**Nanotoxicology: The Asbestos Analogy Revisited**

Direct injection of lung multiwalled carbon nanotubes into the abdominal cavity of mice produces asbestos-like pathogenic behavior. What does this finding mean for nanotube safety?

Determinants of pathogenicity of high aspect ratio nanoparticles:

- **Length**
- **Biopersistence**
- **Surface reactivity**

**Biological consequences of frustrated phagocytosis:**
- Incomplete uptake by macrophages and impaired lung clearance
- Incomplete sequestration in lysosomes → cell death by apoptosis
- Activation of the inflammasome → proinflammatory cytokines
- Altered cytoskeletal function and impaired secretion
- Disruption of mitosis and cytokinesis

**FE-SEM of MWCNTs**

Shi, Von Dem Bussche, Hurt, Kane, Gao, submitted

**Macrophage Activation and Granuloma Formation**

Sanchez et al. Particle Fibre Toxicol. 8:17, 2011

Agnes Kane and Robert Hurt
Brown University

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**Research Challenges at the Nano Bio Interface**

Environmental Science
- rapidly growing data base on fate, transport, and transformation
- less information on environmental impacts of nanomaterials throughout their life cycle
- limited information on ecosystem impacts

Nano Bio Interface
- rapidly growing database in nanotoxicology using prokaryotic and eukaryotic cells
- less information on impact on whole organisms using systems biology, pathology, and toxicogenomics
- limited information about nano bio interactions at the molecular level

Need to establish general principles that integrate physicochemical properties of nanomaterials with biological effects on target molecules, cells, organisms, and ecosystems.

Agnes Kane and Robert Hurt
Brown University
Understanding the Nano Bio Interface at the Molecular Level

1. How do nanoparticles cross biological barriers?
   - Metal oxide nanoparticles and single-wall carbon nanotubes are trapped in the mucus layer:
     - Steric hindrance by pore size of mucus
     - Adhesion to mucin fibers

2. How do target cells recognize nanoparticles?
   - Pattern Recognition Receptors

3. How do nanoparticles interact with subcellular organelles?
   - Release of trace metals from carbon nanotubes block voltage-gated calcium ion channels in neurons

Adapted from Lai et al., Adv Drug Del Rev 2009
Jachek A. et al., submitted
Jakubek et al., Biomaterials, 30: 6351, 2009

Seong and Matzinger, Nat. Rev. Immunol. 4:468, 2004
Agnes Kane and Robert Hurt
Brown University
Current Research Activities:

- Effects of iron hydroxide nanoparticle aggregation on:
  - Metal adsorption/desorption
  - Sorbed metal speciation
  - Metal bioavailability

- Impacts of particle size on physical and chemical properties of mine wastes
  - Toxic metal concentration, speciation
  - Bioaccessibility via ingestion, inhalation

Research Challenges:

1. Thermodynamic vs. kinetic influences on nanoparticle reactivity
   - Size-property relationships not yet established for many nanomaterials
   - Challenges distinguishing between intrinsic properties, kinetic effects, and surface area dependencies
   - Can the intrinsic reactivity of nanoparticles be reliably defined and measured?

2. The nanoparticle-water interface
   - Newer experimental methods of describing hydrated mineral surfaces cannot yet be applied readily to nanoparticle surfaces
   - Structure of water at nanoparticle surfaces and within nanopores may influence surface properties
   - What experimental or simulation methods represent the best approach for constructing models of the hydrated nanoparticle surface?

3. Nanoparticle mobility
   - Nanoparticles/collids can either facilitate or inhibit mass transport
   - Attachment, aggregation, dispersion, dissolution, precipitation
   - To what extent do nanoparticles transport an important/dominant process in transferring material, redox equivalents, and contaminants between different systems?

4. Aggregation of nanoparticles
   - Environmental occurrence of nanoparticles almost always involves aggregation
   - Different aggregation pathways/extents of aggregation can impact nanoparticle reactivity and properties
   - How can the impact of NP aggregation on accessible SA and reaction rates be quantified?

