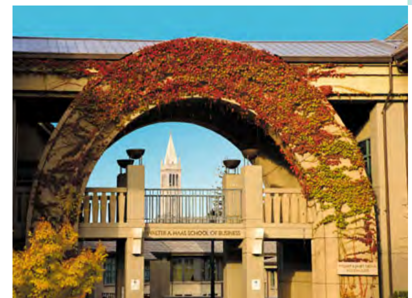
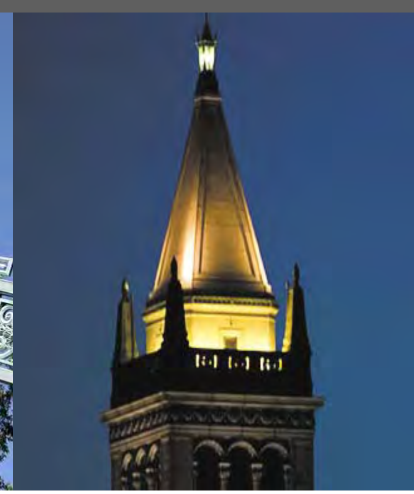
DTSC Berkeley



Marty Mulvihill

October 12, 2011

A Greener Approach to Nanotechnology



How can Green Chemistry be applied to research projects?

- Introduce green chemistry.
- Discuss two examples of green chemistry approaches to nanoscience.

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Sustainability and Green Chemistry

Sustainability

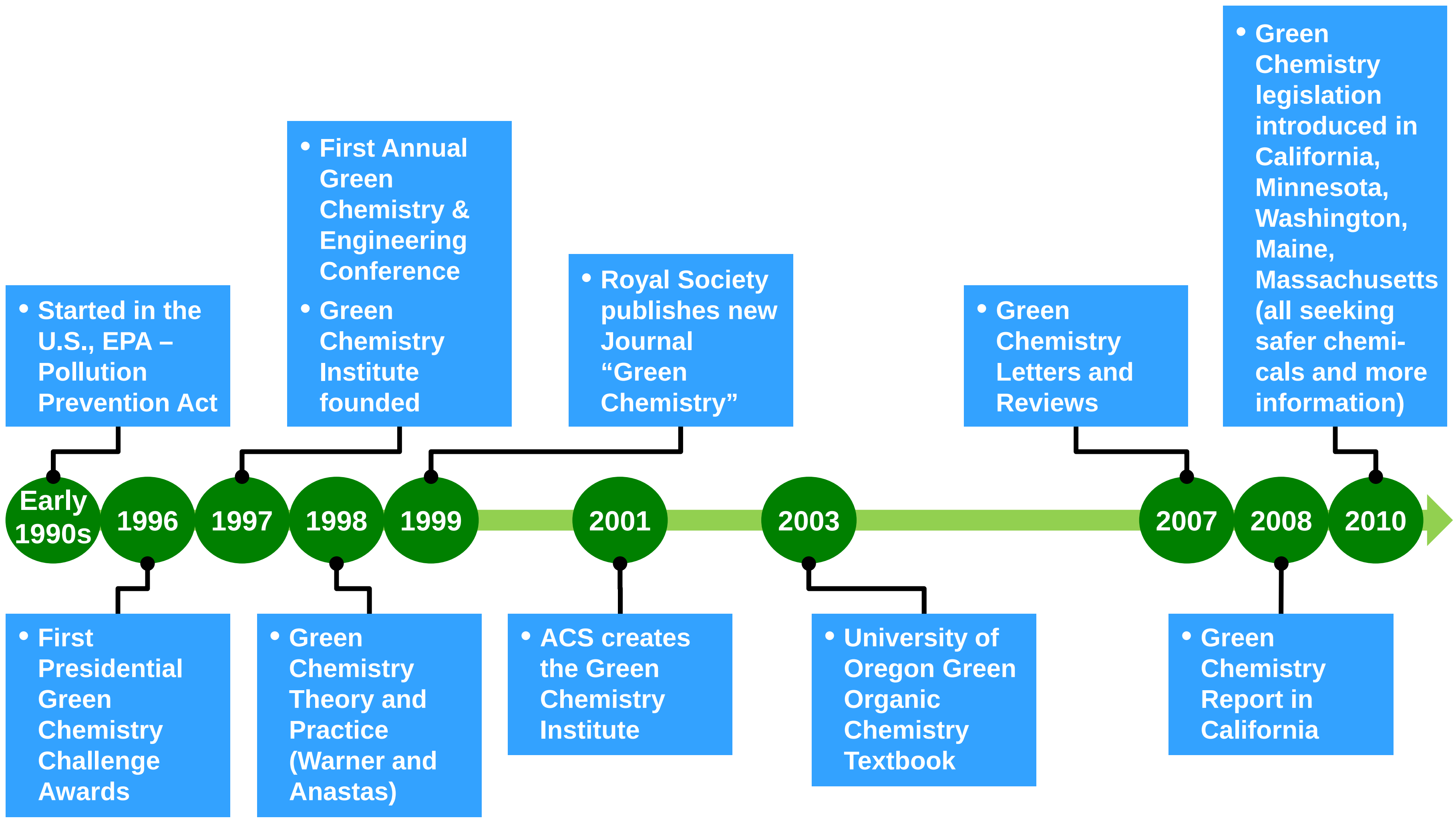
"Meeting the needs of the present without compromising the ability of future generations to meet their needs"

– *Our Common Future,*
Report of the Brundtland Commission,
Oxford University Press 1987

Green Chemistry

- The science behind the discovery and implementation of safer, cleaner, and more efficient chemical processes and products
- Entails design of chemical products and processes that aim to eliminate the use and generation of hazardous substances
  - Seek to minimize:
    - Waste
    - Energy use
    - Resource use (maximize efficiency)
  - Use renewable resources

Green Chemistry Timeline



What Is Green Chemistry?

Materials + **Reactions** = **Products**

Materials

- Bio-based
- Minimize solvent and auxiliaries
- Safer solvents

Reactions

- High yielding
- Atom and energy efficient
- Room temperature and pressure
- Catalytic

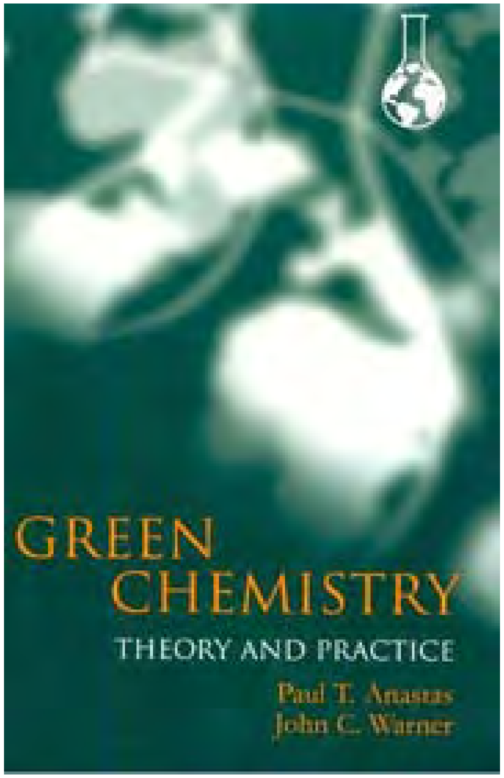
Products

- Design for end of life (degradable or recyclable)
- Consider toxicity

Safer and More Efficient Chemistry

12 Principles of Green Chemistry

1	Prevent waste
2	Design safer chemicals and products
3	Design less hazardous chemicals syntheses
4	Use renewable feedstock chemicals
5	Use catalysts, not stoichiometric reagents
6	Avoid chemical derivatives
7	Maximize atom economy
8	Use safer solvents and reaction conditions
9	Increase energy efficiency
10	Design chemicals and products to degrade after use
11	Analyze in real time to prevent pollution
12	Minimize the potential for accidents



Why Do Green Chemistry?

