Nanotechnology and the Environment

OSWER Conference
July 12-13, Washington DC

Dr. Vicki Colvin
Director, CBEN
Professor of Chemistry
Rice University

Introduction: Overview of Nanotechnology and the Environment

Small is Beautiful

- Highly crystalline
- Huge surface areas

C-sixty
1 nm

Cadmium Selenide nanocrystal
6 nm

Lysozyme
3 nm

Dr. Vicki Colvin
2 of M
Nanomaterials Solve Problems

- Magnetite particles
- Nanogold on silica
- BiMetallic Catalysts

Water purification
Shrinking Tumors
Removing TCE in water

Carcinoma cells
Tumor capillary

Invention and Productivity

- Nanotechnology R&D - US Goal in Millions $$$
- Nanotechnology Publications

Introduction: Overview of Nanotechnology and the Environment
Nanotechnology: It’s Here

<table>
<thead>
<tr>
<th>Product</th>
<th>“Nano Inside”</th>
<th>Value Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Natural Sunscreens</td>
<td>Active Ingredient:</td>
<td>Transparency</td>
</tr>
<tr>
<td></td>
<td>Nanoscopic TiO₂/ZnO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lined with Ceramic</td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td>Nanoparticles</td>
<td>Impermeability</td>
</tr>
<tr>
<td></td>
<td>Embedded with</td>
<td>Stain- and</td>
</tr>
<tr>
<td></td>
<td>“Nano Whiskers”</td>
<td>Wrinkle-Resistance</td>
</tr>
</tbody>
</table>

From “Wow” to “Yuck”?

- DDT cured malaria: Endangered birds
- Pesticides improved crop yields: Toxic to animals
- Refrigerants made houses cool: Lead to ozone hole
- Asbestos improved insulation: Liability expenses
Today’s Talk

Benefits

1. Applications of nanomaterials in water treatment
   *Example: Nanosized magnetite for arsenic removal*

2. Is size dangerous? Implications of nanotechnology

Water Treatment Technologies: A Real Need

- Waterborne illnesses major cause of death
- Increasing contamination in water
- Population growth increasing demand
Nanomaterials in Water Treatment

Small size provides high surface area

In-situ remediation of contaminated wells

Small size provides reactive surface

100-fold improvement in TCE removal

M. Wong, Rice University

Arsenic in Drinking Water

- Arsenic in water linked to cancer
- EPA standards: 50 ug/L to 10 ug/L
- Natural and anthropogenic sources
- Enormous interest in removal
  - Plants (phytofiltration)
  - Muds and sediments
  - Zero valent iron – in-situ
  - Mine tailings (e.g. iron oxides)

Existing Sorbents for Arsenic Removal

“ Our two year study showed that none of the (18) Arsenic Removal Plants could maintain arsenic in … water … below the WHO guidelines ….”
- Hossain et al in ES&T 2005, p. 4300

<table>
<thead>
<tr>
<th>Material</th>
<th>Sorbent (kg) / month</th>
<th>1 gram treats ___ L water</th>
<th>Waste to dispose of kg (1 yr)</th>
<th>Backwash frequency (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina + Metal Oxide</td>
<td>0.24</td>
<td>3.8</td>
<td>2.88</td>
<td>14</td>
</tr>
<tr>
<td>Red Mud [As(III)]</td>
<td>360.7</td>
<td>0.002</td>
<td>4328.1</td>
<td>Periodic</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>No Removal of Toxic As(III)</td>
<td>~ 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For a family of four, using 900 L water/month, at 500 ppb As levels (7.9 pH)

Nanomagnets: Two Advantages

1. Increased surface area for arsenic sorption
2. Enhanced magnetic susceptibilities improve separations
Arsenic sorption onto iron oxides

- Strong and specific sorption
- Chemical transformation
- Subjected to interferences
  - Silicate and phosphates
  - Humic acids

Models for surface interactions*

Are Nanoscale iron oxides are good candidates for sorbents?