5. Scalability/complexity of nanoparticles in environmental systems
   - Model systems (computational, benchtop) may not approximate natural reactions at environmentally-relevant time/length/volume scales
   - Natural systems often have more variables than can be easily controlled
   - How can model systems be designed to better represent natural systems when studying NP behavior in ways that are both scalable and address environmental complexity?
Opportunities for chemists--

Medicine
- NP bioaccessibility, bioavailability, toxicity, transport

Geoscience
- Role of natural NPs in fate and mobility of contaminants

Chemistry of nanoparticles
- Aggregation state
- Growth mechanisms
- Morphology
- Phase stability
- Reactivity
- Redox activity
- Size/size distribution
- Solubility
- Surface structure
- Surface area

Atm. Science
- Atmospheric NP formation, fluxes and transport

Comp. Science
- Inclusion of NP mobility into models of environmental cycles

Env. Engineering
- Engineered NPs for environmental remediation

Christopher Kim
Earth and Environmental Sciences
Chapman University
Research Activities

- Atmospheric oxidation of C₆₀ fullerenes by ozone
- Fate of nanomaterials during incineration
- Characterization of emissions and potential exposure from nanosilver spray products and children’s products

Acknowledgments: NSF (CBET, CEINT), EPA; Erin Davis, Amara Holder, Mike Klapmeyer, John Morris, Marina Quadros, Chris Shores, Andrea Tiwari

Research Challenge

LIFE IS MESSY ⇒ How can we predict impacts of nanomaterials in complex environmental matrices?

Physical, chemical, and biological transformations
Catalysis of byproducts
Fate in the environment

Examples:
CFCs, lead, PCBs, phthalates, endocrine disruptors

And it’s even messier in water!
High-Impact Opportunities

• Improve methods for quantification of nanomaterials in complex environmental matrices
• Shed light on which environmental variables are most important, and define a standard set of environmental conditions for experiments
• Develop structure-activity relationships to predict toxicity
New particle formation is one of the grand challenges of the atmospheric chemical nanosciences. New particle formation is the process of transformation from the molecular scale of individual molecules in the gas phase to a condensed-phase material residing as an aerosol particle in the atmosphere. The process of new particle formation ultimately affects a number of important climate and health-related endpoints of human interest. Important examples are the number concentration in the atmosphere of cloud condensation nuclei (i.e., so-called "indirect effect" of aerosol particles on climate) and the number concentration of sub-100 nm particles in urban environments, which have been directly implicated as a human health hazard.

Key chemical questions of new particle formation include:

(1) What are the atmospheric species that participate in new particle formation?

Some candidates in different atmospheric environments include sulfuric acid, ammonia, oxidized organic molecules, and, most recently, amines. Each of these is strongly influenced by human activities at certain times and locations, especially nearby human populations.
(2) **What are the chemical kinetics of nucleation and new particle formation?**

These experiments are very difficult to perform in the laboratory and require specialized expertise and equipment because of the low concentrations involved (i.e., as directed toward atmospheric relevance) and the importance of minimizing impurities and surfaces under laboratory conditions.

(3) **How can the chemical composition of new particles be measured in atmospheric conditions?**

The relevant size range for composition analysis is 1 to 3 nm because these particles are just past the nucleation barrier; chemical analysis of them can therefore provide information of the molecular precursors. The chemical analytical challenges are to collect these particles effectively into an instrument and to analyze the associated mass of these nanoparticles.

**Entry Points into this Field of Research**


First-Principles Modeling of Mineral-Water Interfaces

Mason Group

Differences in Pb(II)/O Bonding on FLAT vs. CORRUGATED Al₂O₃ revealed through DFT charge density
S. E. Mason et al. JPCC 115 p4008 2011
Implication for nanosurfaces: Sites that support directional bonding are a bigger reactivity control than oxygen coordination

Magnetite Fe₃O₄
Mixed Fe(II,III): interesting redox properties, modeling challenges...

Comparative Oxyanion Adsorption Studies on hydrated surfaces of Al₂O₃/Fe₂O₃/MnO₂
Sb(III,V) adsorption and heterogeneous redox
S. E. Mason et al., Under Review
As(III,V) adsorption: Comparing mono, bi, and tridentate surface complex formation energies, adsorption on defected surfaces, describing As/surface bonding through electronic structure

First-Principles Modeling Challenges: Nanomaterials in the Environment

- How do we identity/justify models that are sufficient for a given reactivity question? How do we design and report theoretical research so that results from one lab propagate?