1 **Innovation:**
An opportunity to guide basic research

2 **Efficiency:**
Material and monetary efficiency

3 **Enhanced Reputation:**
Publications and awards

Natural Synergy between Green Chemistry and Nanotechnology

Dematerialization and Transmaterialization

"use less"

"renewable rather than depleting"

Principles of Greener Nanoscience

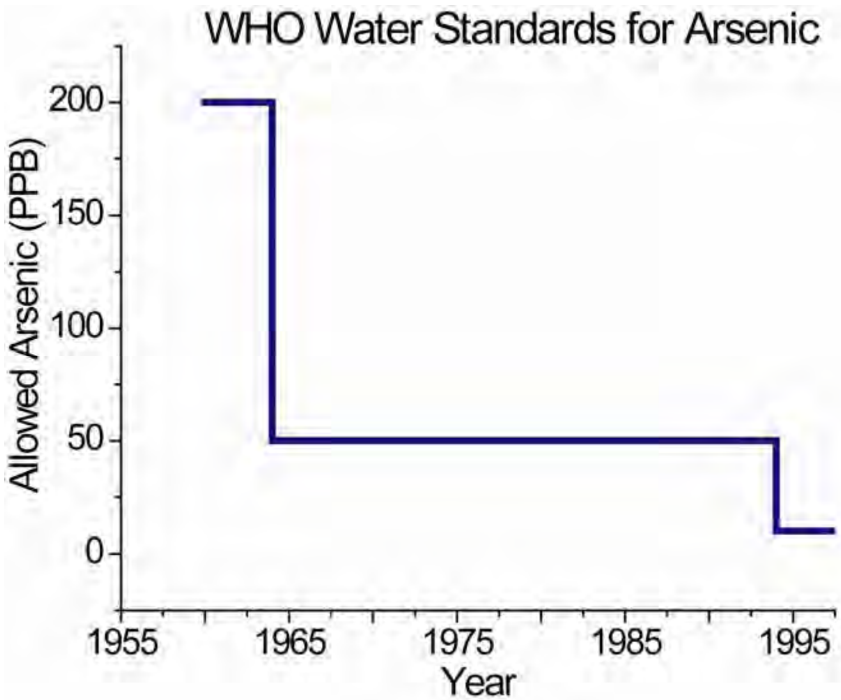
12 Principles of Green Chemistry

1. Prevent waste
2. Atom economy
3. Less hazardous chemical synthesis
4. Design safer chemicals
5. Safer solvents/reaction media
6. Energy efficency
7. Use renewable feedstocks
8. Reduce derivatives
9. Catalysis
10. Design for end of life
11. Real-time process control
12. Inherently safer chemistry

Designing Greener Nanomaterials	Practicing Green Nanoscience
Safer nanomaterials (4, 12) →	Avoid incorperation of toxic elements in nanoparticles; determine biological impacts of nanomaterials based on measureable properties.
Reduce environmental impact (7, 10) →	Determine nanomaterial degradation and fate; design material to degrade into hamless products; use bio-based and renewable feedstocks when possible.
Reduce waste (1, 5, 8) →	Eleminate solvent-intensive purifications; develop new purification methods; utilize bottom-up approaches to enhance materials effeciency and eliminate steps.
Process safety (3, 5, 7, 12) →	Develop replacements for toxic and pyrophoric reagents; use more benign reagents and auxiliaries; when possible use water or other green solvents.
Material effciency (2, 5, 9, 11) →	Optimize incorperation of raw material bottom-up and self assembly processes; use real-time monatoring to guide process control.
Energy effciency (6, 9, 11) →	Run reactions under ambient conditions, utilize non-covalent and self assembly methods, use real-time monitoring to optimize reaction chemistry.

Hutchison, J. et al, *Chem. Rev.* 2007, 2228.

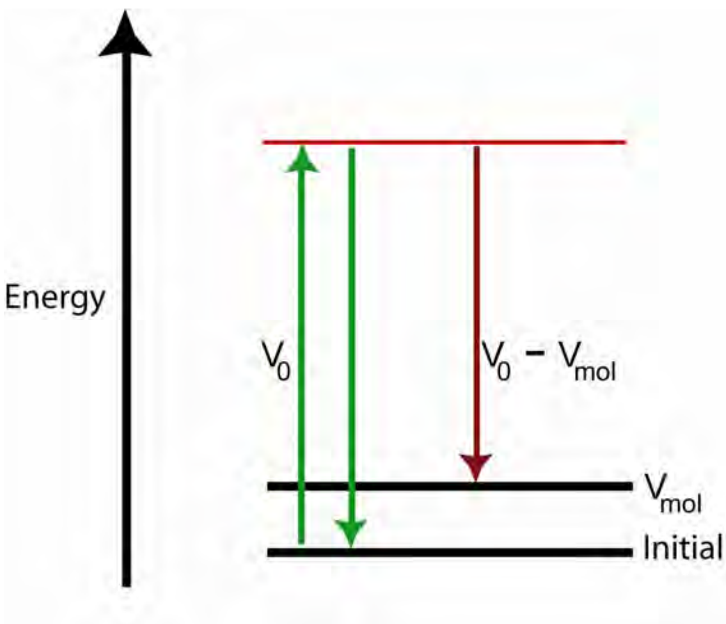
Example 1: Arsenic Sensor Development



- Both chronically and acutely poisonous.
- 28-35 million people are exposed to Arsenic levels of 10 ppb or greater.
- Need for rapid detection.

Surface Enhanced Raman Spectroscopy

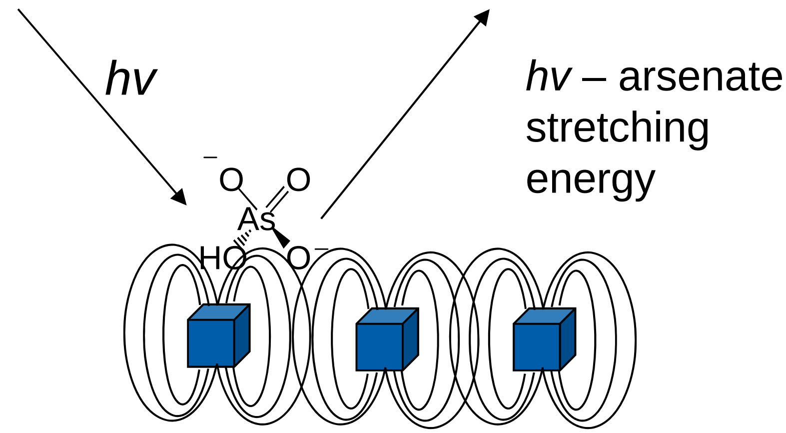
Traditional Raman Scattering



Only 1 in 100,000,000 photons

Detection limits ~100 ppm.

Surface Enhanced Raman Scattering



Concentrates light near analytes.