MASON TOMSON, AMY KAN, SUJIN YEAN

* D. M. Sherman, S. R. Randall Geochimica et Cosmochimica v. 67 no. 22 p. 4223

Commercial nanoscale iron oxides

D = 25 nm
σ ~ 35%

As particle size gets smaller sorptive area increases with R^2

http://www.kemcointernational.com/IronOxide.htm
Sorption of Arsenic Onto Magnetite

- 20 nm Magnetite can sorb both As(V) and As(III)
- Sorption capacities (△) of 0.1 % (w/w)
- Arsenic is irreversibly sorbed (▲) stable in storage

MASON TOMSON, AMY KAN – Rice University

Size dependence: Surface Area

Surface area in 1 gram ~ 4 \( \pi \) r^2 / (4/3 \( \pi \) r^3 · density)
Synthesis of monodisperse nano-Fe₃O₄

Commercial nano-oxides have problems
- Agglomerated → poor magnetic separation
- Larger nanoparticles → lower sorption
- Bad size distribution → no optimization


Nanomagnets: Large Sorption Capacity

Volume of water treatable by 1 Kg magnetite

<table>
<thead>
<tr>
<th>Particle Size (nm)</th>
<th>Volume of Water (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 As(III)</td>
<td>2,283</td>
</tr>
<tr>
<td>20 As(III)</td>
<td>594</td>
</tr>
<tr>
<td>300 As(III)</td>
<td>21</td>
</tr>
<tr>
<td>12 As(V)</td>
<td>1,435</td>
</tr>
<tr>
<td>20 As(V)</td>
<td>1,145</td>
</tr>
<tr>
<td>300 As(V)</td>
<td>150</td>
</tr>
</tbody>
</table>

Remaining Challenge: Nanoparticles are difficult to remove
Nanomagnets: Two Advantages

1. Increased surface area for arsenic sorption
2. Enhanced magnetic susceptibilities improve separations

“Nano” Improves Magnetic Behavior

Small cluster: Supraparamagnetic
   Easy to magnetize

Larger cluster: Single Domain
   Magnetization can shift

Bulk solid: Permanent magnet
   Small magnetization

Nanocrystals are better magnets than larger bulk materials
Magnetic Filtration for Nanosorbents

- Requires no pressure gradients
- No fouling of separation system

Magnetic Separations in Water Treatment

- Gravitational settling
- Filtration
- Induced coagulation
- Magnetic Separations

External fields >> 1-2 Tesla
Particle sizes >> 50 nm

A surprise: Low fields can remove nanocrystals

0.0 Tesla  →  0.36 Tesla

Lower fields = Simpler Systems
Library of nanoparticles for optimization

Retention of Particles by Columns

Dr. Vicki Colvin -- Presentation Slides
Nanocrystals must be supraparamagnetic

\[ \text{Fe}_3\text{O}_4 \text{ particles} \]

Field on (1 T)

Rinse water

Field Off

Existing Sorbents for Arsenic Removal

<table>
<thead>
<tr>
<th>Material</th>
<th>Sorbent (kg)/month</th>
<th>1 gram treats</th>
<th>Annual waste to dispose kg [3]</th>
<th>Backwash Frequency (day)</th>
<th>Efficiency[1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina + Metal Oxide</td>
<td>0.24</td>
<td>3.8</td>
<td>2.88³</td>
<td>14</td>
<td>0.003</td>
</tr>
<tr>
<td>Red Mud [As(III)]</td>
<td>360.7</td>
<td>0.002</td>
<td>4328.1³</td>
<td>Periodic</td>
<td>~0.003</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>No Removal of Toxic As(III)</td>
<td>~ 3</td>
<td></td>
<td></td>
<td>0.014</td>
</tr>
<tr>
<td>Nanoscale Iron Oxides</td>
<td>0.09</td>
<td>10</td>
<td>1.1</td>
<td>0</td>
<td>~7.5 to 75 [2]</td>
</tr>
</tbody>
</table>

1. “Efficiency” as defined by NAE in the “Granger Challenge, June, 2005” The object is to maximize the efficiency.
2. 12 nm magnetic cost estimated as a synthesized chemical at $2.00/lb and a multiplication factor of cost by 3x to 30x for estimated conditioning chemicals and packaging.
3. The amount (kg) + the backwash frequency
Roadblocks for Nanotechnology

