

Peter  
Vikesland



# Opportunities and Challenges for the Nanotechnology Research Community



# Opportunity and Challenge I

*Novel nanomaterials are continually being developed...*

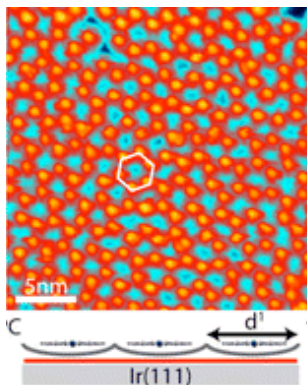
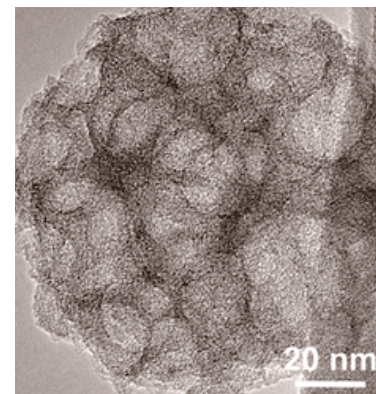
ACS NANO

## **Solution-Based Carbohydrate Synthesis of Individual Solid, Hollow, and Porous Carbon Nanospheres Using Spray Pyrolysis**

Chengwei Wang, Yuan Wang, Jake Graser, Ran Zhao, Fei Gao, and Michael J. O'Connell

Publication Date (Web): November 25, 2013 (Article)

DOI: 10.1021/nn4048759



## **Tailoring Molecular Self-Assembly of Magnetic Phthalocyanine Molecules on Fe- and Co-Intercalated Graphene**

Maciej Bazarnik, Jens Brede, Régis Decker, and Roland Wiesendanger

Publication Date (Web): November 26, 2013 (Article)

DOI: 10.1021/nn405172q

## **Gold Catalyzed Nickel Disilicide Formation: A New Solid–Liquid–Solid Phase Growth Mechanism**

Wei Tang, S. Tom Picraux, Jian Yu Huang, Xiaohua Liu, K. N. Tu, and Shadi A. Dayeh

Publication Date (Web): November 25, 2013 (Letter)

DOI: 10.1021/nl4032023

NANO LETTERS

# Opportunity and Challenge I

*...yet nanomaterial fate studies generally lag behind.*

**Cerium Oxide Nanoparticles Modify the Antioxidative  
Stress Enzyme Activities and Macromolecule  
Composition in Rice Seedlings**

**Photochemical Transformation of Carboxylated Multiwalled Carbon Nanotubes:  
Role of Reactive Oxygen Species**

**Influence of Bovine Serum Albumin and Alginate on Silver Nanoparticle  
Dissolution and Toxicity to *Nitrosomonas europaea***

**Potential Mechanisms and Environmental Controls of TiO<sub>2</sub> Nanoparticle Effects  
on Soil Bacterial Communities**

**The Impact of Silver Nanoparticles on the Composting of Municipal Solid Waste**

**Porous Media Induced Aggregation of Protein-Stabilized Gold Nanoparticles**

Matthew Chan and Peter J. Vikesland

Publication Date (Web): December 3, 2013 (Article)

DOI: 10.1021/es404455w

# Life cycles of nanomaterials



Well studied 'pure' nanomaterials:

'Isotropic' NMs:  $\text{CeO}_2$ ,  $\text{C}_{60}$ ,  $\text{FeO}_x$ ,  $\text{Fe}^0$ , AgNP, AuNP

'Anisotropic' NMs: CNTs, AuRods

'Pure' nanomaterials requiring further study:

Graphene (although this is changing rapidly...)

Organic nanostructures (nanocellulose, dendrimers, conductive polymers)

Novel shapes/morphologies



# Life cycles of nanomaterials



Nanoassemblages – combinations of nanomaterials in various configurations

Metal oxides on carbon

Carbon nanotubes/quantum dots

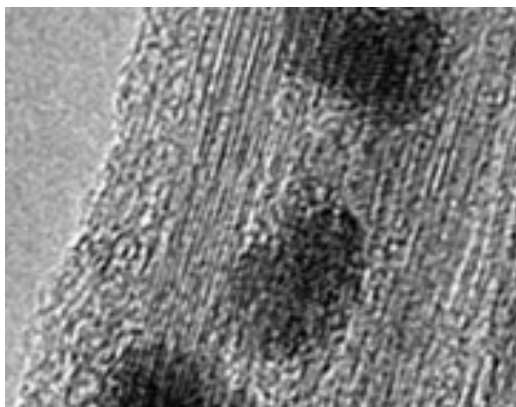
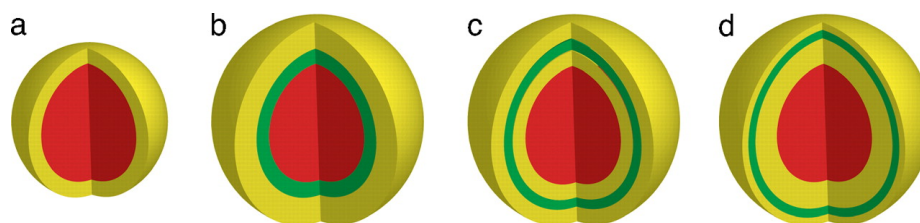
Electron donors/electron shuttles

Photon harvesters/electron shuttles

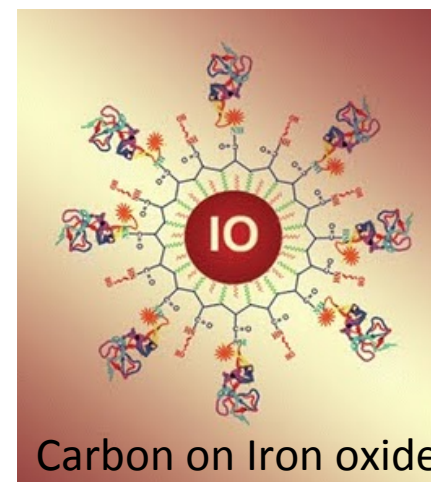
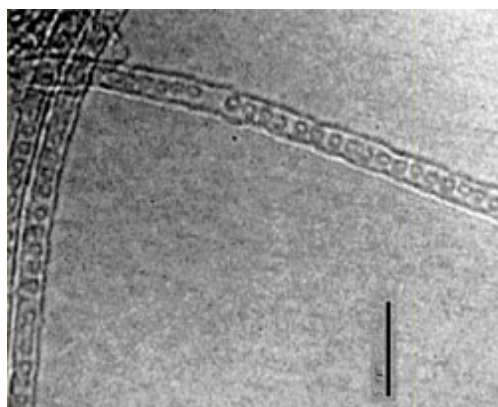
Core-shell structures

Nanotubes filled with nanomaterials

Organic/inorganic hybrids



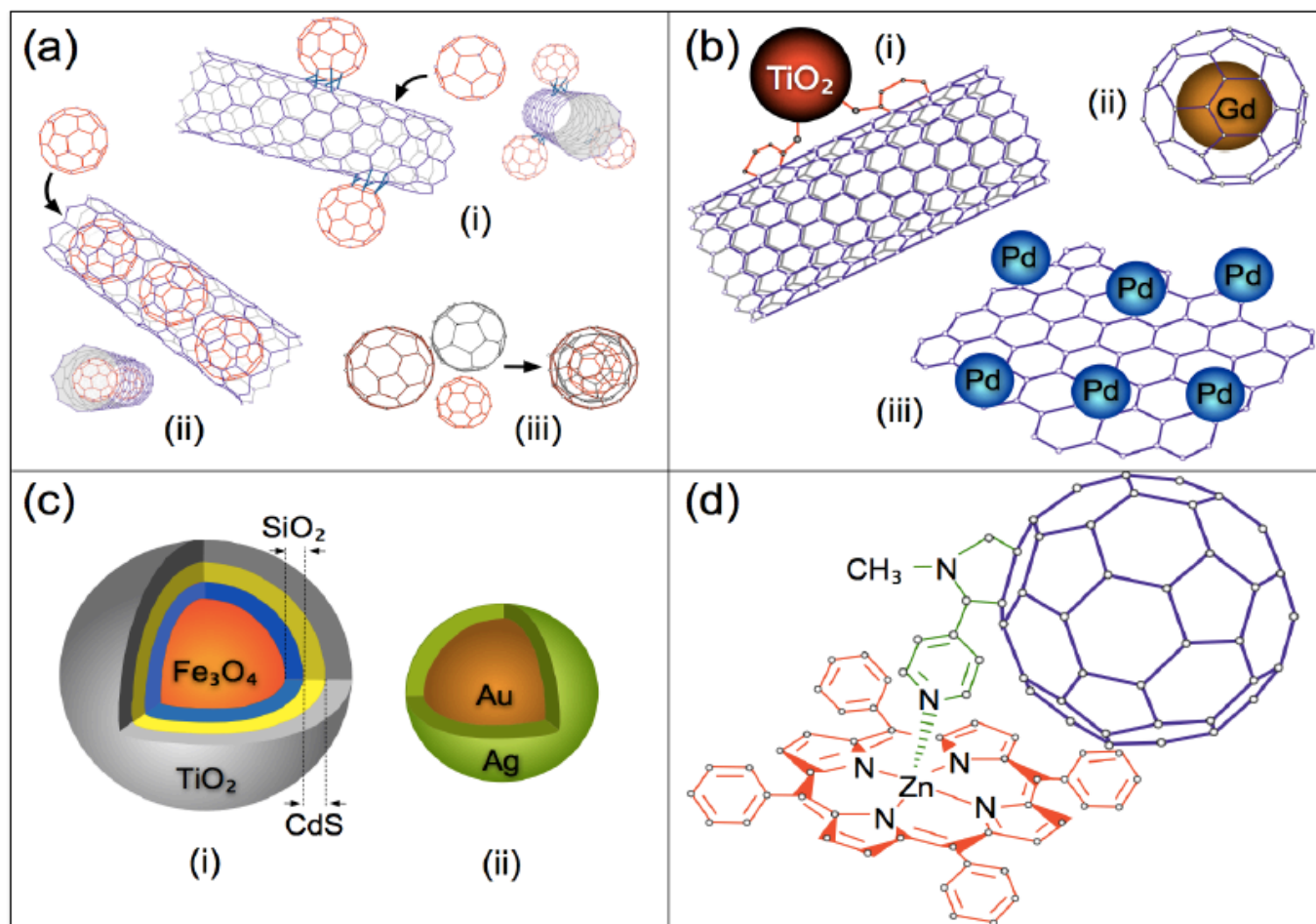
CdSe on CNTs



Carbon on Iron oxides

# Are Nanohybrid Environmental Implication Studies Overdue?

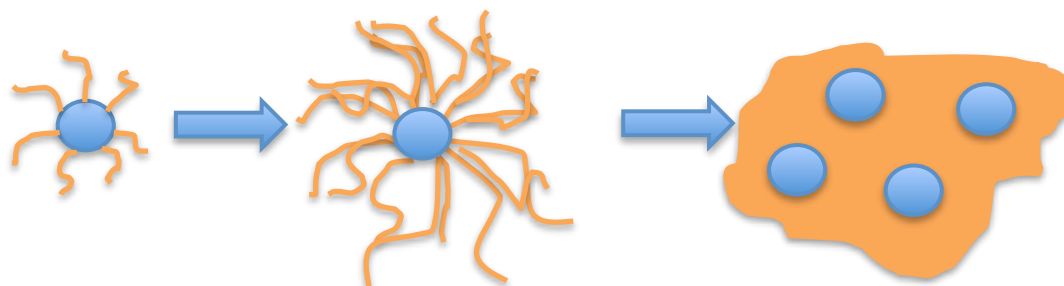
<sup>1</sup>Navid Saleh, <sup>2</sup>Xinyu Huang, <sup>3</sup>Jamie Lead,  
<sup>1</sup>Nirupam Aich, <sup>2</sup>William Rigdon, <sup>1</sup>Jaime Plazas-Tuttle