SERS Enhancements

$$EF = (I_{surface})/(I_{solution}) \times N_{solution}/N_{surface}$$

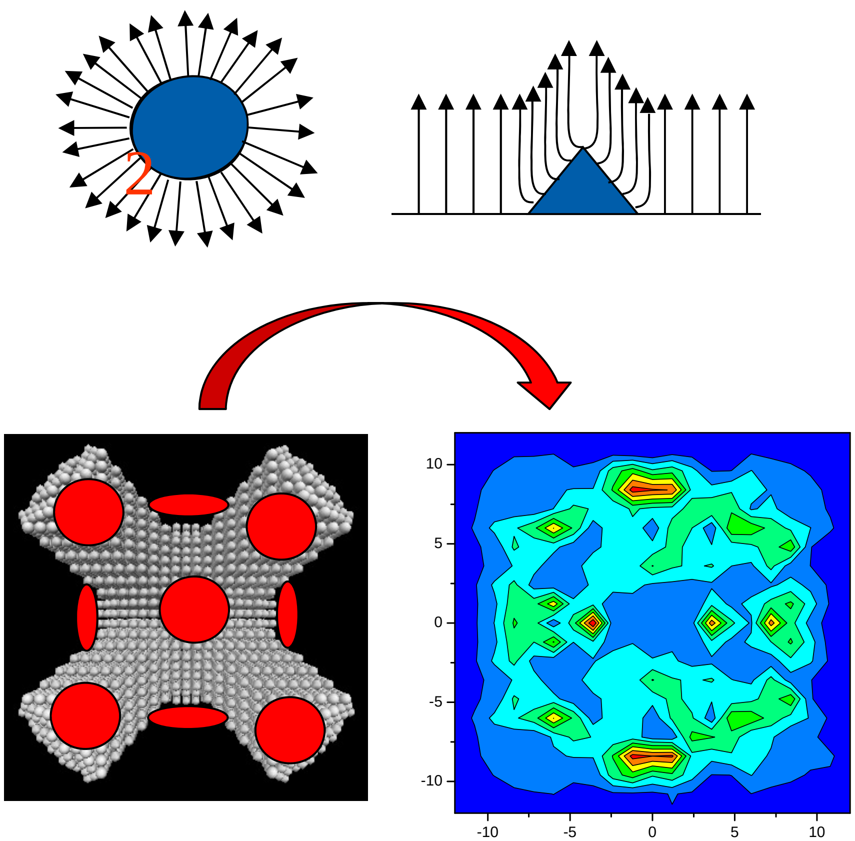
Typical Enhancement Factors (EF) for non-resonant analytes are 10^6-10^8.

Detection limits in ppb (10^{-8} M) or even ppt (10^{-10} M) range.

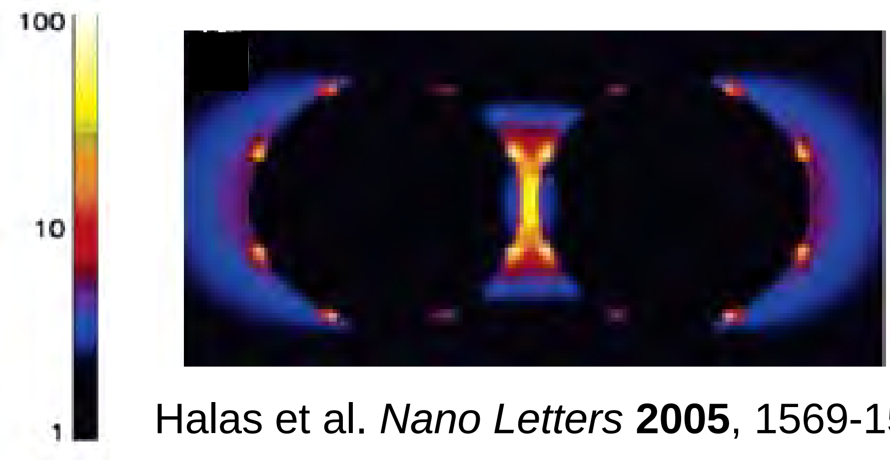
Designing an Effective SERS Substrate

<u>Field Enhancement at sharp corners</u>

<u>Field Enhancement particle junctions</u>

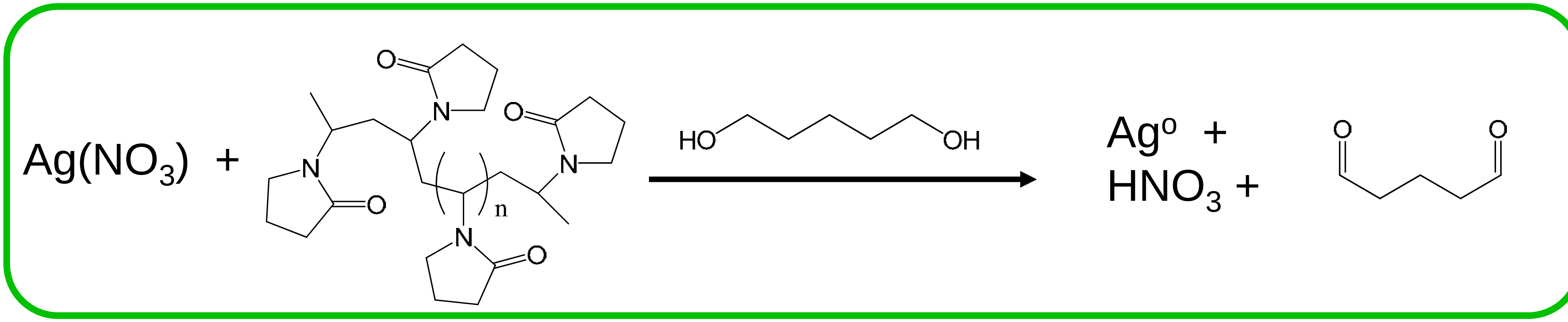


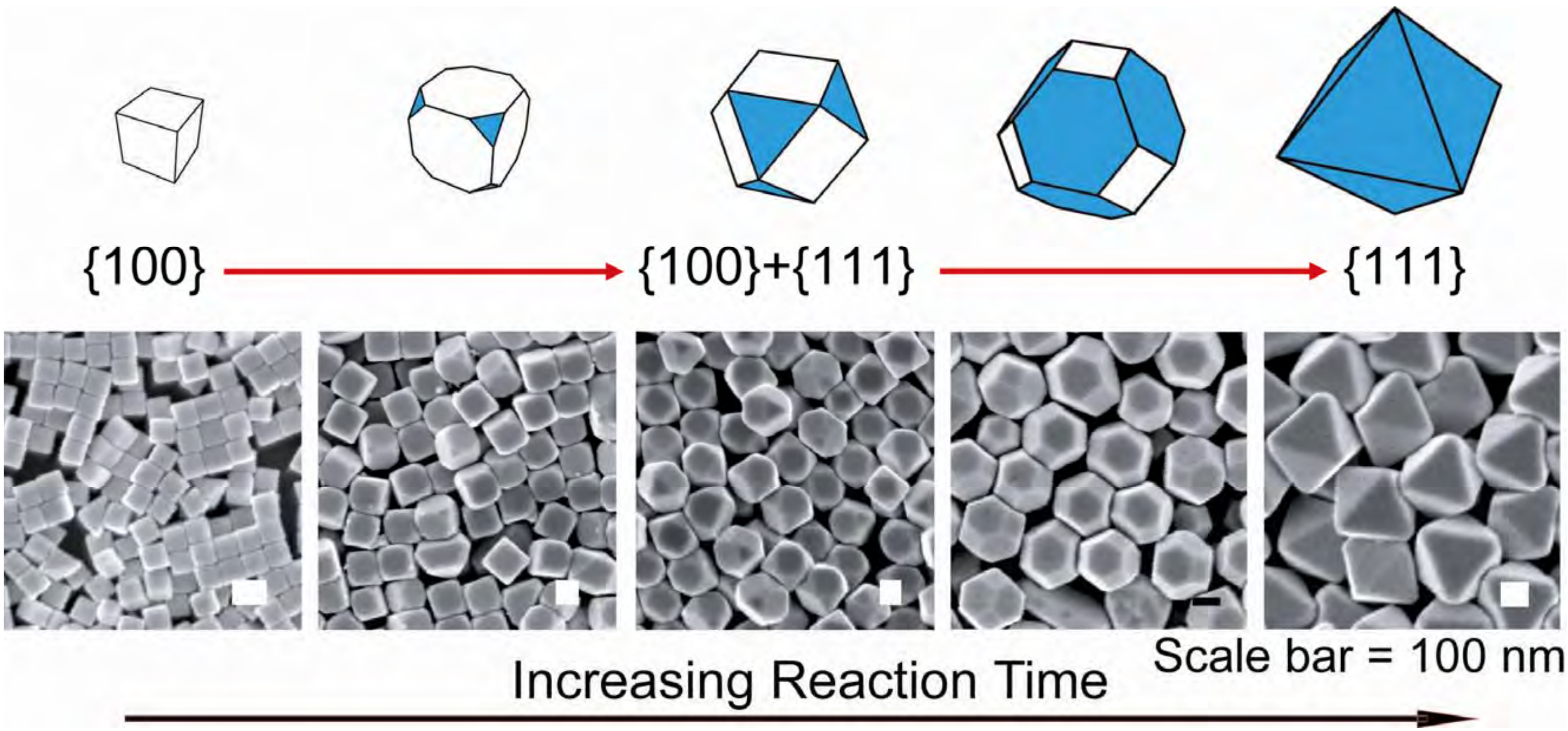
Naumov, I. et al. Applied Physics Letters **2010**, 033105.



