Aqueous Dispersions of Post-Graphene 2D Nanomaterials

2D nanomaterials can be dispersed in aqueous environments using biocompatible block copolymers

MoS$_2$ in Pluronic F87

MoS$_2$, SnSe, WS$_2$, WSe$_2$

Hersam, et al., in preparation.

Fate and transport of 2D MoS$_2$ is highly dependent on surface chemistry

In collaboration with Walker Lab, UC Riverside


Exfoliation of MoS$_2$ attenuates toxicity in lungs

In collaboration with Nel Lab, UCLA

Agg MoS$_2$, Lit MoS$_2$, PF MoS$_2$

Nel, Hersam, et al., Nanoscale., under review.
Abiotic ROS generation is decreased with increase in doping concentration. The surface framework structure in the fumed SiO$_2$ NPs (3MR, Si-O-Si) is known for inducing ROS is changed due to the formation of Si-O-Ti after doping.

IL-1$\beta$ production is proportionally reduced with Ti doping concentrations in Fumed SiO$_2$ NPs.
**Method:** We used zebrafish embryo as a screening tool to study the potential impact of two nano Cu-based materials, in comparison to nano sized and micro-sized Cu and CuO particles as well as following their transformation in an experimental wastewater treatment system.

**Result:** Nanoscale materials showed greater hatching interference, Cu passed through the septic tank underwent transformation to nonbioavailable species that failed to interfere with the zebrafish hatching enzyme.
Toxicity trends of 24 Metal Oxides in *E. coli* parallel those seen in mammalian cells

**Implications:** *E. coli* can be used to help predict toxicity patterns in higher organisms

Comparative studies on libraries of engineered carbon nanomaterials show the dispersal state and surface reactivity play key roles in triggering pro-fibrogenic AOP, which could prove helpful for hazard ranking and a proposed tiered testing approach for large carbon NM categories.

**In vitro**

- Macrophage
- Epithelial cells
  - IL-1β
  - TGF-β1

**Co-culture**

- PDGF

**Day 1:** IL-1β

**Day 7-21:** TGF-β1, PDGF-AA

*Wang et al ACS Nano, 2015 9(3) 3032-3043*
Rare earth oxides display a mechanism of toxicity unique from other metal oxides. REO NPs interfere in autophagosome fusion in the lysosome and disrupt the structural phosphates leading to chronic inflammation.

Ruibin Li et al. ACS Nano 2014, 8(10) 10280-10292
**Objective:**
Determine the rate of release of Cu from antifouling paint, nano fraction, and effect on organisms

**Findings:**
- Release of Cu decreases rapidly with time;
- Nano fraction released is small but measurable
- Release varies with drying time & surface
- Within 7 days [Cu] affects survival of zebrafish embryos (collaboration with Theme 2)

**Range of nano fraction**
- Estuary = 0 - 2.19 mg/L
- Seawater = 0 - 7.46 mg/L

Marine Antifouling Paint releases nano-scale Cu and affects fish embryos

Adeyemi Adeleye and Arturo Keller, UCSB
• Uptake, translocation, and physiological impacts of metal oxide engineered nanomaterials in soil-grown plants
  • Plants (Clarkia) grown under stressful environmental conditions accumulate more ENMs and are more susceptible to photosynthetic interference. (collaboration with Theme 4)

• Transport and effect of metal oxide ENMs on soil properties
  • Larger aggregates are restricted by pore size of soil and are retained near surface while smaller particles are transported further
  • ENMs appear to exchange with ions in soil and increase bioavailability of phosphorous

Fate & Transport of ENMs in Terrestrial Environments

Jon Conway & Arturo Keller, UCSB
Fluorescent latex nanoparticle characterization:

**Objective:**
Determine the effect of nanoparticle size on removal efficiency in filtration media.

**Findings:**
Removal efficiency is a strong function of particle size.

**Transport experiments in micromodel:**

- **Clean**
- **1mM KCl, 20min**
- **100mM KCl, 20min**

**Removal efficiency as a f(size)**

\[ \eta = \frac{I_{\text{Total}}}{h_C R_C u C_0} \]