# Life cycles of nanomaterials



Formulations - Chemical modifications to stabilize nanomaterials  
Nanoparticle-polymer composites (a continuum)

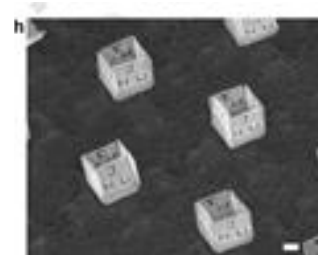
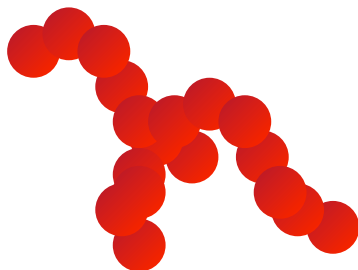
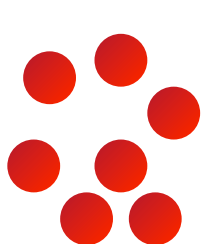


Nanoparticle surface functionalization

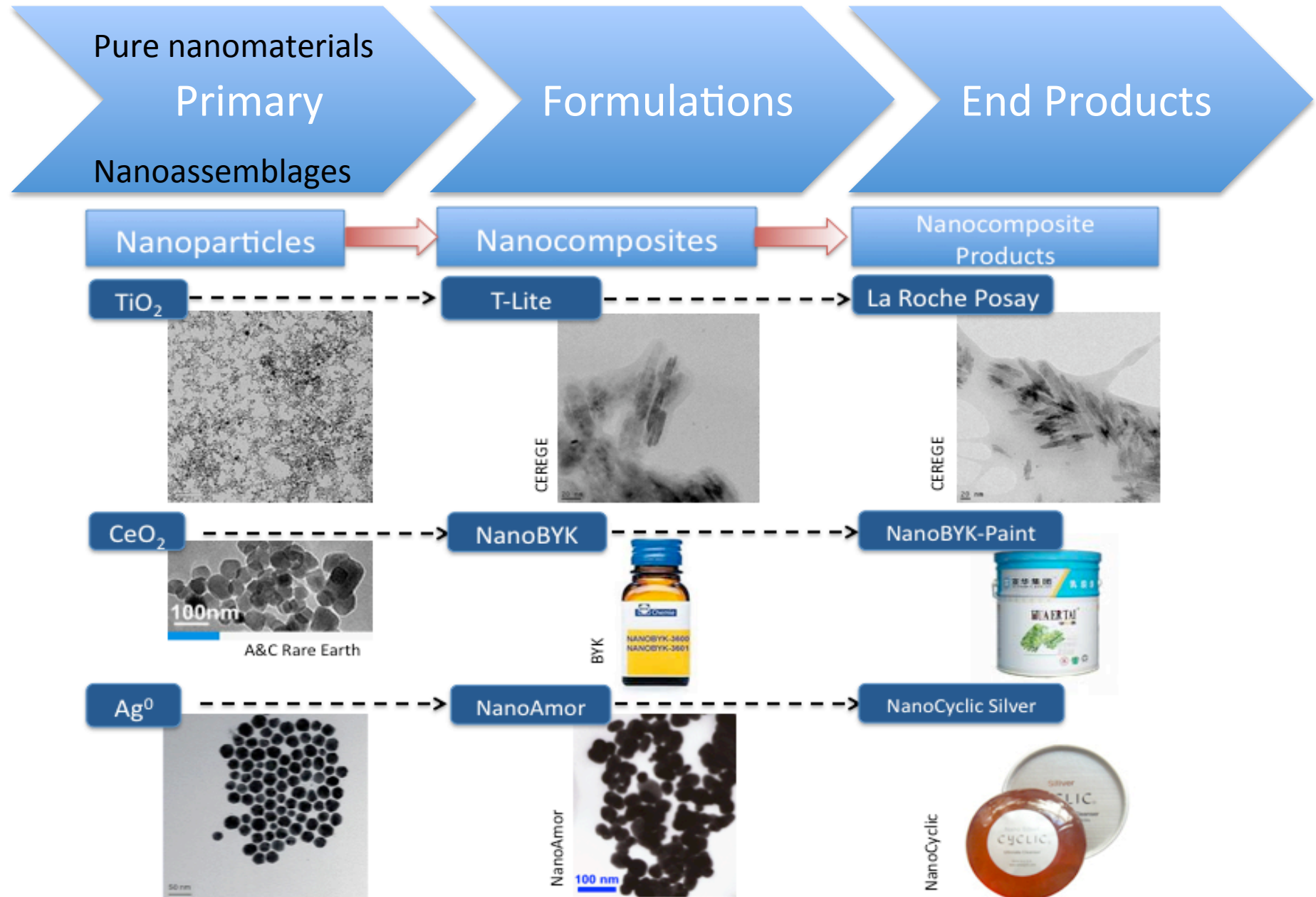
$\text{-NH}_2$   
 $\text{-OH}$

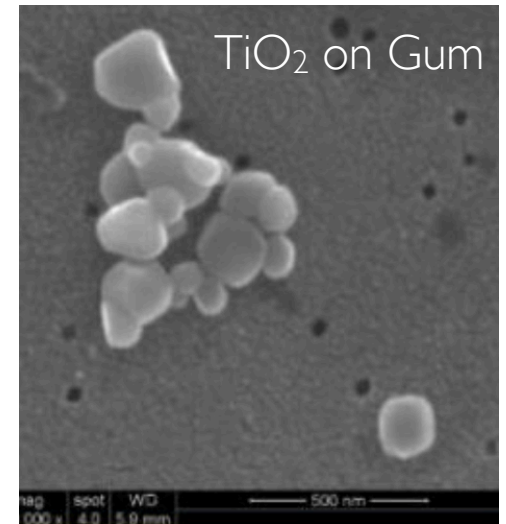
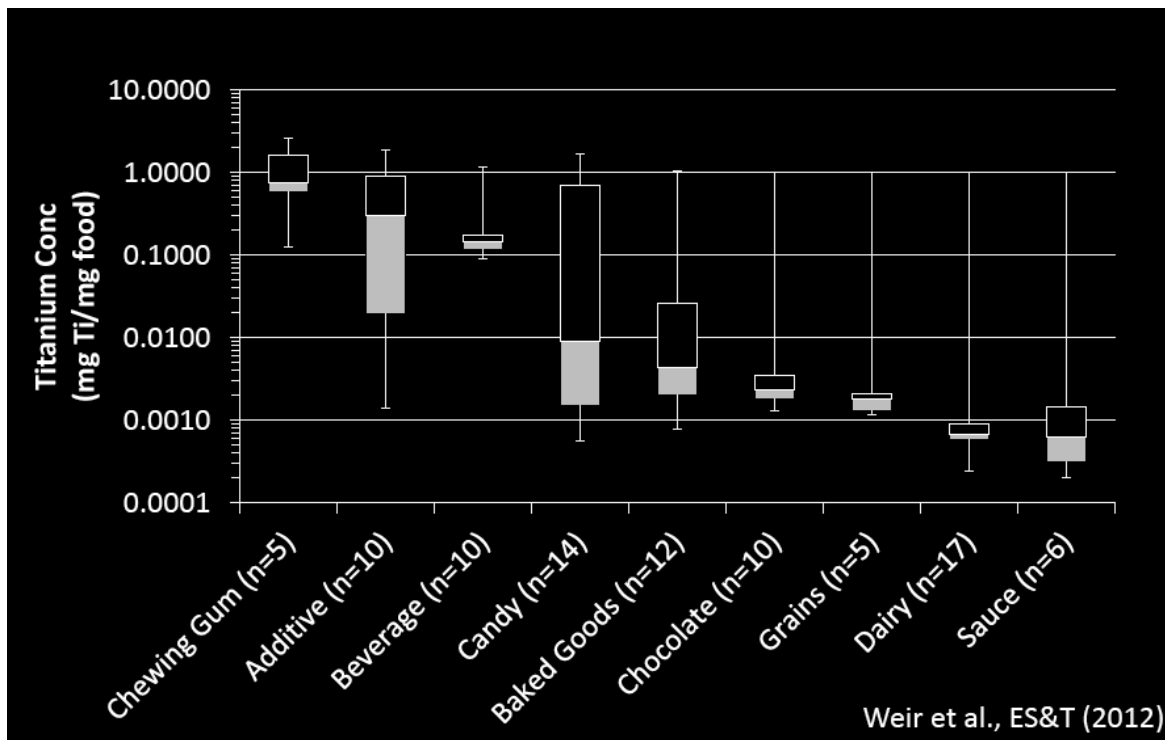
$\text{-COOH}$   
 $\text{-SH}$

Physical processing (3-D structures, aggregate structures, thin films, patterns)