Halas et al. *Nano Letters* **2005**, 1569-1574.

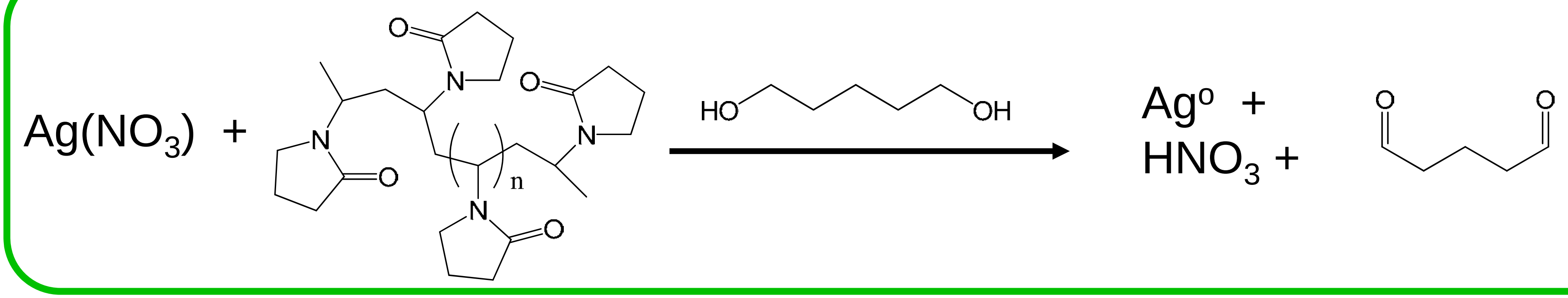
Chemically Induced Shape Control





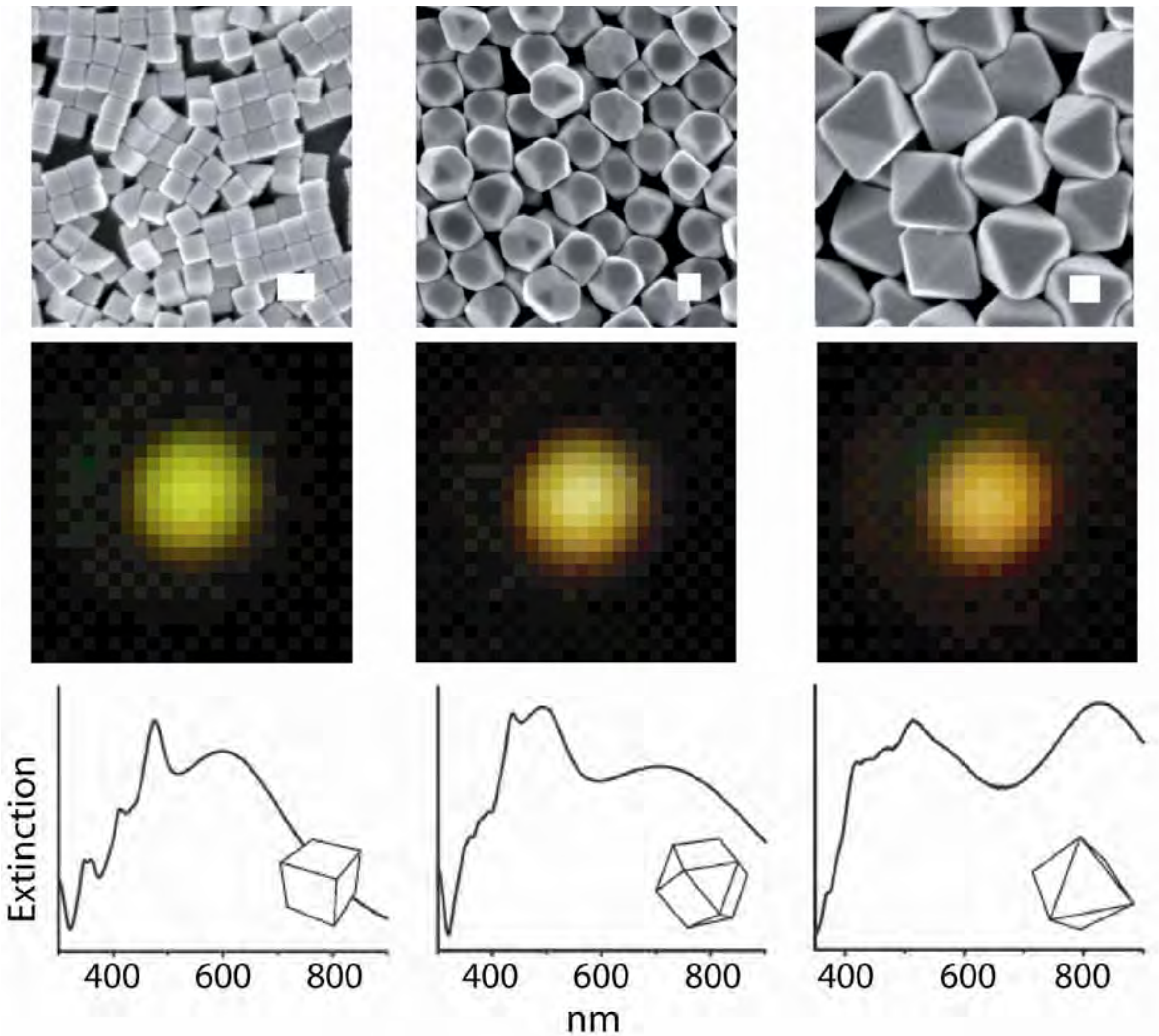
A.Tao et al, *Angewandte* **2006**, 4597 –4601

What Makes This Reaction Green?



- One-pot synthesis.
- Tunable reaction.
- No purification needed.
- Moderate temperatures: 190 °C
- Benign capping agent: PVP
- Reasonably safe reagents and solvents.