- How do we move into modeling nanominerals/mineral nanoparticles when our understanding of mineral-water interfaces of ideal, single-crystal surfaces is still developing? When do particulate properties matter? When does surface science dominate?

- How do we explore the potential energy surface? How do we decipher the electronic structure?

- How can we build the “next generation” of (semi-) empirical methods for predicting interface stoichiometry/structure? How do we account for the subtle changes in bonding of a collection of atoms?
First-Principles Modeling Opportunities: Nanomaterials in the Environment

- Fully detailed, fully reported, systemic benchmarking and fully reported aspects of structural model geometries
- Make use of 2-D periodic models for point/line defect structures as models for mineral nanoparticles
- “Stand on the shoulders” of the theoretical surface science catalysis community. Design comparative studies in which reactivity factors are independently varied. Employ real-space electronic structure analysis. Don’t stop at reproducing experimental observations, instead aim to explain them.
- Extensions of bond-valence empirical relationships by accounting for directional bonding and bond-valence-based energy models
**In Situ AFM of Clay Mineral Swelling**

Major component of soils/sediments
Swelling (incorporation of interlayer water) affects:
- Contaminant adsorption and transport
- Permeability

Clay mineral particles composed of overlapping layers can be monitored by AFM in an aqueous environment.

Height profiles provide direct measurement of extent of swelling.

**Exchange of Na⁺ for K⁺**

Challenge: Predicting Mobility of Nanomaterials in Soils/Sediments

Nature of interactions with soil particles dependent on many variables
- particle size/charge
- surface coatings, adsorbed species
- composition, pH, ionic strength of aqueous phase

Aggregation affected by adsorption on clay minerals and/or natural organic matter (NOM).

Environmentally relevant properties (e.g. anti-microbial activity) may not be affected by adsorption → reservoir of reactive nanoparticles.
Opportunities for Chemists in Nano/Environment

Deciphering complex relationships between chemical interactions and physical properties of soil and nanoparticles

Chemical interactions

Adsorption → Swelling → Permeability/ pore size

Physical changes in soil properties

Nanomaterial mobility

Physical size/shape effects

McGuire
Alexandra Navrotsky, UC Davis, Research
Thermochemical stability of nanoparticles, their surfaces and interfaces, and their hydration and transformation (unique calorimetric approach)
Transformation of nanoparticles in the environment
Large thermodynamically driven shifts in redox and other phase equilibria at the nanoscale
Example: Fe – O phase diagram (Navrotsky et al. Science 330, 199 (2010))

Research Challenges

• Identifying nanoparticles, their sources, and transformation products in the environment
• Understanding nanoparticle surfaces and reactivity, separating thermodynamic from kinetic factors
• Nanoparticle interactions with organics and with living matter, including toxicity, bioavailability, transformation
  – A. Navrotsky
Molecular Frontier: Opportunities for Chemists

- Nanoparticle surface structure and dynamics by spatially and temporally resolved spectroscopic techniques. Isotopic and elemental analytical techniques with nanoscale resolution.
- Analytical techniques applied to environmental settings.
- Tracing the molecular evolution of aqueous systems from dissolved species to clusters, to nanoparticles, to bulk precipitates, and back again.
- Molecular basis of organic and biological interactions with nanoparticles.
- **Strong interaction with geochemistry community.**

— A. Navrotsky
Research activities relevant to nano/environment
Galya Orr, Pacific Northwest National Laboratory

Tying Distinct Nanoparticle Properties to Cellular Interactions, Fate and Response

1. Identify molecular interactions that mediate the internalization pathways and intracellular fate of bare and surface modified nanoparticles in alveolar epithelial cells.

2. Determine the impact of aerosolized nanoparticles in alveolar and bronchial epithelial cells at the air-liquid interface to better mimic in vivo exposures to inhaled nanoparticles.

3. Identify the role of nanoparticle dissolution in toxicity at the respiratory tract by focusing on aerosolized ZnO nanoparticle exposures at the air-liquid interface.