- \( \eta \) = removal efficiency
- \( I_{\text{Total}} \) = average attachment rate
- \( h_C \) = height of the cylinder
- \( R_C \) = radius of the cylinder
- \( u \) = Darcy velocity
- \( C_0 \) = the particle concentration

Chen Chen, Sharon Walker
MNMs in Soil: Plants Modified the Bacterial Community Effects

ZnO Toxicity was Decreased by Plants

Plants Caused “New” Effects w/ low CeO₂

Ge et al. 2014. ES&T
Interaction of MNMs with Plants: Effects on yield and nutritional quality

**CeO$_2$: Decrease in Barley Spikes**

*Rico et al. 2014 ES&T*

**CeO$_2$: Decrease Spikes in Wheat**

*Rico et al. 2014 ES&T*

**CeO$_2$ and ZnO: Changes in Soybean Nutrients**

Peralta-Videa et al. 2014 PPB

**Cu-based products: Changes in Alfalfa and Lettuce Nutrients**

Hong et al. 2014 Environ Sci: Processes & Impacts
Objective:
Link cellular toxicity of engineered nanomaterials (ENMs) in High Content Screening (HCS) assays to ecological effects at the population level (in mesocosms).

Findings:
- Metal and metal oxide ENMs induce multiple cytotoxic injuries at 0.1-10 mg L\(^{-1}\) (ppm) concentrations;
- Cytotoxic injuries predicted population growth effects;
- Cytotoxic mechanisms differ for different ENMs;
- HCS screens effective in first 24 hrs;
- Aging of ENMs reduced cytotoxicity, indicating reduced toxicity potential in nature;
- HCS-to-population studies with phytoplankton reflect bacteria work in Theme 4.

Robert Miller, Bryan Cole, Hunter Lenihan, & Gary Cherr, UCSB & UC Davis
Objective: Test effects of nano-CuO exposure on embryonic development in sea urchins in 96 hr microcosm experiments

Findings:
- Toxic response to Cu metals observed as disruption of the developmental axis;
- Cu ions from micro-contaminant CuSO₄ more toxic than nano-CuO forms, due to high dissolution rate;
- Purified nano-CuO has a higher dissolution rate, higher surface area, and a higher zeta potential than commercial nano-CuO, factors that can contribute to higher toxicity;
- Cu accumulation in embryos and oxidative damage (total antioxidant capacity) caused by nano-CuO not explained by amount of solubilized Cu;
- Hypothesis: Cu NPs are internalized, and once inside the embryos, dissolve creating copper “hot-spots” that cause significant oxidative damage.

<table>
<thead>
<tr>
<th>Copper source</th>
<th>EC₅₀ (ppb)</th>
<th>Dissolution in FSW (%)</th>
<th>Z-potential in FSW (mV)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄</td>
<td>33</td>
<td>100</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Purified nano-CuO</td>
<td>463</td>
<td>2.5</td>
<td>-1.15</td>
<td>78.5</td>
</tr>
<tr>
<td>Commercial nano-CuO</td>
<td>5,565</td>
<td>0.73</td>
<td>-2.81</td>
<td>12.3</td>
</tr>
</tbody>
</table>

ND: not determined. FSW: filtered seawater
Mesocosm exposure to Nano-CuO injures killifish and impairs osmoregulation

Jeffery Miller, Andrew Whitehead, & Gary Cherr, UC Davis

Objective:
Test effects of CuO engineered nanomaterials (ENMs) on osmoregulation in killifish using estuarine mesocosm system with varying salinity

Findings:
- Exposure to CuO ENMs causes gill tissue damage and inflammation, and reduces enzymatic activity (Na/K ATPase);
- Impacts of CuO ENMs due to nanoparticle effects not ionic effect;
- Gill impairment comprises ability to adapt to salinity changes;
- Salinity challenged fish exposed to nano-CuO NPs loose plasma chloride homeostasis

Coastal salinity (red line) varies widely due to tidal cycles (daily) and seasonality: To deal with salinity changes in estuaries, killifish possess physiological and morphological gill plasticity to maintain homeostasis
Objective:
Test interactive effects of exposure to nano-Silver and food limitation on the reproduction of Daphnia in aquatic mesocosms

Findings:
- Daphnia reproduction highly sensitive to phytoplankton availability;
- Exposure to nano-Ag at only low parts per billion concentrations substantially enhanced effects of food limitation;
- Effects on Daphnia observed as increasing variability in reproduction through time (0-40 days);
- Daphnia usually lives on the edge in terms of resource availability, so exposure to small amounts of ENMs can have large effects;
- Effects now being modeled with DEB models.