Shape Dependent Properties

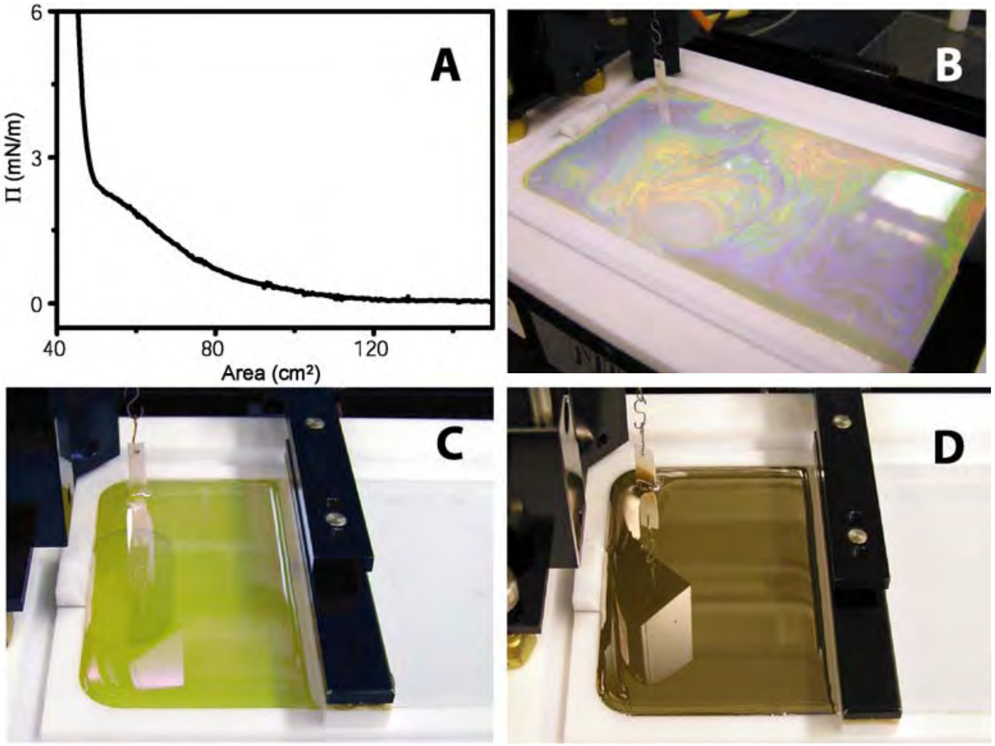


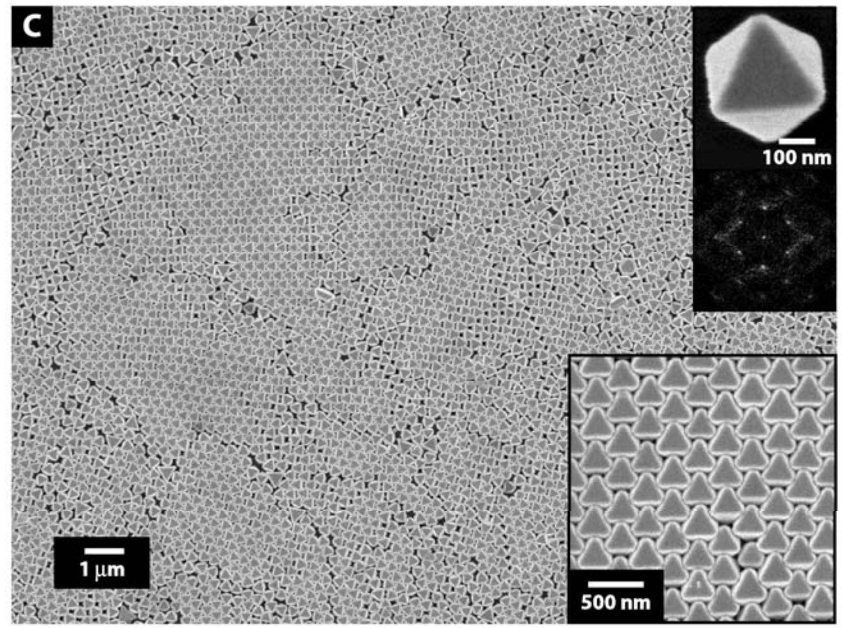
Scanning Electron Microscopy (SEM)
Particle Morphology

Darkfield Optical Microscopy
Particle color

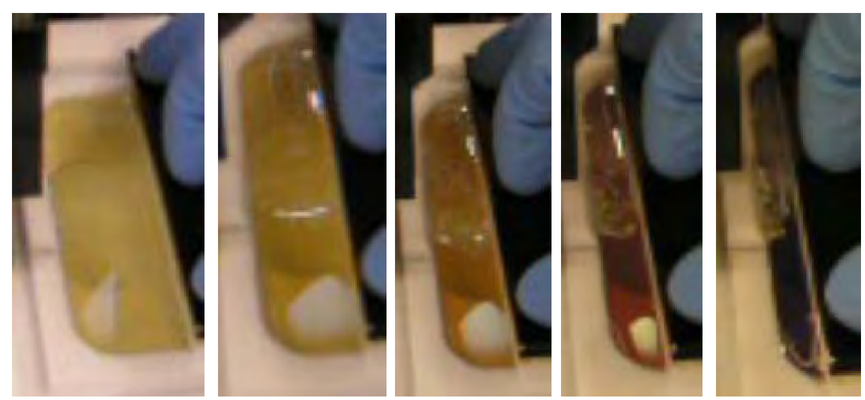
UV-Vis Spectroscopy
Particle Absorption.