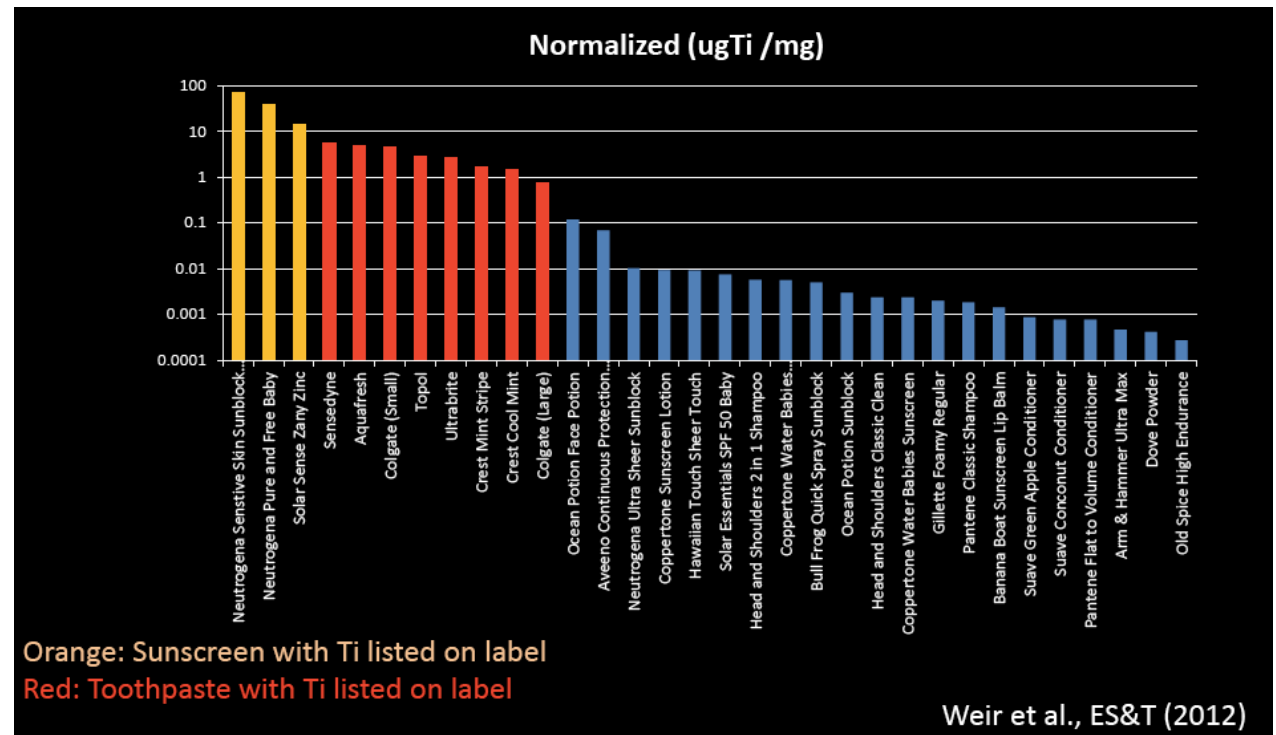
# Life cycles of nanomaterials





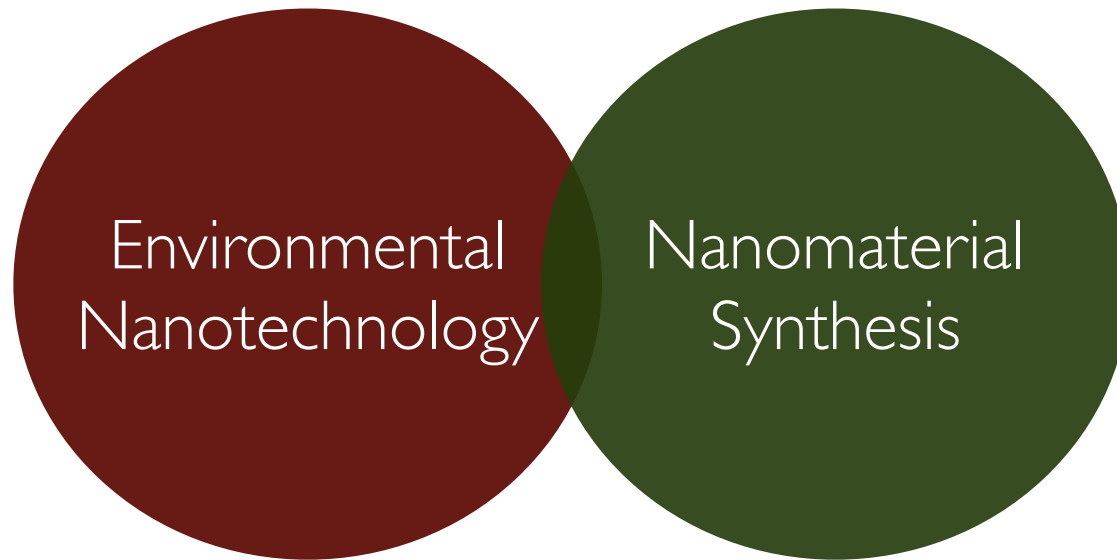
# TiO<sub>2</sub> NPs in Foods, Personal Care Products

Westerhoff group  
Arizona State

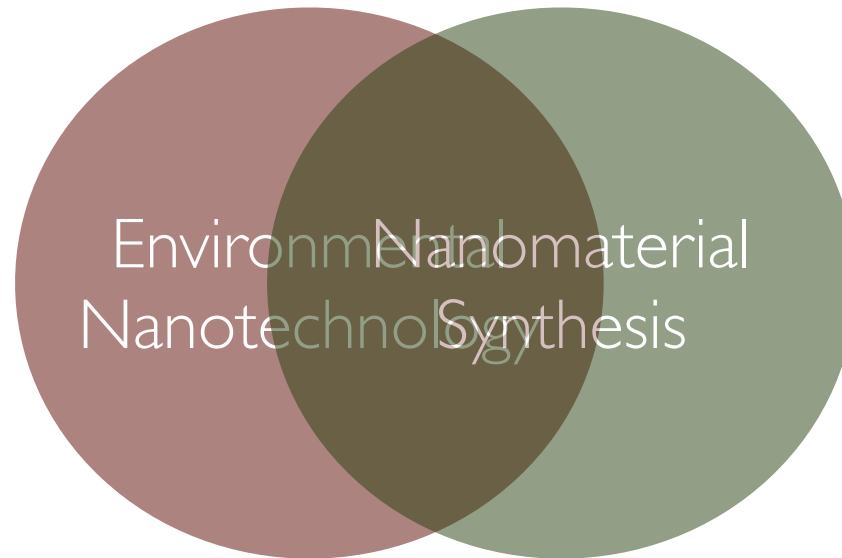




Initially, those with the expertise to produce nanomaterials often did not interact with those interested in the environmental fate of nanomaterials.



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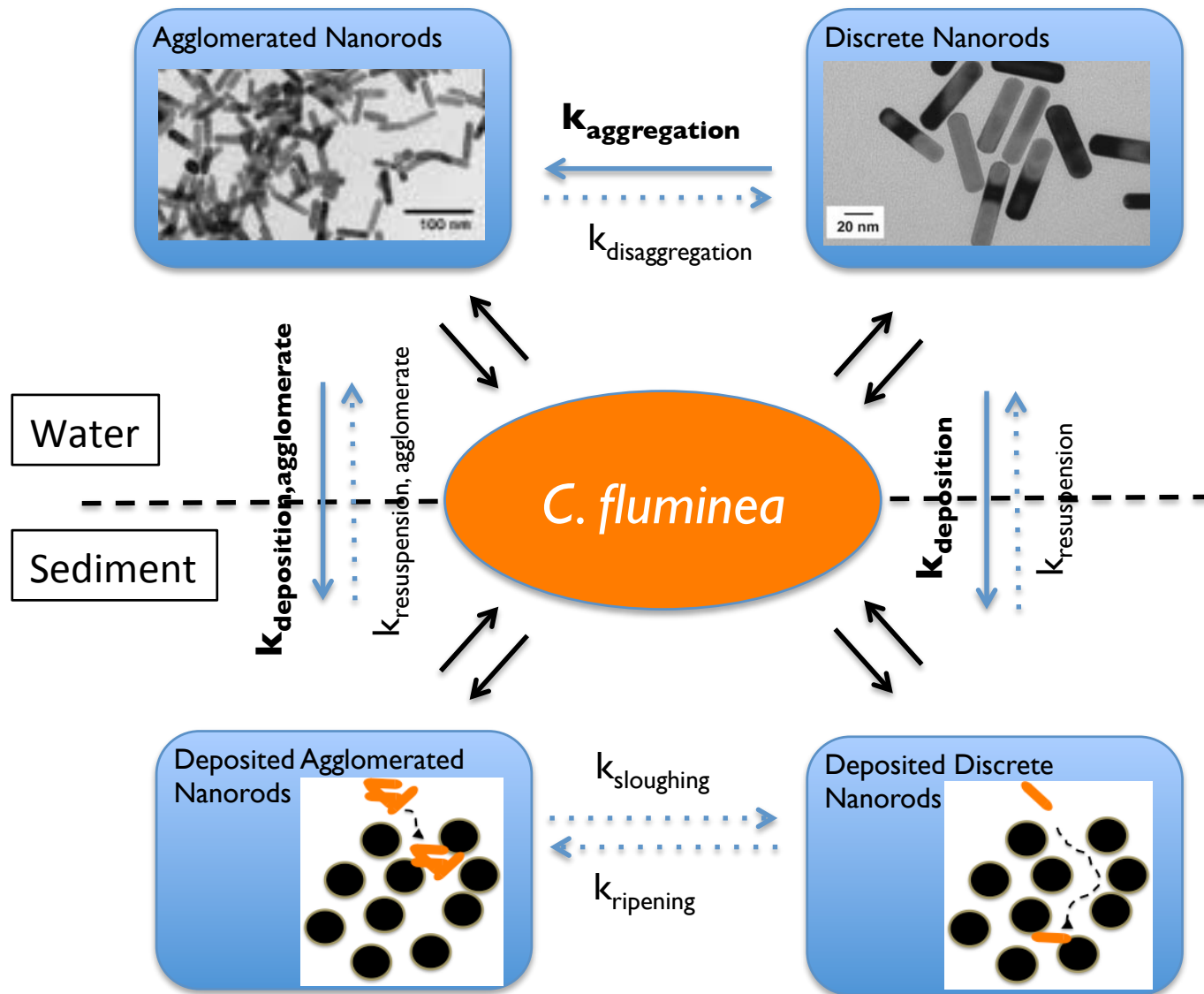


**This, however, has changed substantially since both groups began to realize the benefits of working together.**

Improved  
Colloidal Stability

Design for  
Decreased Toxicity

Environmental  
Applications



## Important System Variables

### Nanorod

Aspect Ratio (AR): 1-20

Identity: Au

Au@SiO<sub>2</sub>

Au@γ-Fe<sub>2</sub>O<sub>3</sub>

Au@CeO<sub>2</sub>

Concentration

### Solution Chemistry

Simple salts (NaCl, CaCl<sub>2</sub>)