Important research challenge(s) at the intersection of nanotechnology and environmental science (Galya Orr)

The cellular interactions and fate of the nanoparticles, which dictate the cellular response and ultimately the impact on human health, are governed by the physical and chemical properties of the particle.

These properties are modified not only by the external environment but also by the biological environment. Inhaled nanoparticles change as they enter the respiratory tract, reach the alveolar region and penetrate distinct cells and organelles.

This transformation, which is determined by the tissue-, cell- and organelle-specific molecules, is critical for delineating the relationships between particle properties and toxicity or biocompatibility.
High-impact opportunities for chemists to contribute to molecular-level science at the nano/environment interface (Galya Orr)

Characterize nanoparticle properties that are relevant to the investigated tissue, cell and organelle to enable drawing accurate relationships between particle properties and cellular response.

Establish approaches for predicting particle properties within distinct biological environments to support predictions of particle destination and fate and the consequent response.

Simulate the biological environment to investigate changes in nanoparticle properties over time, which will enable predicting the target tissue, cells and organelles.

Focus on protein coronas that are typical to distinct tissues/organs; pH that is typical to distinct organelles; aggregation/agglomeration size that will determine internalization and trafficking mechanisms; charge that will determine interactions at the cell surface.

Links between chemical reactivity and nanoparticle properties (e.g., size, shape, composition, microstructure, phase)

Aggregation kinetics and reversibility

Crystal growth mechanisms

Characterization of natural nanomaterials

NEW to our group - nanecotoxicology

Research Challenges

• Characterizing nanoparticles in general
• Characterizing natural nanomaterials
• Characterizing (and detecting) anthropogenic nanomaterials collected from the environment
• Understanding how nanoparticles change in response to dynamic and reactive environments
• Understanding particle-particle interactions as well as particle interactions with other species in environmental systems
How can Chemists contribute?

- First and foremost – COLLABORATING with Earth and environmental scientists
- Quantitatively characterizing surface chemistry (spectroscopic methods)
- Characterizing short-lived adsorbates and intermediates (e.g., species residing at the solid-liquid interface for short times)
- Detecting chemical and structural changes in solid nanomaterials
- Application of molecular kinetics to understanding reaction mechanisms
- Detecting exceedingly small “concentrations” of anthropogenic nanomaterials in environmental systems
- MODELING
Metrology and Nanoremediation

● **Novel Metrology Tools for ENMs**
  - CID - Capture, Isolation and Detection of Nanoparticles (JEM, 9, 657-665, 2007; JEM, 11, 1782–1800, 2009)
  - Electrochemical Sensors for Ag-NPs and Carbon Nanotubes (JEM, 9, 1154, 2007; Biosensors & Bioelectronics 24, 2749-2765, 2009)
  - Size-exclusive nanosensor for fullerene (EST 45, 5295-5300, 2011)

● **Nanoremediation Materials**
  - Reduction of Cr(VI) to Cr(III) using PAA and PdNPs (Applied Catalysis B Environmental, 76, 158-176, 2007)
  - Provide conversion at 99.98% efficiency (ACS Catalysis, 1, 139-146, 2011).
  - Exhibit spatio-selective via 3D binding interaction with ENMS
  - Allows controlled porosity with size between 2.8 - 50nm.


Research Challenges

● **Diversity**: Complexity of environmental or biological matrices. Diversity of the engineered nanomaterials. Size, shape, morphology, porosity

● **Sample preparation**: Need to separate, pre-concentrate & detect with minimal alteration to their properties.

● **Methodology**: Need to develop, standardize and validate a toolbox of robust analytical methodologies and new instrumentation.

● **Transformation**: ENMs may agglomerate, acquire or lose coatings and experience dissolution, or redox reactions that alter surface charge, reactivity & toxicity.

● **Dynamic characterization & toxicity Testing**: Urgent need to rapidly monitor and discern the nature of ENMs.