Langmuir Blodgett Assembly





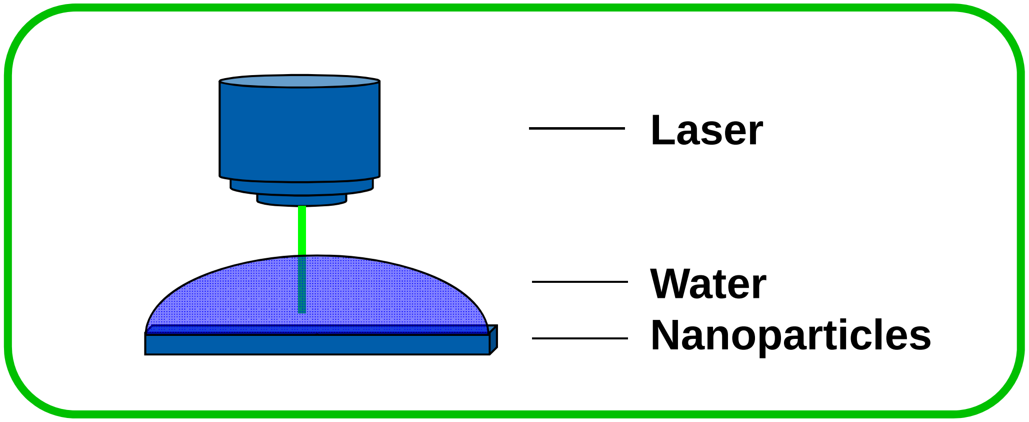
Increasing Surface Pressure

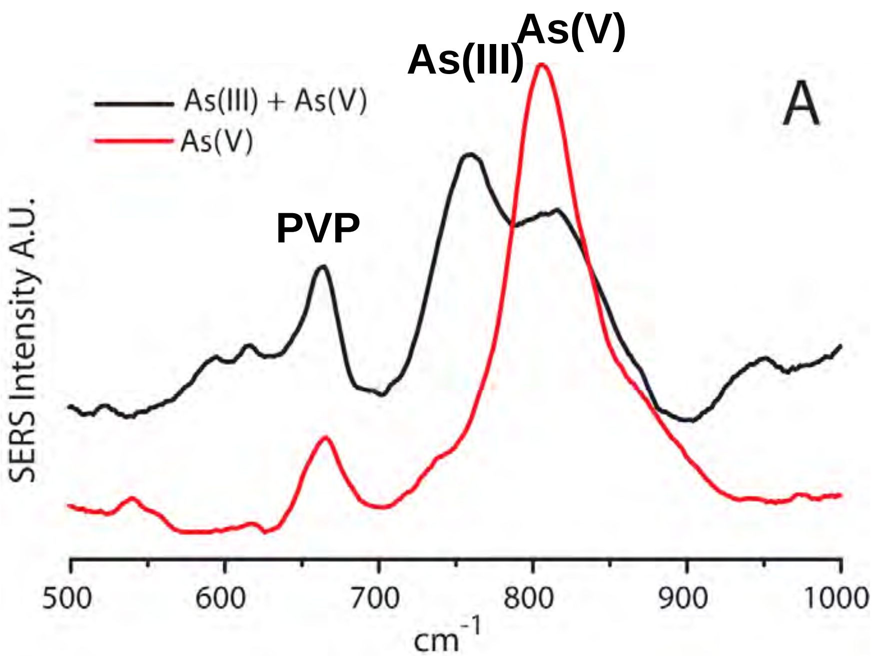


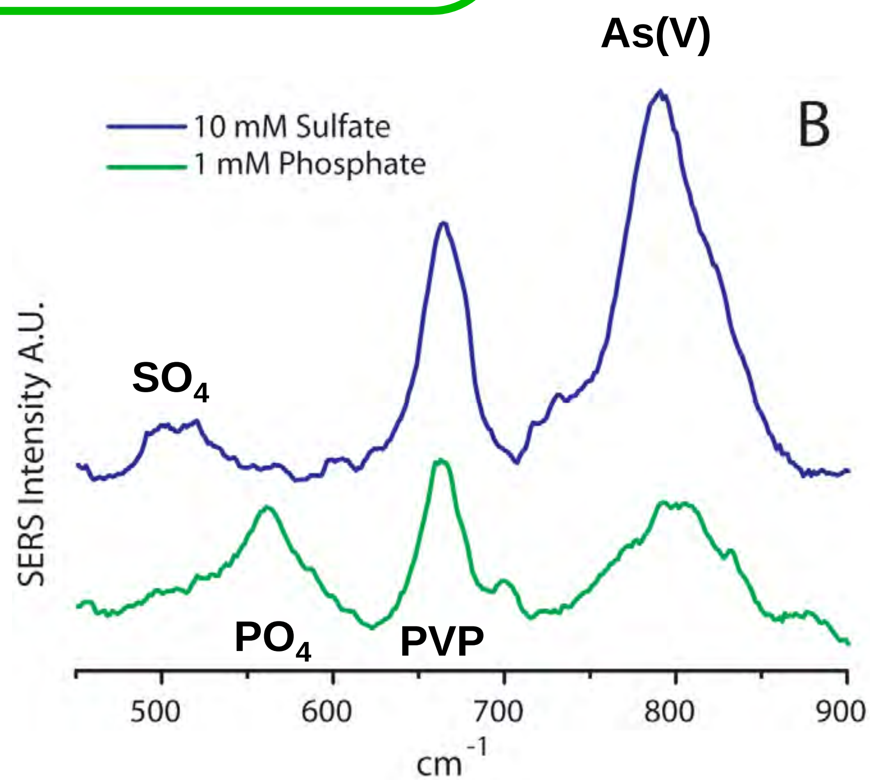
- High surface area
- Control over packing density

A. Tao, et. al, *Nat. Nanotech.* **2008,** 435-440.

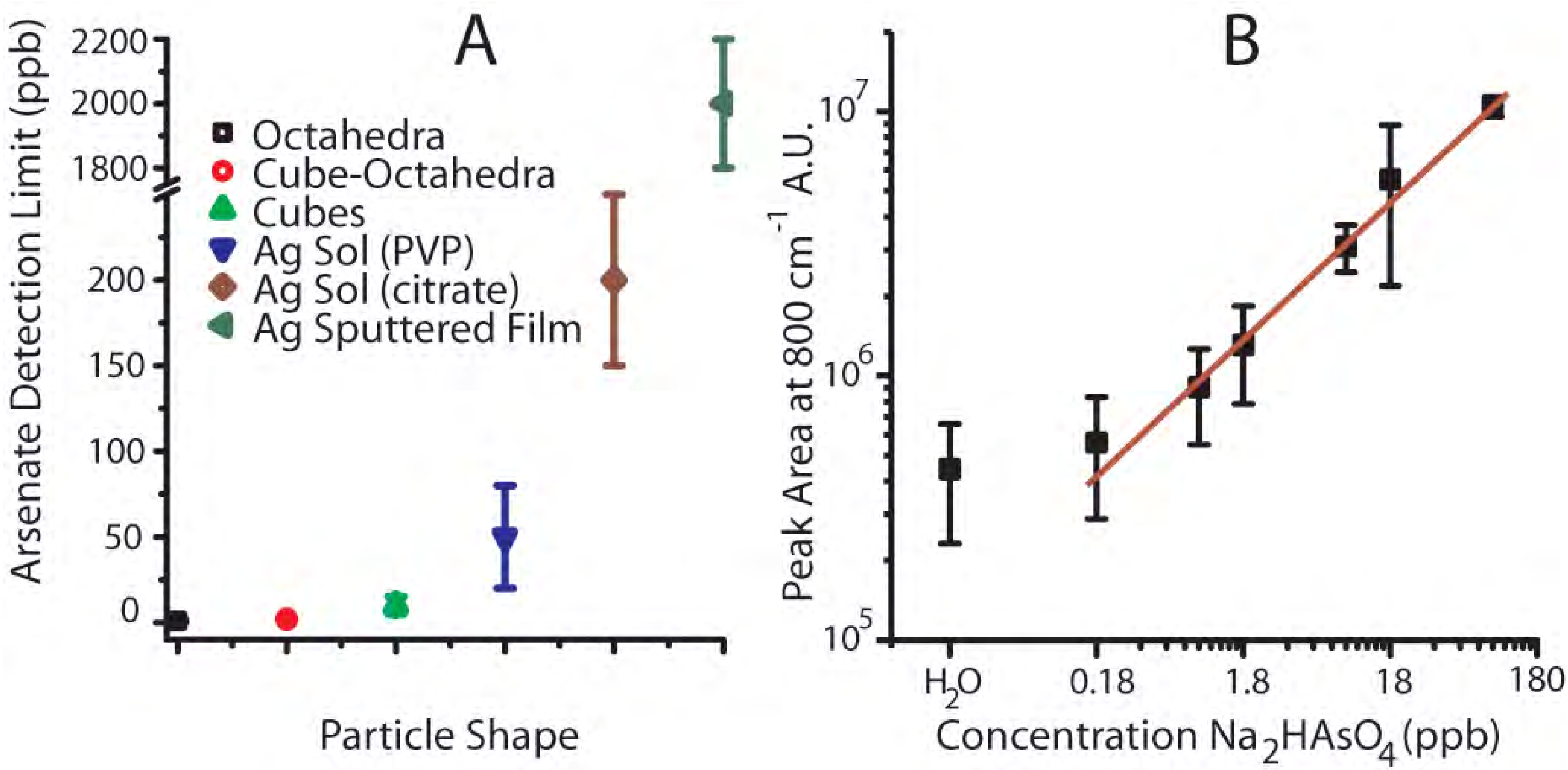
The Arsenic Sensor







Sensing at ppb in ground water

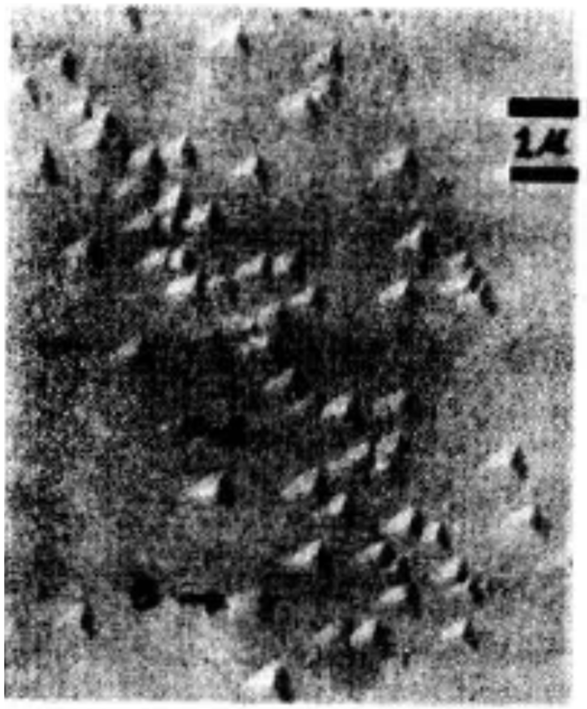


<u>Shape Effect</u>
- Both Shape and PVP improve the sensitivity of particle assemblies.

<u>Sensitivity</u>
- Linear over three orders of magnitude.
- Well below WHO limits.