Moderately hard saline

Humic acid

### Collector Type

Silica beads

Sand grains

### *C. Fluminea*

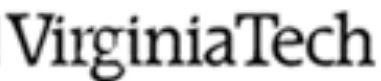
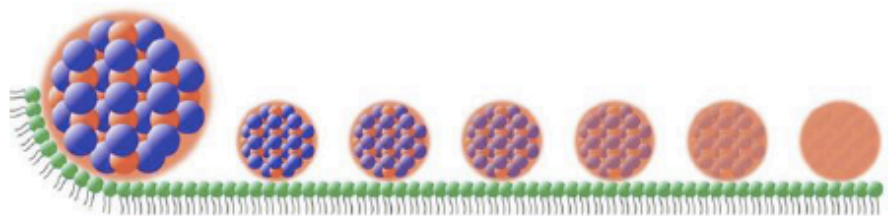
Concentration

Age

NSF CBET 1336353 *Fate, Transport, and Organismal Uptake of Rod-Shaped Nanomaterials*

Vikesland - VT  
Saleh - UT-Austin  
Murphy - U.Illinois

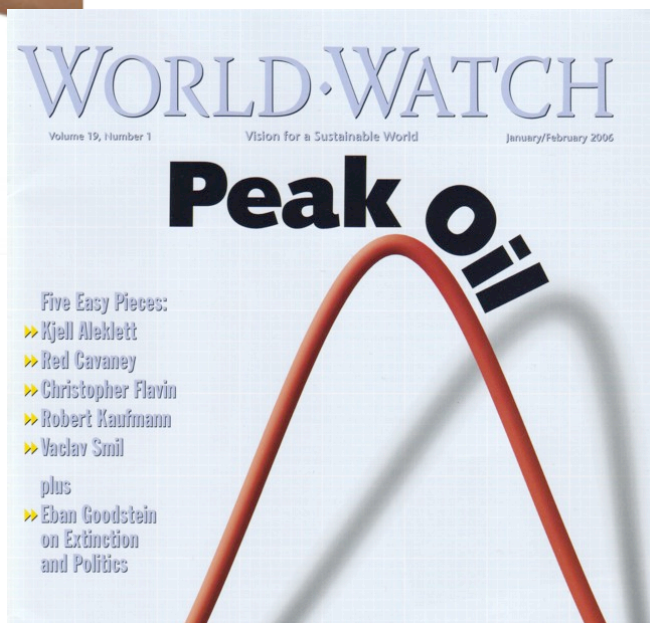
# Center for Sustainable Nanotechnology



# Opportunity and Challenge II

*Many nanomaterial syntheses are reliant on unsustainable materials and/or energy intensive processes.*

scientificamerican.com



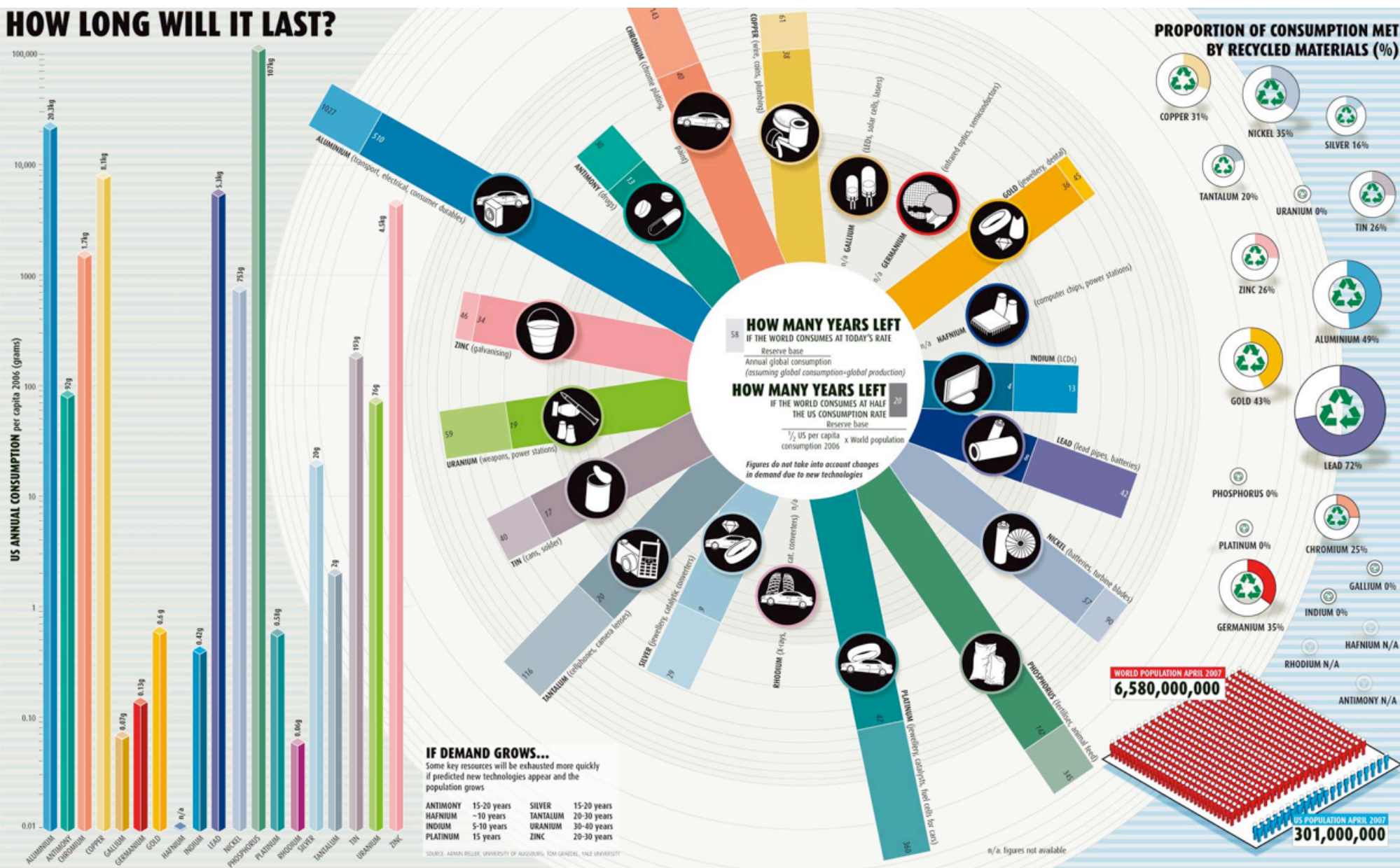
sciencemag.org

MINERAL RESOURCES

**Is the World Tottering on  
The Precipice of Peak Gold?**



# HOW LONG WILL IT LAST?



Earth's natural wealth: an audit (23 May, 2007), NewScientist.com  
<http://www.newscientist.com/data/images/archive/2605/26051202.jpg>

**GOLD** (jewellery, dental)



36 45

**INDIUM** (LCDs)



4

13

**SILVER** (jewellery, catalytic converters)



29

9

How many different nanotechnologies are based on **resources that are limited** and on **non-renewable** precursors?

What are the projections of the growth of the nano-industry?

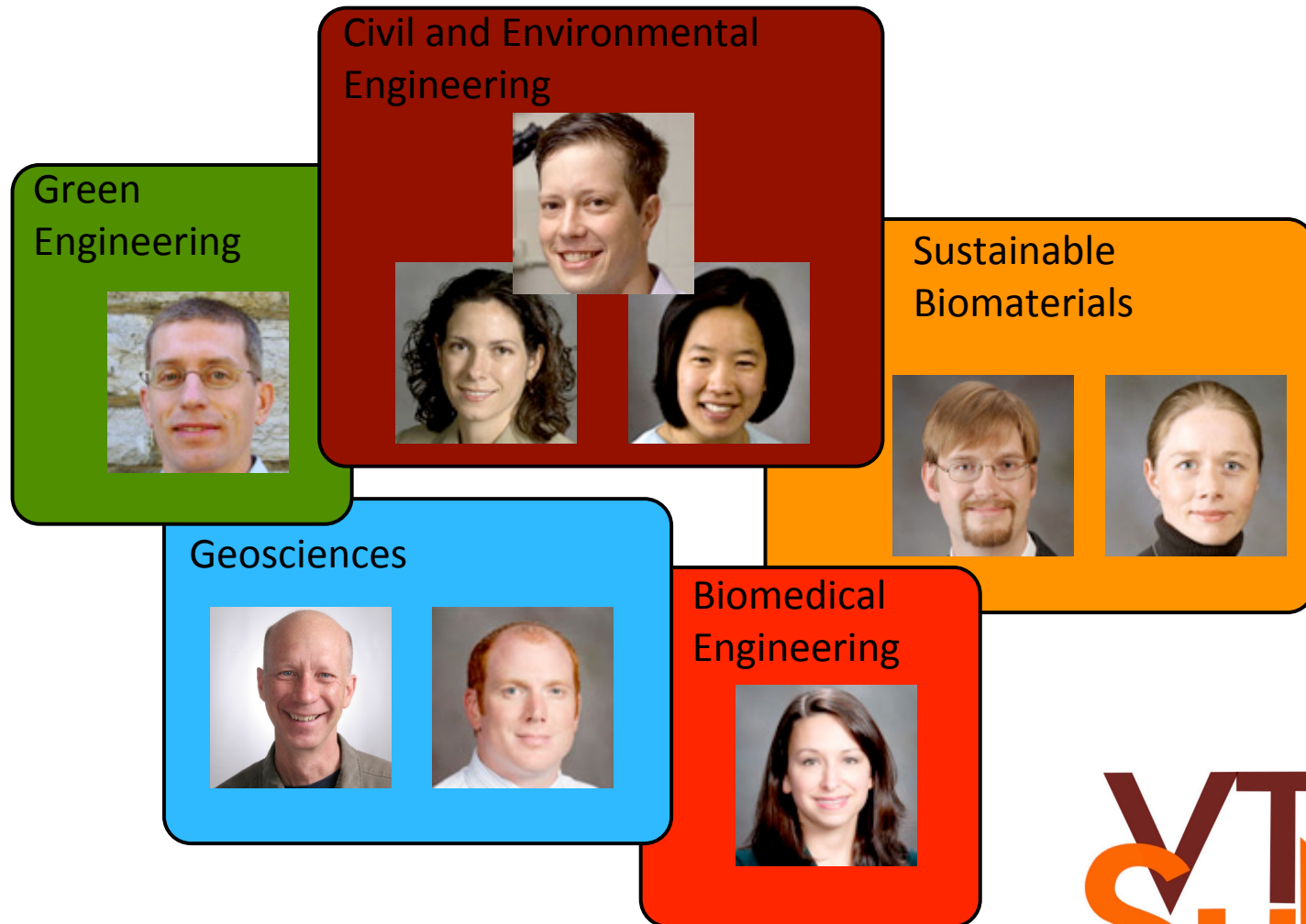
...the growth of world population?

...the decline of non-renewable resources?