**Grand Challenges**
- Effective water treatment systems using nanoparticles

**2011 Outcomes**
- A nano-enabled water treatment system applied on a large scale

- MARKET: Nano needs a market to pay cost
- MONEY: Investments in new technologies
- ACCEPTANCE: public confidence in safety

Today’s Talk

**The Public**

1. Exploiting size in environmental remediation
   - *Nanosized magnetite for arsenic removal*

2. Is size dangerous? Implications of nanotechnology
**Is Small Dangerous?**

- **Highly crystalline**
- **Huge surface areas**

- C-sixty
  - 1nm

- Cadmium Selenide nanocrystal
  - 6 nm

- Lysozyme
  - 3 nm

---

**Nanotechnology’s Risks are Distributed**

- **End-of-use issues:** Ecological impacts
- **Worker and laboratory safety**
- **Direct consumer contact**
Carbon nanostructures: Model Systems

C-sixty or C\textsubscript{60}
- Factory production (Frontier Carbon)
- Highly controlled “molecular” species
- Fuel cells, face creams, medical treatments
- Extremely hydrophobic in pristine state

Single-walled Carbon Nanotubes (SWNT)
- Factory production (CNI, NEC, Samsung)
- Complex mixtures, distributions of types
- Flat panel displays, composites
- Extremely hydrophobic in pristine state

Risk : From Source to Receptor

2. TRANSPORT

Risk = Exposure • Effect

1. CHEMISTRY

3. TOXICITY
Environmental Chemistry of Fullerenes

Hydrophobic fullerenes CLUSTER when they sit in water.

Preparation conditions affect CLUSTERING and BEHAVIOR.

Dirt and other residues stick to CLUSTERS in groundwater.

Movement of Nanoparticles in Soils

- SMALL ≠ MOBILE (nanoparticles are sticky)
- MODELS too predict distribution in soil/water

Wiesner (Duke); Hughes (GaTech)
Nanoparticles and Microorganisms

Less toxic
10^4
10^3
10^2
10^1
10^0
MIC in ppm
Nano-SiO₂
Nano-TiO₂
Nano-ZnO
C₆₀ w/PVP
C₆₀/toluene
C₆₀/THF

More toxic
10^1
10^2
10^3

"Nano" does not mean toxic for many materials

C₆₀ effects depend on how it is water solubilized


Developmental toxicity of nano-C₆₀

Mitigation by GSH suggest that toxicity is related to oxidative stress

Zebrafish larva with pericardial edema due to nC₆₀ exposure

Alvarez, Tomson (Rice); Zhang (China)
Risk: From Source to Receptor

1. CHEMISTRY

2. TRANSPORT

3. TOXICITY

Risk = Exposure • Effect

In-Vitro Cytotoxicity

C_{60} colloidal particles (4 ppm) + DMEM → HDP cells, seeded (Human Diploid Fibroblasts)

48 Hours

Live Dead

Introduction: Overview of Nanotechnology and the Environment

Dr. Vicki Colvin -- Presentation Slides

Dose Response Curve for n-C$_{60}$

<table>
<thead>
<tr>
<th>Human Cell Line</th>
<th>LC$_{50}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HepG2</td>
<td>0.05</td>
</tr>
<tr>
<td>HDF</td>
<td>0.02</td>
</tr>
<tr>
<td>NHA</td>
<td>0.002</td>
</tr>
</tbody>
</table>

n-C$_{60}$ Relative Cytotoxicity

<table>
<thead>
<tr>
<th>Toxin</th>
<th>LC$_{50}$, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$(OH)$_x$</td>
<td>&gt; 100,000</td>
</tr>
<tr>
<td>Ethyl Alcohol*</td>
<td>17,000</td>
</tr>
<tr>
<td>THF</td>
<td>11,000</td>
</tr>
<tr>
<td>Toluene</td>
<td>1,600</td>
</tr>
<tr>
<td>Paraquat</td>
<td>100</td>
</tr>
<tr>
<td>Benzo[a]pyrene*</td>
<td>10</td>
</tr>
<tr>
<td>n-C$_{60}$</td>
<td>0.02</td>
</tr>
<tr>
<td>Dioxin*</td>
<td>0.001</td>
</tr>
</tbody>
</table>

* National Institute of Health, Registry of Cytotoxicity Data (ZEBET)