M. Mulvihill, *Angew. Chem. Int. Ed.* **2008**, 6456.

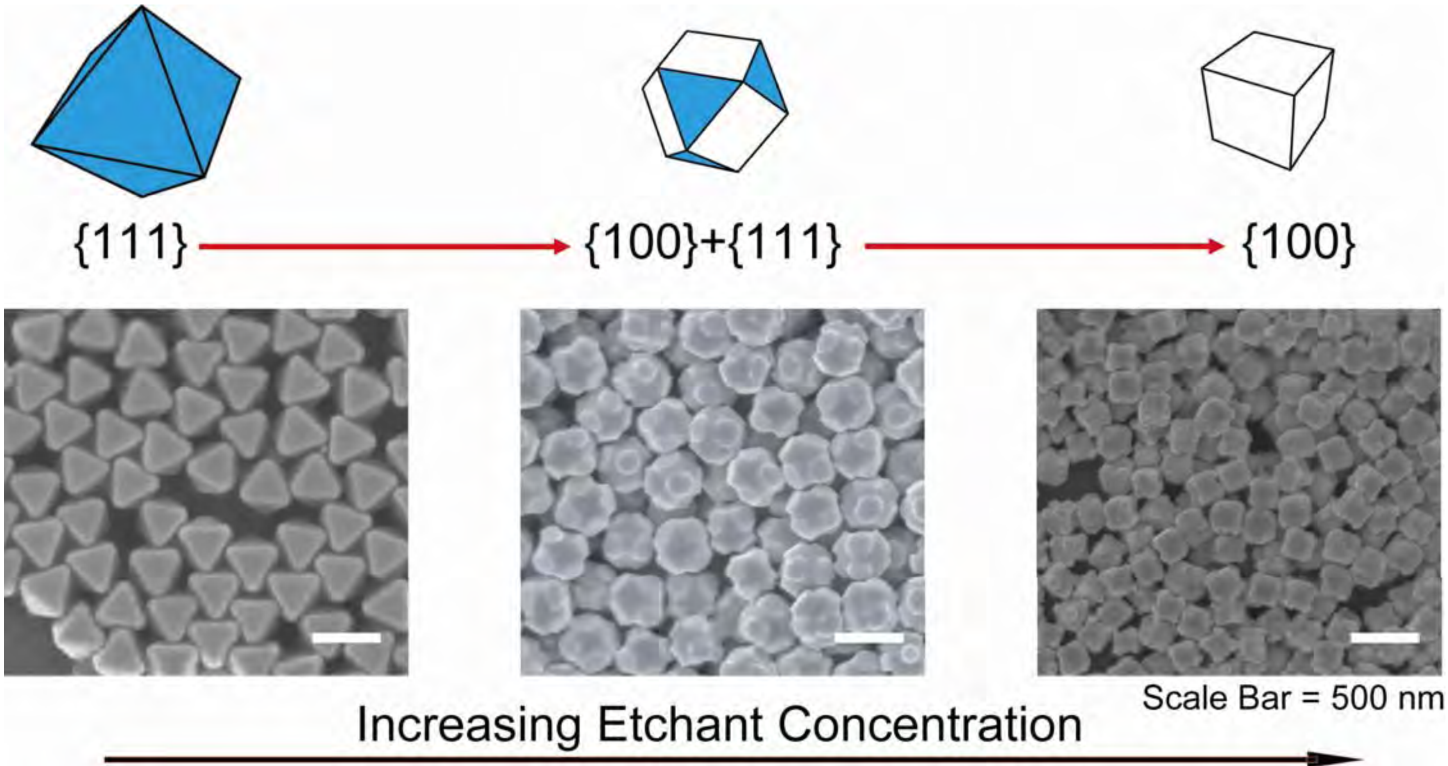
A recipe for improvement?

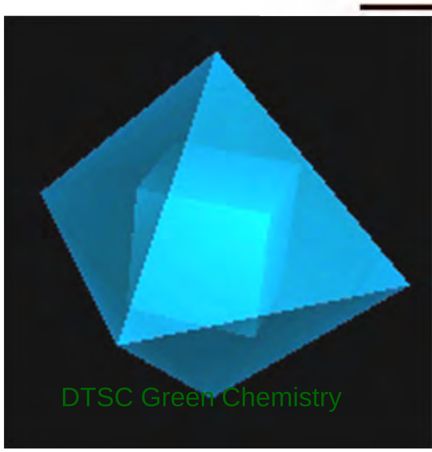


1 parts 30% H_2O_2
5 parts conc. NH_4OH
0.08 parts CrO_3 in HCl

Levinstein and Robinson, *Journal of Applied Physics.* **1962**

Selective, but not interesting





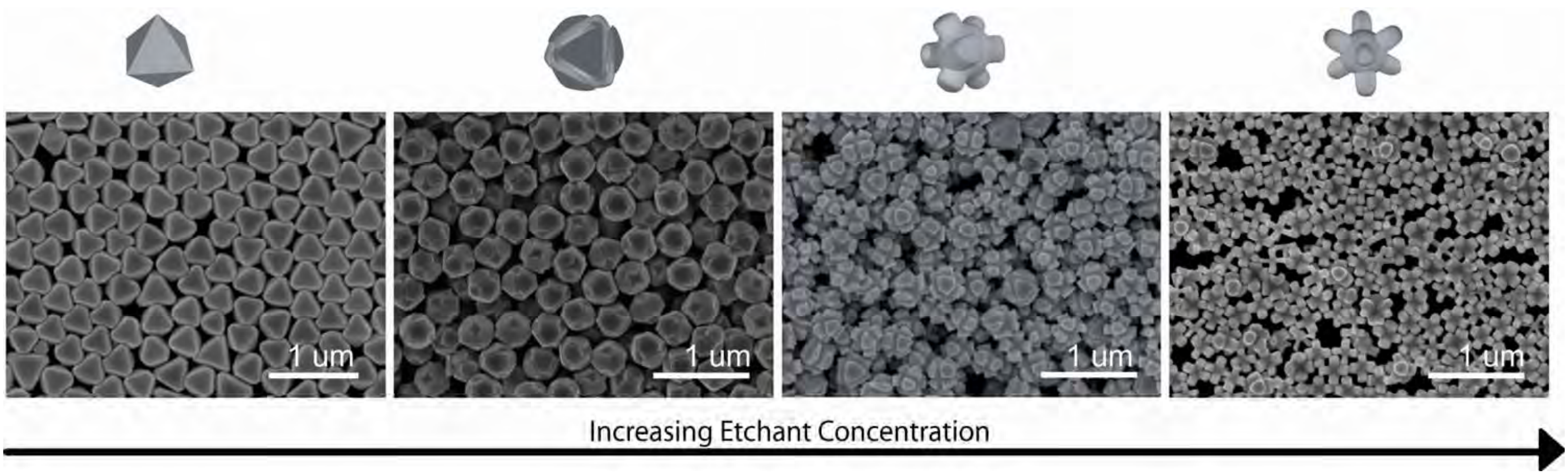
The diagonal of the resulting 150 nm cube is about 270 nm, which is the face to face distance in the starting octahedra.

Improved Selectivity and Sustainability

To determine the driving force of the reaction: $\Delta G = -nFE$.