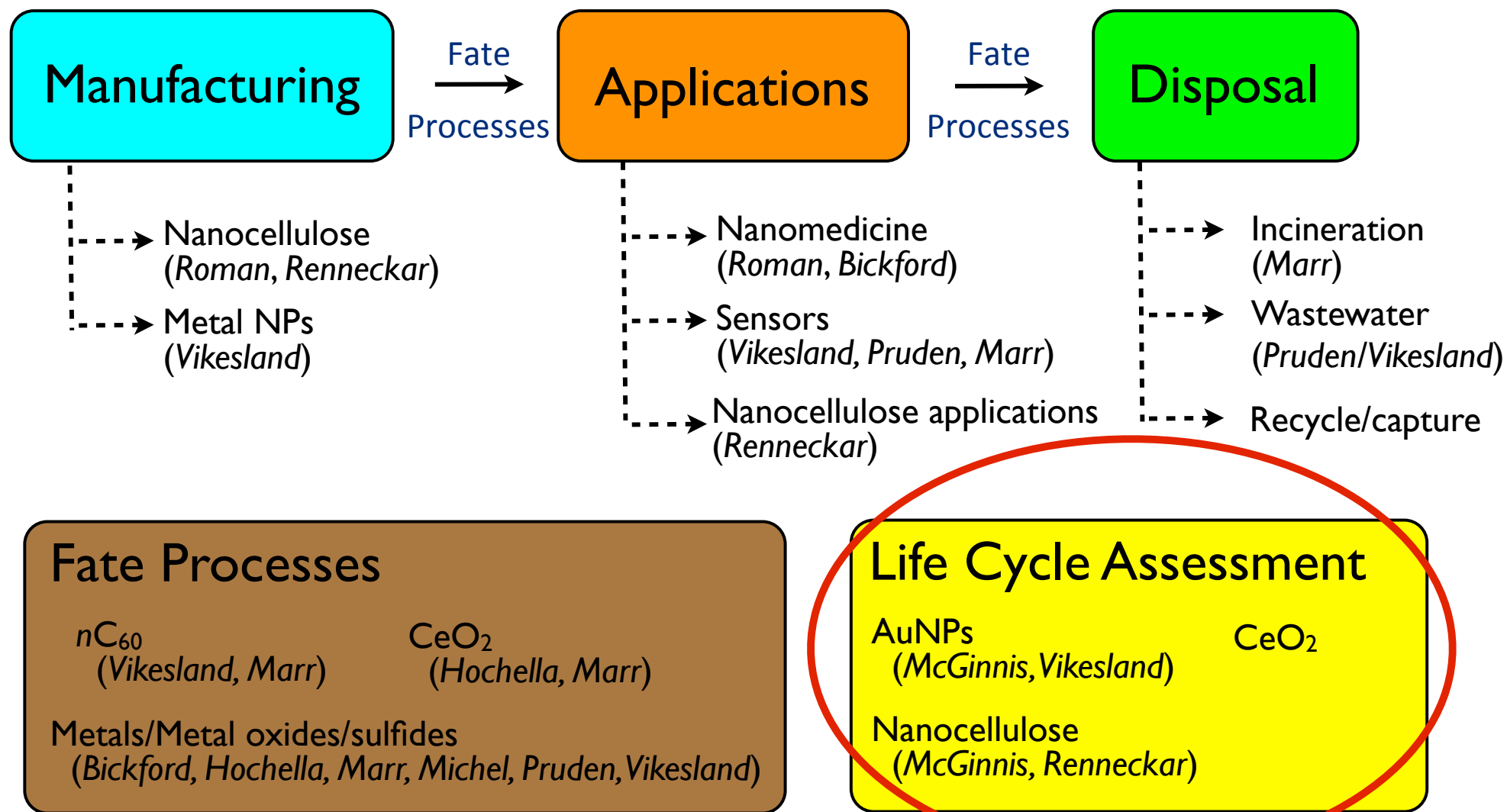
...and the synergistic effects of all of the above?



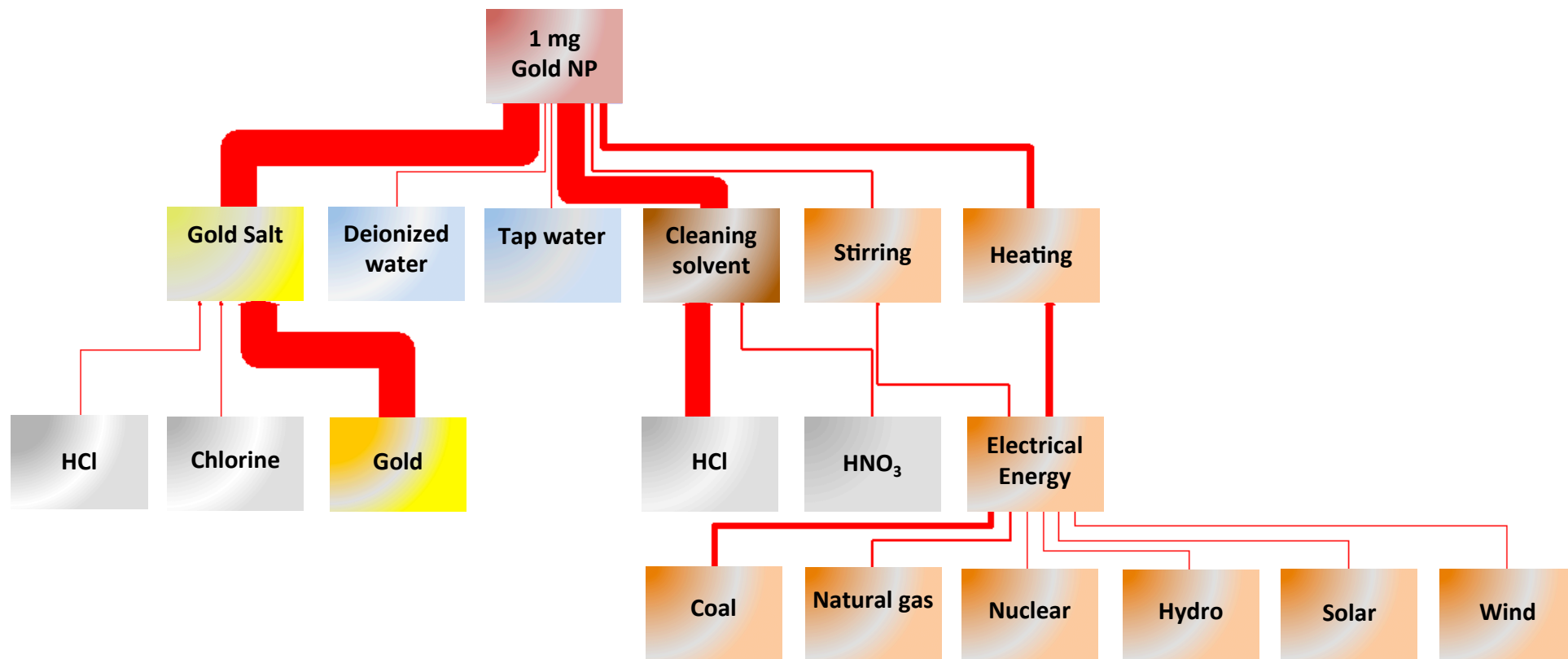
# VTSuN: Sustainable Nanotechnology



# Sustainable Nanotechnology





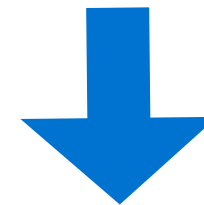
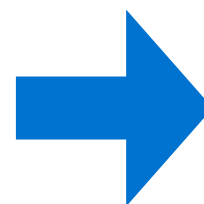
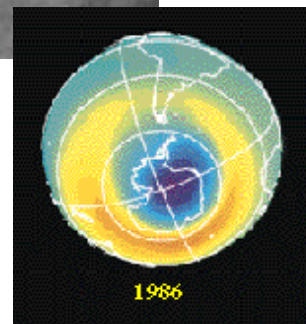
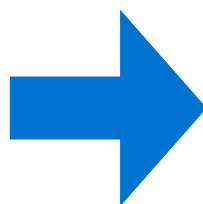
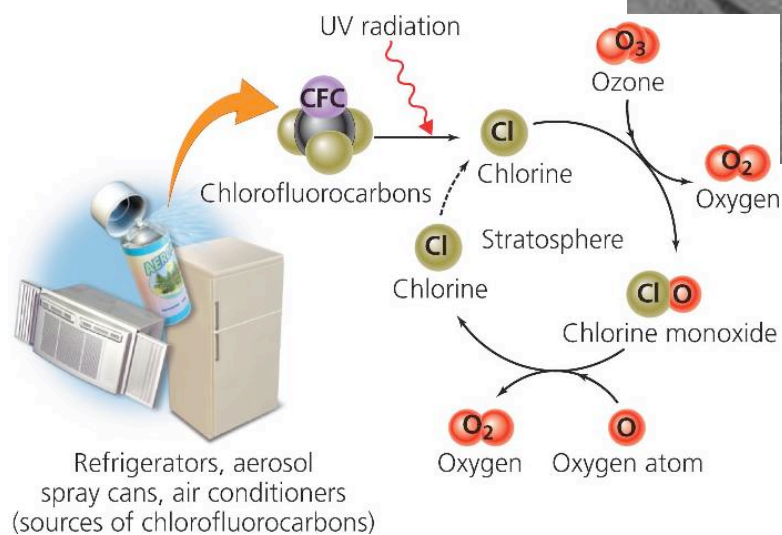
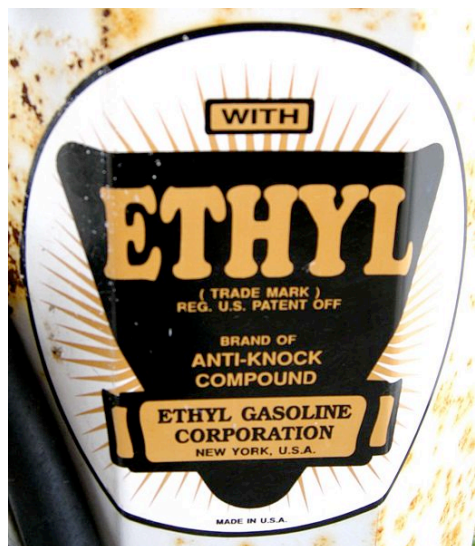


# Opportunity and Challenge III

*What if we are asking the wrong questions?*

History is replete with examples where our solutions to one problem have unforeseen consequences.