Exposure to nano-Silver enhances population impacts of food scarcity in Daphnia

Louise Stevenson & Roger Nisbet, UC Santa Barbara

- Many animals in natural environments live at risk of starvation;
- Daphnia populations graze on phytoplankton populations;
- Combined effects of food limitation and toxicant stress are rarely studied, especially for ENMs;
- Aquatic chemostat mesocosm experiments controlled nutrient levels, phytoplankton growth, and Daphnia population abundance and growth.
A Web-Based Platform for ENMs Environmental Impact Assessment (EIA)

1. ENM Mass Distribution among environmental compartments
   - Sediment
   - Air
   - Water

2. Multimedia Analysis
   - HTS/LTS Analysis Tools
   - Data
   - Studies

3. Emissions

4. Knowledge Extraction:
   - Toxicity Metrics & QSARs

http://www.nanoinfo.org
CEIN NanoDatabank, Data Analytics and NanoEHS Decision Support Tools

Input raw Data, conduct detailed analysis, share findings (using different settings) using Centralized Nanodatabank

ENM users
Manufacturers
Regulators
Researchers

Data storage, Retrieval

Data Mining

Environmental Impact Assessment

Physicochemical characterization, toxicity data
HTS ENMs experimental data
Literature mined toxicity data
Biological Response

http://www.nanoinfo.org

NSF: DBI-1266377

UC Center for Environmental Implications of Nanotechnology

Year 7 Progress Report
Engagement of Academia, Industry, and NGOs in Two Day Workshop on ENM Categorization (May 2014)

Discussion on how data from alternative testing strategies (ATS) can be used to facilitate ENM categorization to risk potential and how such an approach could facilitate regulatory decision-making in the future.

Categorization strategies are needed to allow regulators and industry to predict ENM risk and to prioritize the level of testing (hazard, exposure, physicochemical) needed to estimate potential risk while minimizing time-consuming and costly in vivo studies that characterize traditional risk assessment.

Insights on Current Utility of Categorization of ENMs:
- Physicochemical properties not currently sufficient for ENM categorization for regulatory purposes
- Categorization methods for regulatory purposes should include indicators of hazard and exposure potential
- ATS may provide useful means for expedited hazard screenings for ENMs
- Decision-tree approaches for categorizing CNTs according to risk potential post-manufacturing could facilitate decision making in the EPA’s New Chemicals Program and in other frameworks
- Targeted cross-comparison of ATS with standard assays may be needed for ATS to be incorporated as an accepted component of categorization strategies in some regulatory contexts

Godwin et al, ACS Nano 2015
Published Project
11,000+ page views since June 2013

Topic: How do nano-based antibacterial products work?

Audience: 8th grade+

Select Vocabulary:
- Antibacterial; Antimicrobial
- *Escherichia coli* (*E. coli*)
- Kirby-Bauer antibiotic testing method
- Nanoscale, Nanoparticles, Nanometer
- Parts per million (PPM)
- Zone of inhibition

Fundamental Science Concepts Include:
- Select & use appropriate tools & technology to perform tests, collect data, analyze relationships, display data
- Distinguish between variable & controlled parameters in a test
- Formulate explanations by using logic and evidence
An IRB-approved curriculum development project

Incorporating CEIN-developed HTS assays into an undergraduate chemistry curriculum to provide students with an authentic, interdisciplinary research experience with real-world applications

Curriculum

Week 1: Nanoparticle synthesis & characterization
Week 2: Nanoparticle ecotoxicity assay
Week 3: Research evaluation and (re)design

Students

Undergraduates enrolled in CHEM 12H at a primarily undergraduate university

Presentations & Publications

Presentation accepted:
Presentation submitted to MSTEM 2015: www.materialsinstem.org

Journal article(s) in progress

Catherine Nameth (UCLA) & Korin Wheeler (Santa Clara University)