High Impact Opportunities

- Understanding the environmental fate, transport and transformation of ENMs
- Development of standard materials & standard measurement techniques
  - Can it distinguish between different types of nanomaterials (e.g. functionalized, un-functionalized, organic, inorganic or hybrid)?
  - Can it distinguish between intentionally-produced nanomaterials from ultratine, incidental nanomaterials (e.g. pollen, viral components, dead vs. living bacteria)?
  - Does it allow multi-platform testing? Is method interference-free?
  - Is further development, standardization or validation required
  - Is the method able to detect & accurately quantify nanomaterials in complex systems
  - Is the method suitable for determining nanomaterial toxicity
  - Are orthogonal measurement techniques needed?
  - Can it address discrepancies between laboratory vs. environmental/biological environment
- Understanding the toxicity mechanisms of ENMs
- Development of sustainable synthetic approaches for ENMS

Sadik, O. A, SUNY-Binghamton [http://chemiris.chem.binghamton.edu/SADIK/sadik.htm](http://chemiris.chem.binghamton.edu/SADIK/sadik.htm)
Schneider Group: Computational Environmental Catalysis

- Environmental effects on surface structure and reactivity
- NO$_x$/NO$_3^-$ catalytic redox chemistry
- WGS catalysis
- Novel CO$_2$ capture chemistries
- Chemically reactive ionic liquids

Atomic scale simulation, based on Density Functional Theory

- Alumina/water interface
- Structure and stability
- Reactivity
- Reaction dynamics

(Computational) Research Challenges

- Chemical reactivity is different at intermediate (nano) length scales
  - Geometric, electronic, environmental, and interfacial effects

- First-principles simulations ably describe <20 atom and semi-infinite systems

- 100’s-1000’s of atom length scales remain challenging
  - Electronic structure problem
  - Configurational problem
(Computational) Research Opportunities

- Computational tools that bridge the length- and time-scale gaps

- How can we predict the static, dynamic, and evolutionary properties of nanoscale materials in realistic, complex environments?

- Opportunity to impact both the design and the safe stewardship of nanomaterials

Computational engines

- First principles ↔ Empirical

Configurational engines

- Structure searching
- Equilibrium properties
- Chemical kinetics
- Chemical dynamics
Electrochemical carbon nanotube filter for water purification
- At 2 V, > 95% of influent dyes (1 mM) are removed and oxidized and 100% of bacteria/virus (10^7/mL) are removed and inactivated

-majority of the environmental research to date on engineered nanoparticles (NPs) has focused on implications i.e., they are considered as micropollutants in terms of fate, transport, distribution, transformations, bioavailability, toxicity, health

-the general conclusions made from the summation of this research indicate that NP micropollutants should not be an area of major concern. For example, all ecotoxicity studies utilize NP solutions that are obviously contaminated i.e., they are colored or contain large aggregates

-in regards to implications the energy/CO₂ used to synthesize and purify these energy-dense NPs and the wastes generated during these processes are becoming of greater concern

-the lesser concern towards NP micropollutants should result in a greater number of environmental applications of engineered NPs such as water purification, atmospheric pollution control, and alternative energy production

-better understanding of engineered NP surface/interfacial chemistry, photo/electro/redox mechanisms and kinetics, and self-assembly critical to environmental applications
- development of energy efficient methods to synthesize NPs of specific physical dimensions, surface structure, and composition
  - reduction of environmental implications of engineering NPs in terms of synthesis energy requirements
  - standardized NPs for comparison between labs
- development of routine physical characterization and chemical analysis methods for NPs under dynamic and environmentally-relevant conditions
  - most methods are ex situ, in vacuo, and time-consuming
- investigation of relationships between NP structure and surface chemistry and chemical reactivity (photo/electro/redox) and mechanisms and kinetics
  - identification of specific surface functional groups responsible for NP reactivity resulting in chemical control of reactions ie, to reduce environmental implications or alternatively to increase for applications
- investigations of heterogeneous NP-NP interactions and interfacial chemistry and effects on aggregation and reactivity (catalysis)
  - most aggregation studies are with single NPs – unrealistic
  - take advantage of multiple NP properties, for example one for adsorption of contaminant and another for catalytic destruction
- development of chemical self-assembly methods to construct ‘periodic’ three-dimensional NP structures to be used for applications
  - translation of individual NP properties to macroscopic structures yet to be attained due to inability to manipulate NPs Chad D. Vecitis – Harvard University