Thomas Midgley  
1889-1944



Hydrofluorocarbons (HFCs)  
100-10000x larger GWP than CO<sub>2</sub>

# Principles of “Green” Nanomaterial Production

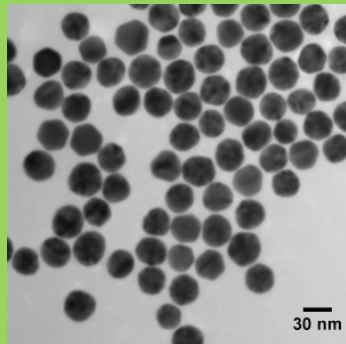
1. **Design safer nanomaterials**
2. Design for reduced environmental impact
3. Design for waste reduction
4. Design for process safety
5. Design for materials efficiency
6. Design for energy efficiency

Hutchison *ACS Nano*, 2008

# I) Design Safer Nanomaterials

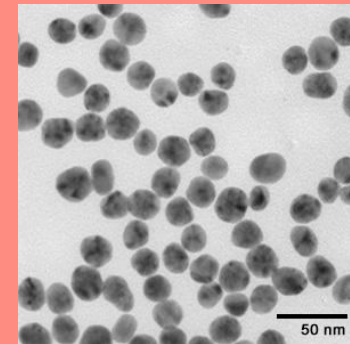
***Replace toxic materials with non-toxic counterparts***

Gold NPs



Nanocomposix

Silver NPs



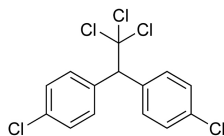
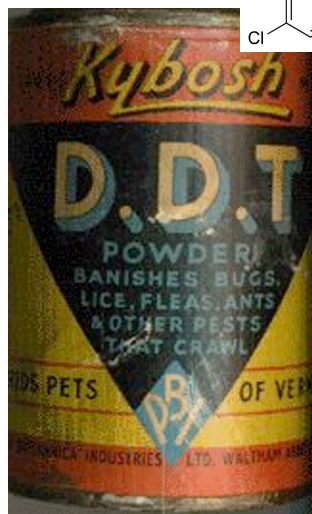
Nanocomposix

What if persistence is of greater concern than short-term reactivity?

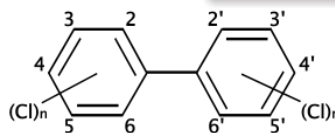


# Persistent Bioaccumulative Pollutants

## DDT

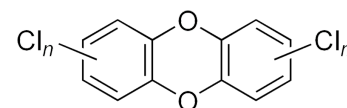


“[DDT] is cheap, easily manufactured, and exceedingly stable...”  
Nobel Prize Citation, 1948



## PCBs

## DIOXINS



<http://www.niehs.nih.gov/>

Each of these compounds is chemically **persistent**, is subject to **bioaccumulation** via trophic transfer, and is inherently **toxic**.

Persistent?

Bioaccumulative?

Toxic?

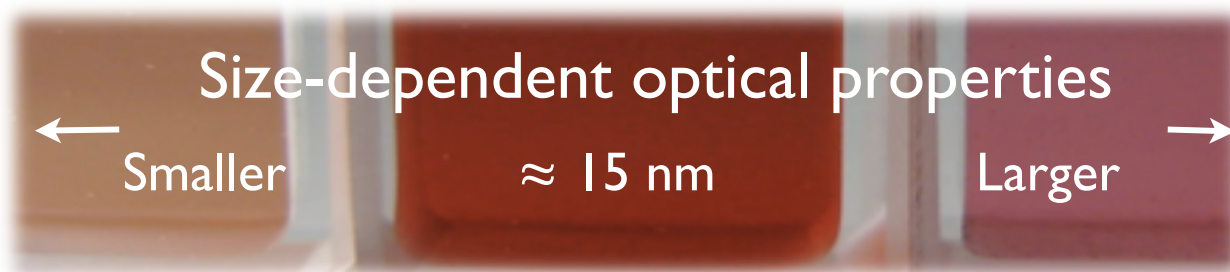
# Gold nanomaterials are one type of nanomaterial with many commercial applications

## Applications

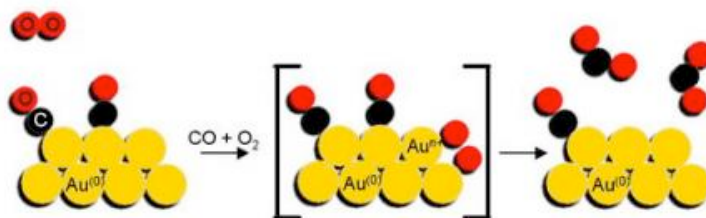
- Pharmaceuticals
- Biosensors
- Catalysis

## Advantages

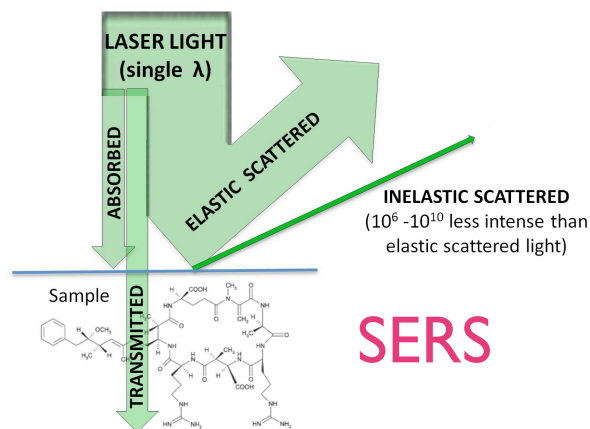
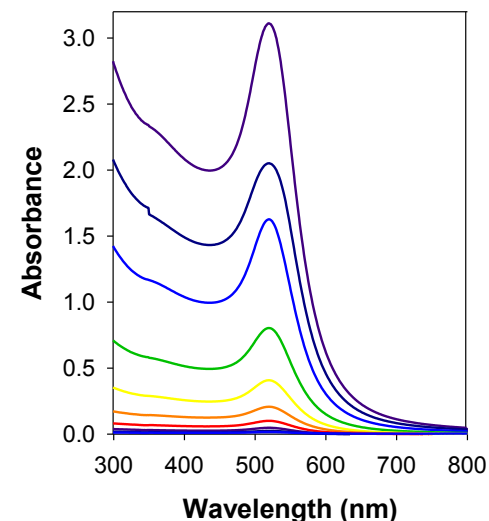
- Ease of synthesis
- Size and shape control
- Characterization
- Plasmonics
- Surface functionalization



## Catalysis

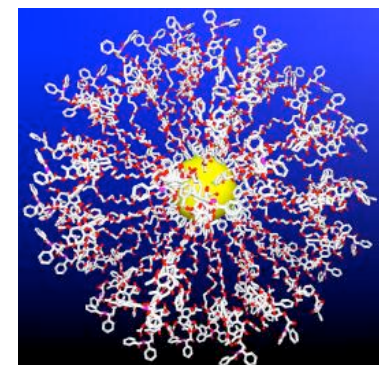


## Plasmonics



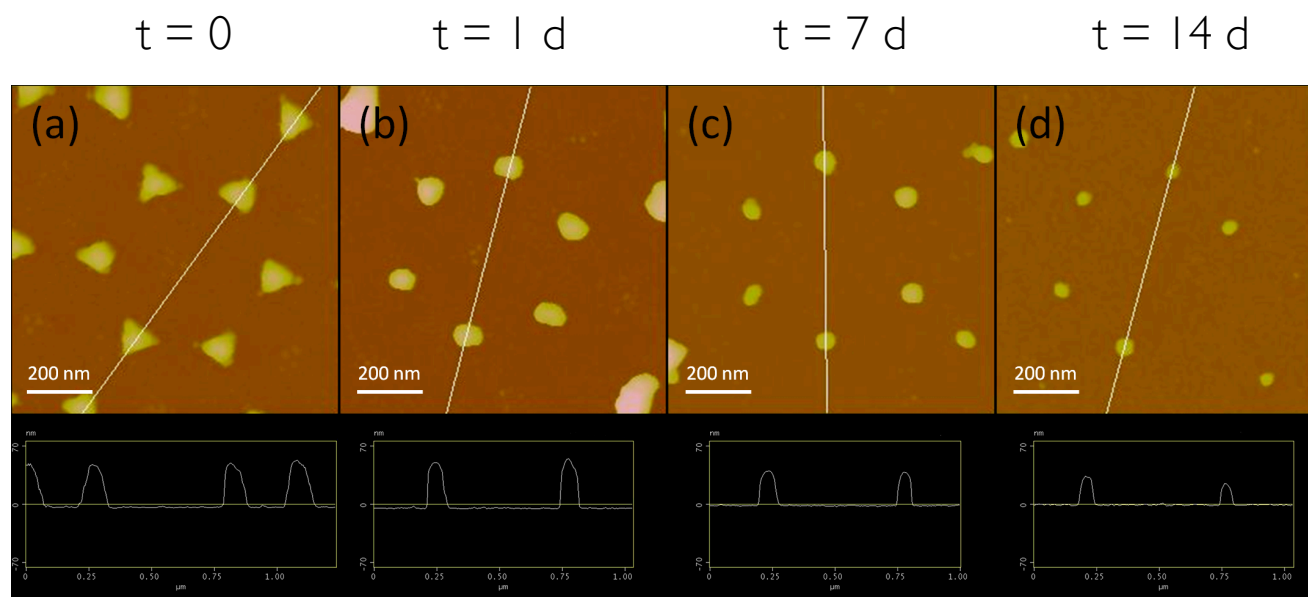
## SERS

## Pharmaceuticals

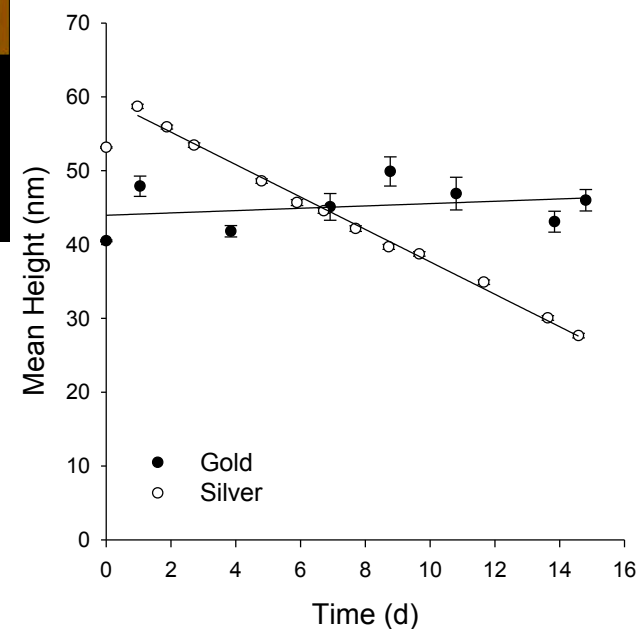


# Gold nanomaterials are chemically persistent

We recently developed an AFM based method to evaluate the chemical stability of gold and silver nanomaterials.