Aggregated C-sixty is a very toxic substance in cell culture
Membrane Leakage

Control

No dye 10,000 70,000 500,000

HepG2 and C₆₀

No internal organelle oxidation: only outer membrane damage

Yang, Hafner

Dr. Vicki Colvin
41 of 56
Origins of fullerenes bioactivity

C$_{60}$ can form superoxide anion, and singlet oxygen
C$_{60}$ is also a highly lipophilic substance

*Cytotoxic substance which destroys lipid membranes*

Systematic Variation of Surface Chemistry

Increasing derivatization lowers photoinduced singlet oxygen generation
More polar functionality creates higher water solubility in materials
Structure/Activity Relationship Revealed

Information Supports Risk Management

• Development of pre-treatment schemes for waste
  ➢ Mild oxidation for fullerenes
  ➢ Thermal treatments for titania

• Simple ex-vivo screens for nanoparticle formulators

• Foundation for testing structure-function hypotheses
Framing a new question

*Are engineered nanoparticles dangerous?*

> How can we engineer safe nanoparticles?

**Today’s Talk**

**Benefits**

1. Nanocrystalline magnetite irreversibly sorbs Arsenic
2. “Nano” makes magnetic separations practical
   1. *Higher removal at lower fields*
   2. *Very high surface areas increase capacity*
3. Ongoing implications work improves technology

**Risks**
Acknowledgements

• Dr. Christie Sayes
• John Fortner
• Dr. Joe Hughes
• Dr. Jennifer West
• Joe Mendez
• Delina Lyon
• Adina Boyd
• Andre Gobin
• Yi Yang
• Raj Wahi
• Dr. David Warheit (DuPont)
• Dr. Wenh Guo
• Dr. Yizhi Jane Tao
• Dr. Mason Tomson
• Dr. Kevin Ausman
• Dr. Jane Grande-Allen
• Dr. Lon Wilson
• Dr. Jason Hafner

Want to learn more? Do more?

• Copies of presentation: colvin@rice.edu
• Center web page: http://cben.rice.edu/
• Check-out
  – ICON: http://icon.rice.edu/. Multi-stakeholder
group devoted to minimizing risks of
nanotechnology
  (E56) Help write standards on nanotechnology
  and risk assessment, management.
NanoX: Not Toxicology As Usual

Are single-walled carbon nanotubes toxic?

- 20 major types of SWNT
- 4 manufacturing types (trace impurities)
- Lengths ranging from 5 – 300 nm
- 5 methods of purification
- 10 possible surface coatings

> 50,000 SWNT samples

Basic structure-function relationships for nanomaterials and biological impacts are necessary

Acknowledgements

- Professor Mason Tomson
- Dr. Amy Kan
- Sunjun Yean
- Cafer Yavuz
- J. T. Mayo
- Arjun Prakash
- Dr. William Yu
- Yi Hua
- Josh Falkner

NSF-NSEC CBEN
www.rice.edu/~cben
Colvin@rice.edu
Magnetic Separations Optimized

- 30 nm Fe₃O₄ commercial
- 10 nm Fe₃O₄ in water
- 22 nm Fe₃O₄ in hexanes

Arsenic Removal, with Magnetic Field

<table>
<thead>
<tr>
<th>Particle Size (nm)</th>
<th>As(V) or As(III)</th>
<th>Initial As Concentration (mg/L)</th>
<th>Residual As Concentration (mg/L)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>As (III)</td>
<td>500</td>
<td>3.9</td>
<td>99.2</td>
</tr>
<tr>
<td>20</td>
<td>As (III)</td>
<td>500</td>
<td>45.3</td>
<td>90.9</td>
</tr>
<tr>
<td>300</td>
<td>As (III)</td>
<td>500</td>
<td>375.7</td>
<td>24.9</td>
</tr>
<tr>
<td>12</td>
<td>As (V)</td>
<td>500</td>
<td>7.8</td>
<td>98.4</td>
</tr>
<tr>
<td>20</td>
<td>As (V)</td>
<td>500</td>
<td>17.3</td>
<td>96.5</td>
</tr>
<tr>
<td>300</td>
<td>As (V)</td>
<td>500</td>
<td>354.1</td>
<td>29.2</td>
</tr>
</tbody>
</table>