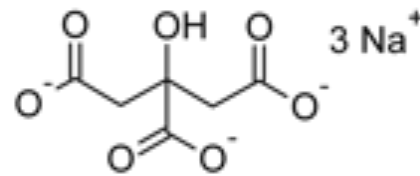
AgNP dissolution in 550 mM NaCl



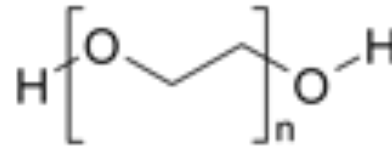
To enhance the colloidal stability of AuNP we can functionalize its surface.

## Functional Group

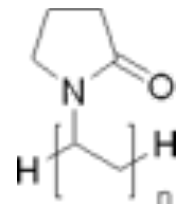
Citrate



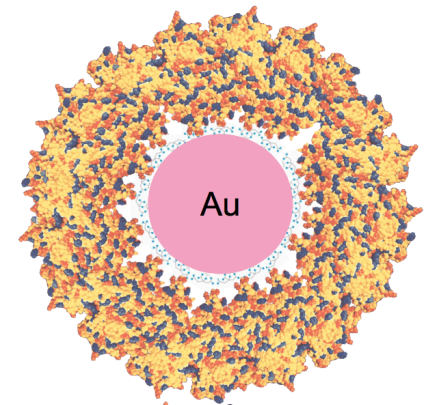
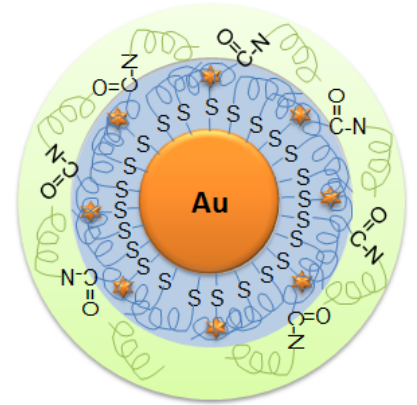
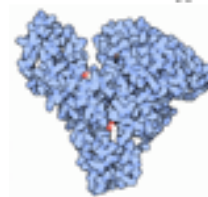
Polyethylene glycol (PEG)



Poly(N-vinyl-2-pyrrolidone) (PVP)



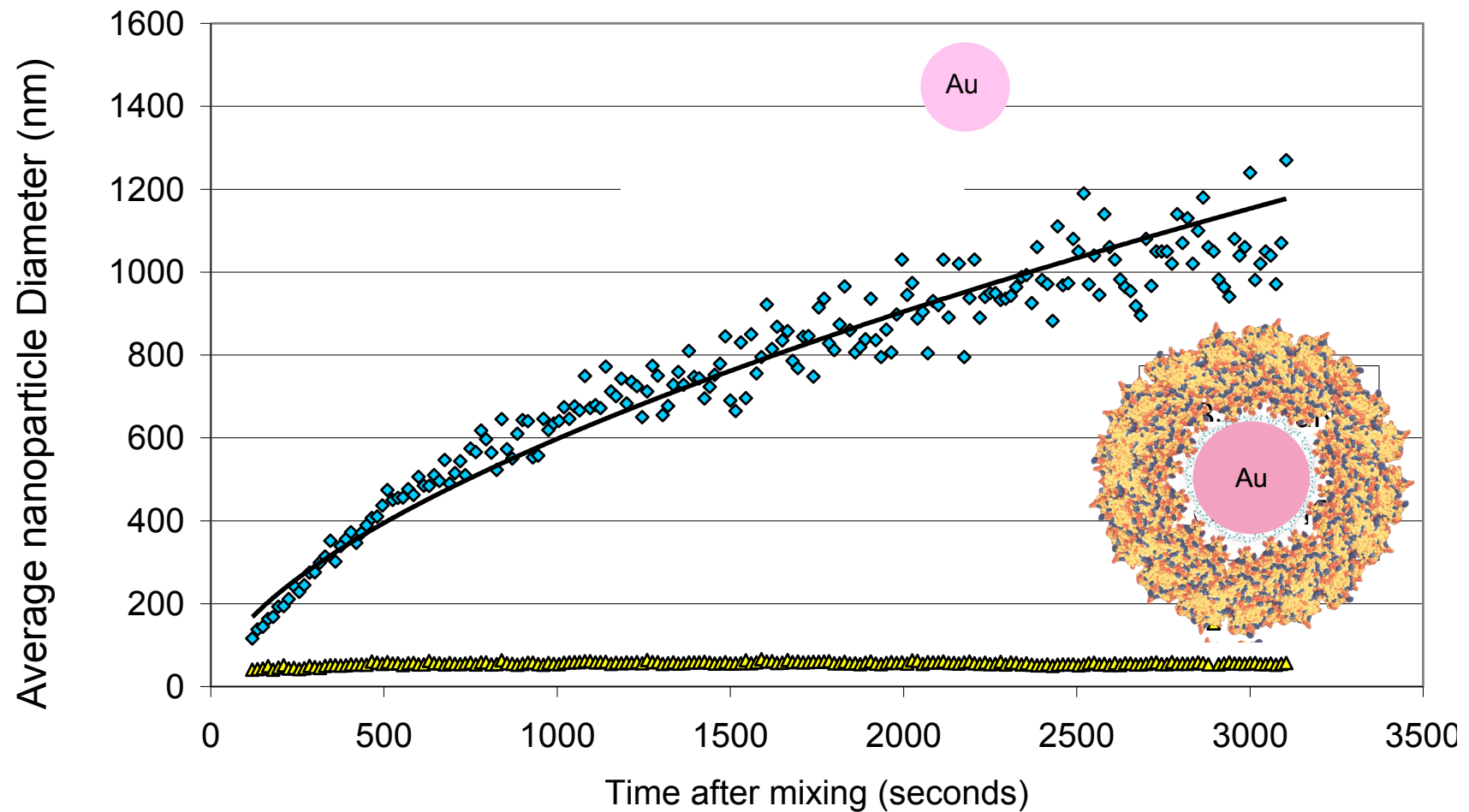
Biologically and environmentally relevant macromolecules (proteins, NOM)



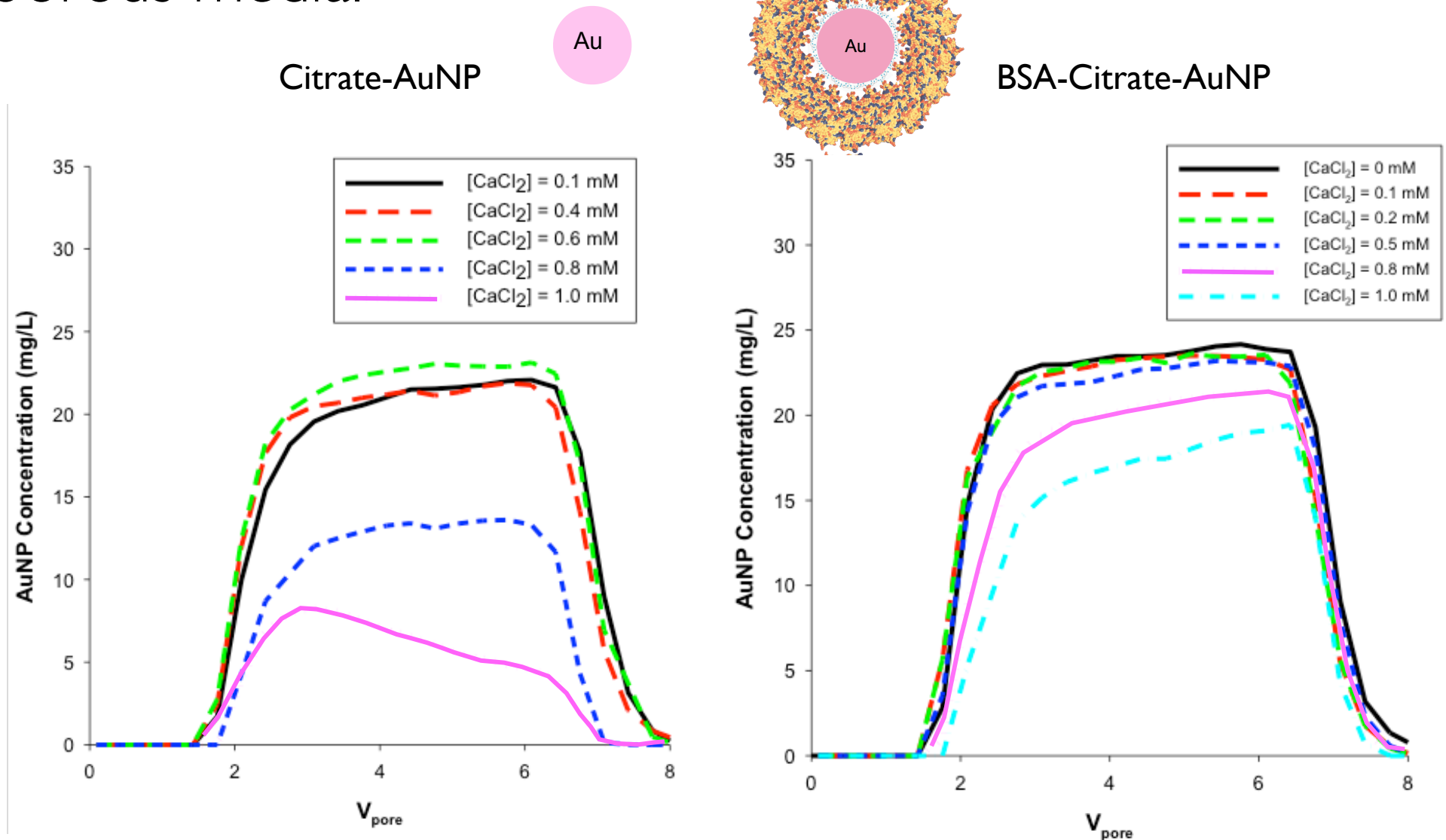
An endless variety of surface functionalities are possible due to the capacity for gold to form strong covalent thiol bonds.



# Surface coatings enhance gold nanoparticle stability.



# BSA enhances gold nanoparticle transport through porous media.



Chan and Vikesland, *ES&T* 2014

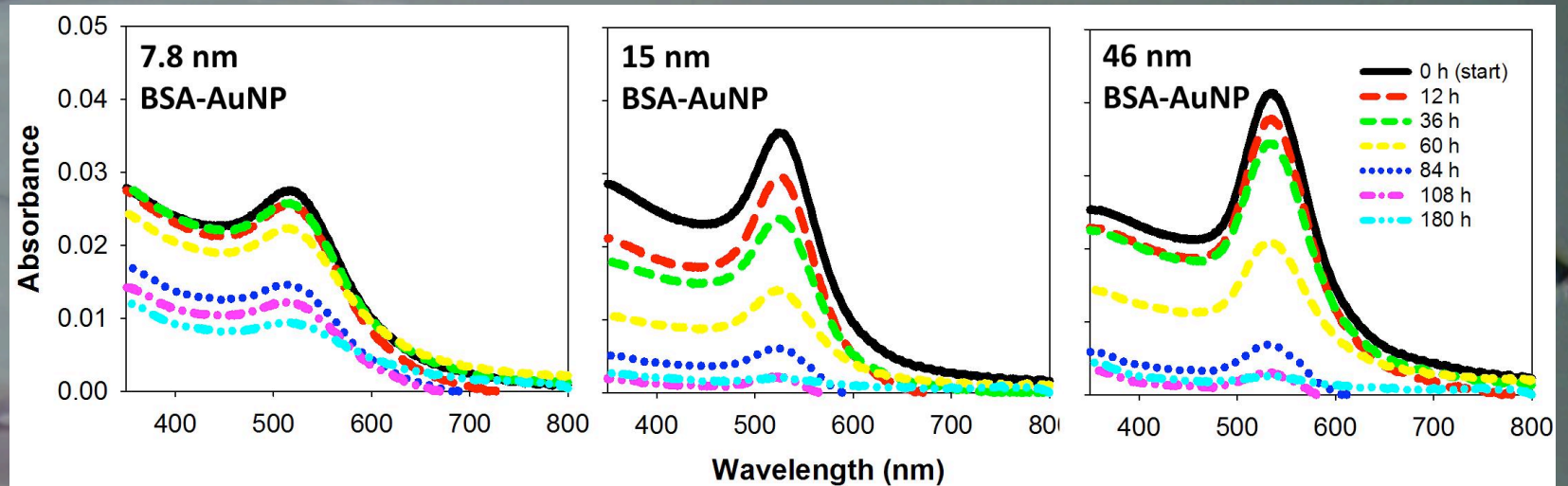
$C_0 = 24.5$  mg/L 15 nm AuNP; 260 nm glass beads

Persistent?



Bioaccumulative?

Toxic?



Gold nanoparticle  
suspension 48 hrs after  
exposure to *C. fluminea*

Gold nanoparticle  
suspension in the  
absence of *C. fluminea*

Daily sampling by UV-Vis shows time-dependent decrease in absorbance intensity at the SPR band  
for BSA-AuNP  
(controls without clams were stable throughout)

# Gold nanoparticles biomagnify.

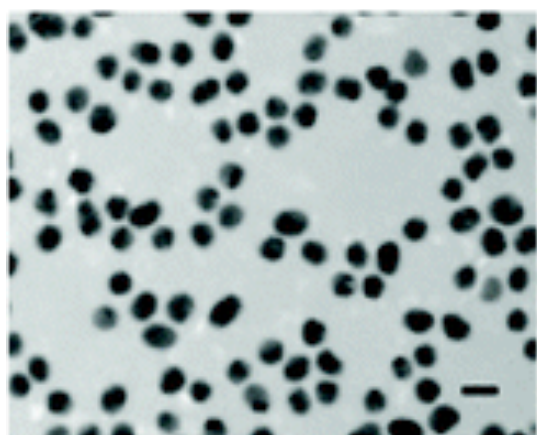
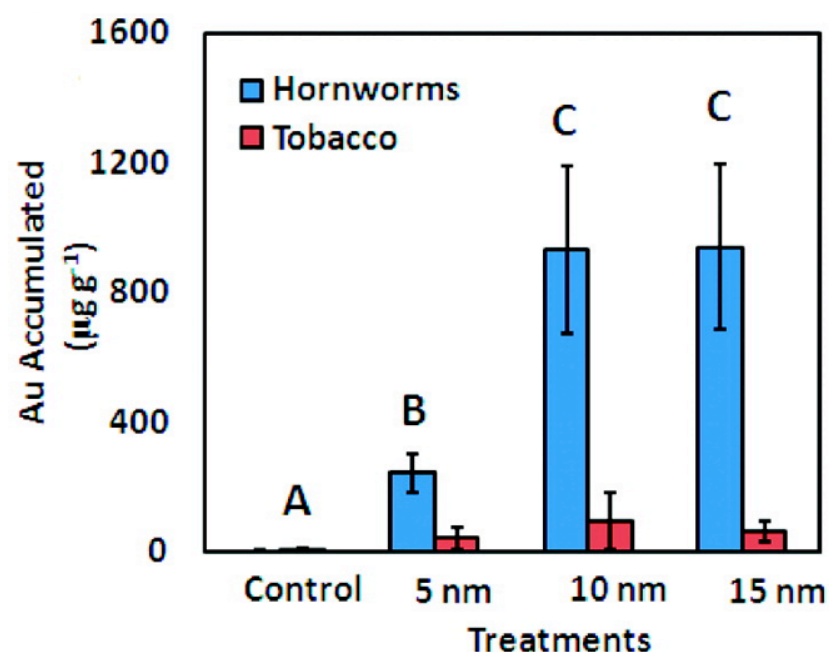
## Evidence for Biomagnification of Gold Nanoparticles within a Terrestrial Food Chain

JONATHAN D. JUDY, JASON M. UNRINE,  
AND PAUL M. BERTSCH\*

*Department of Plant and Soil Sciences, University of  
Kentucky, Lexington, Kentucky 40546, United States*

*Received September 3, 2010. Revised manuscript received  
November 9, 2010. Accepted November 18, 2010.*

*Environ. Sci. Technol.* **2011**, *45*, 776–781



Au NPs



*Nicotiana tabacum*  
L. cv *Xanthi*



*Manduca sexta*  
(tobacco hornworm)



Persistent?



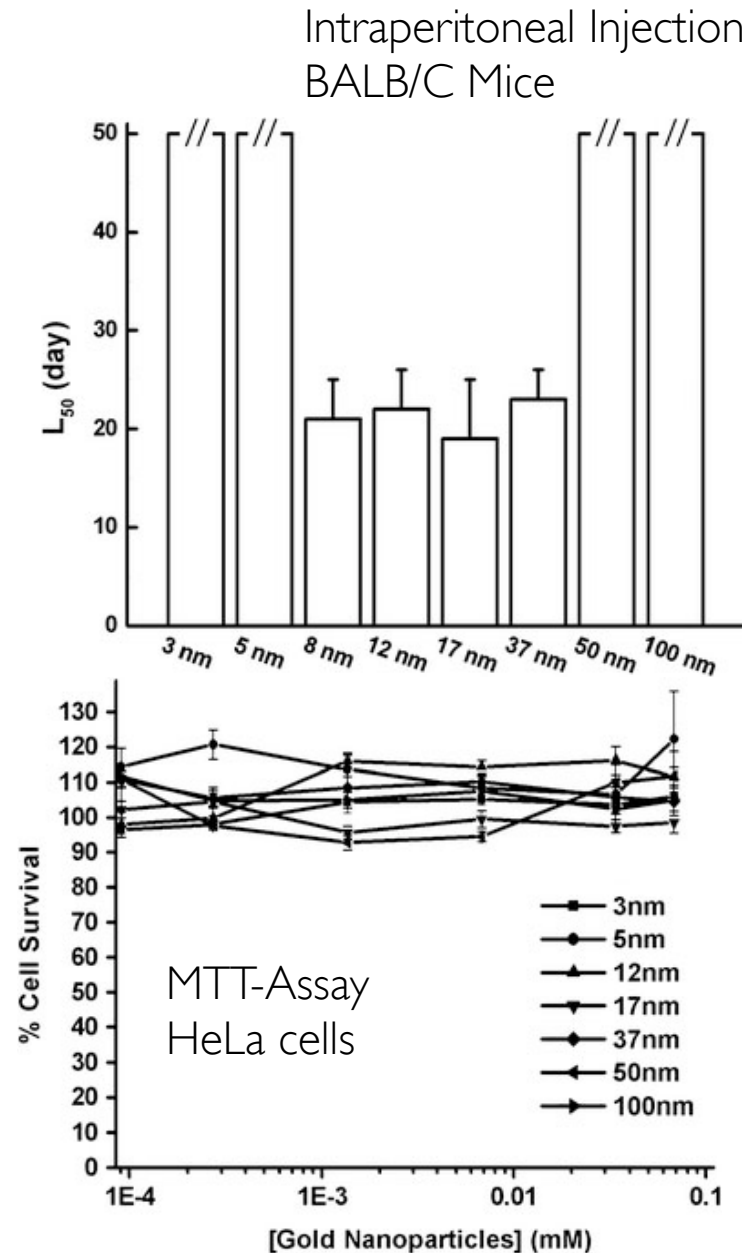
Bioaccumulative?



Toxic?

It is currently unclear whether gold nanomaterials are toxic since major inconsistencies plague the literature.

- *In vitro* studies are inconclusive - some reports suggest toxicity, while others report none using the same nanomaterial.
  - Coatings are important
  - Cell lines matter
- More *in vivo* studies are required.
  - Localization of AuNP to liver and kidneys in vertebrate studies
  - 8-37 nm citrate-AuNP toxic to mice.
  - Localization of AuNP to digestive tract and digestive gland in invertebrate studies
  - No apparent toxicity to *C. fluminea*



Persistent?



Bioaccumulative?



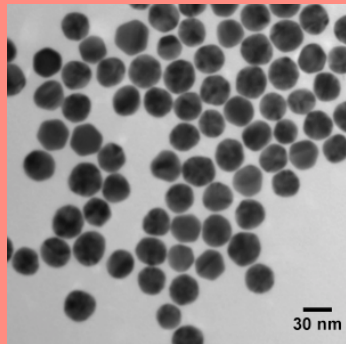
Toxic?



# I) Design Safer Nanomaterials

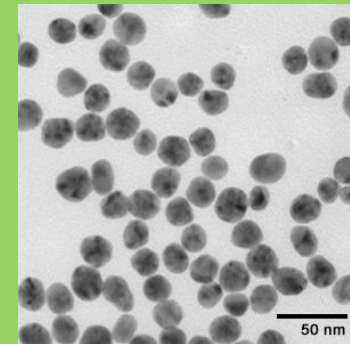
***Replace toxic materials with non-toxic counterparts***

Gold NPs



Nanocomposix

Silver NPs



Nanocomposix

What if persistence is of greater concern than short-term reactivity?

# Opportunities:

1. Materials scientists, chemists, environmental scientists and engineers should continue to expand the types of nanomaterials being collectively studied.
2. Systems approaches (e.g., life cycle assessment) should be applied to ensure nanotechnologies develop in a manner that considers societal sustainability.
3. The nanotechnology community needs to continually ensure that we ask the right questions with respect to the environmental implications of nanomaterials.