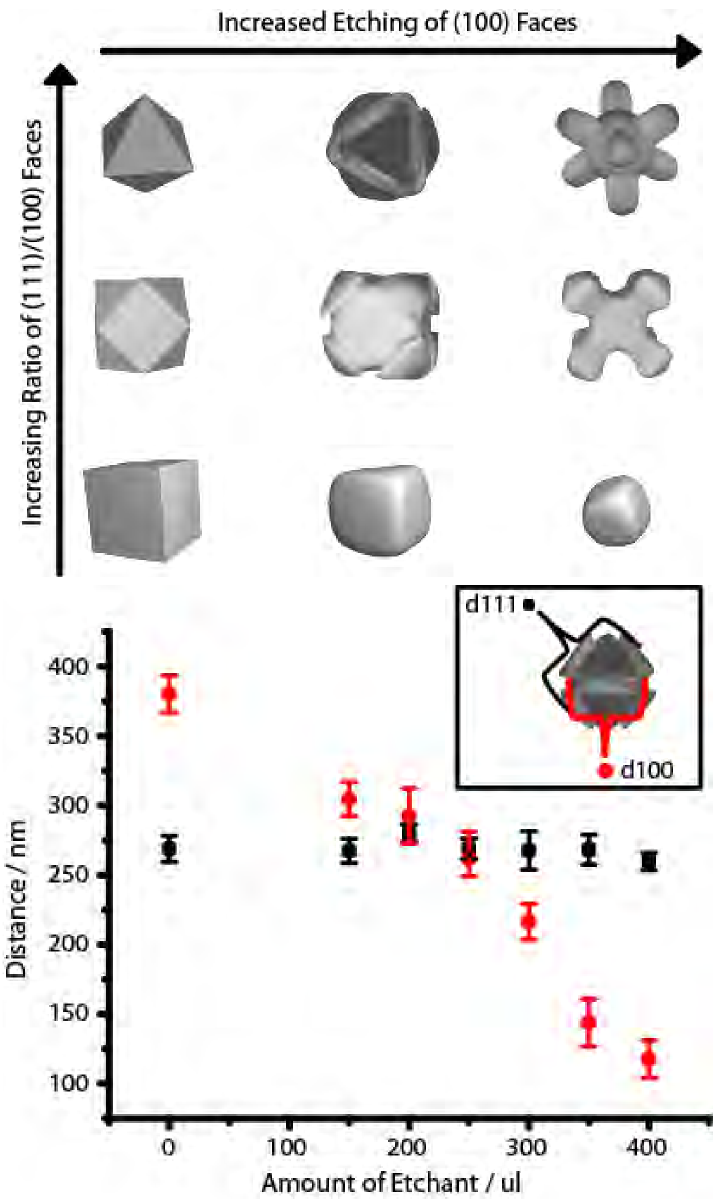
$H_2O_2 + 2H^+ + 2Ag \rightleftharpoons 2Ag^+ + 2H_2O$	$E = 0.694$ V
$NH_3OH + 2H^+ + 2Ag \rightleftharpoons 2Ag^+ + NH_4^+ + H_2O$	$E = 0.531$ V
$CrO_4^{2-} + 4H_2O + 3Ag \rightleftharpoons 3Ag^+ + Cr(OH)_3 + 5OH^-$	$E = -0.919$ V

<u>The CrO_3 was removed and the etching improved.</u>



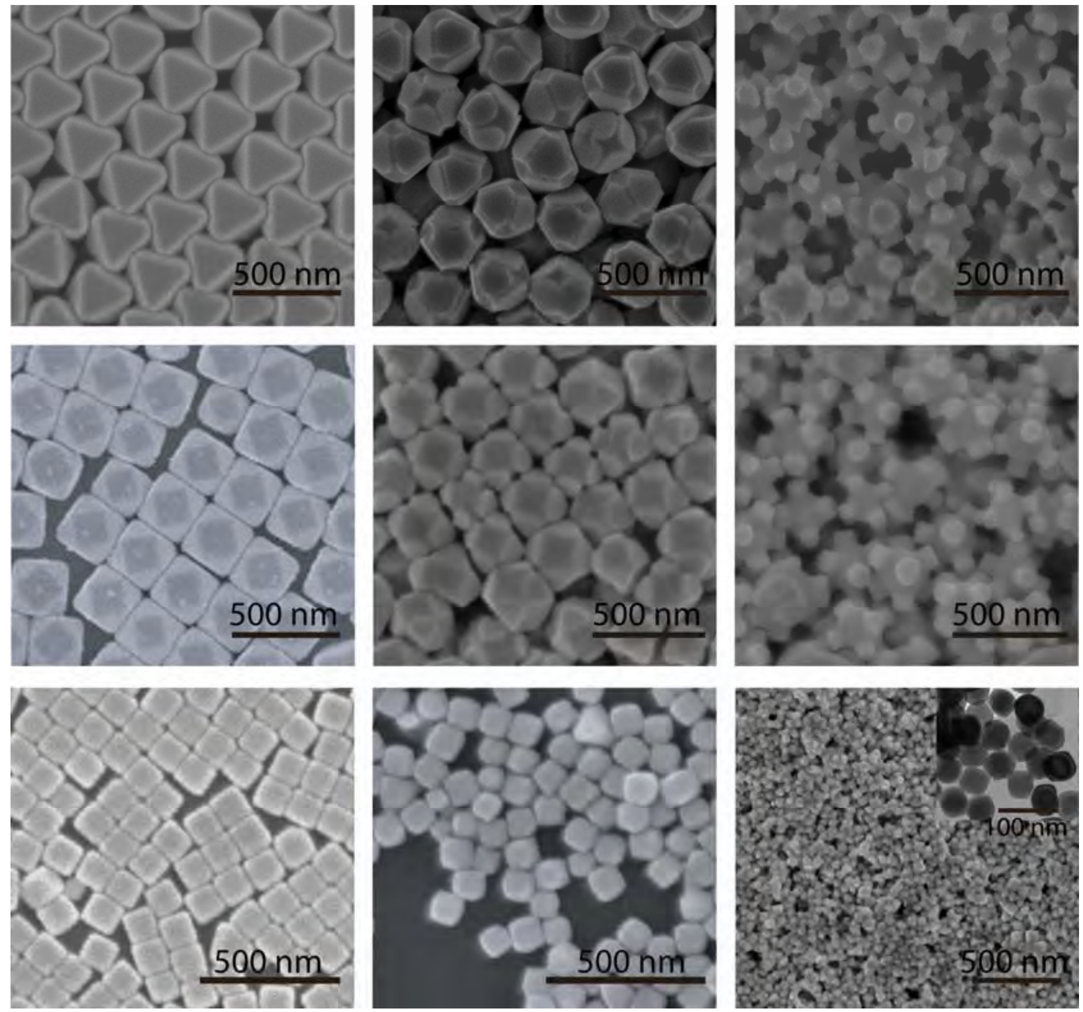
M. Mulvihill, JACS **2010**, 268

Chemically Induced Shape Control

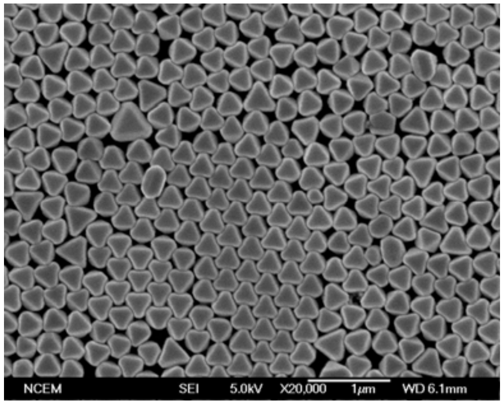


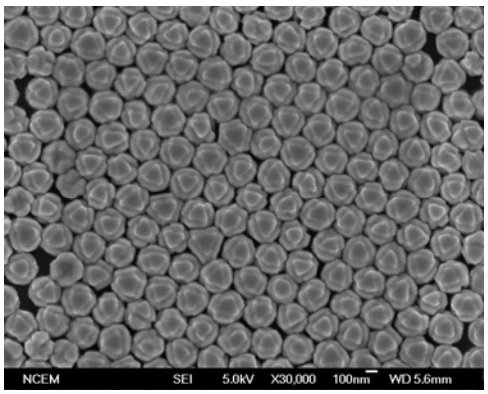
$$H_2O_2 + 2H^+ + 2Ag \rightleftharpoons 2Ag^+ + 2H_2O$$

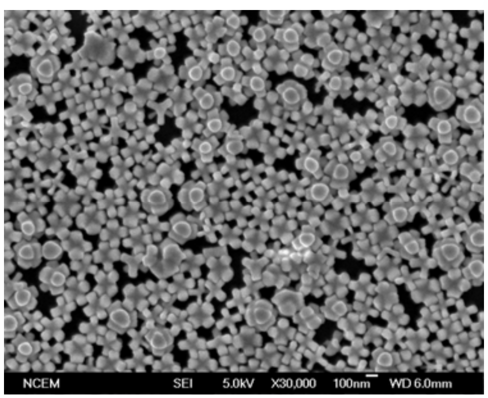
$$NH_3OH^+ + 2H^+ + 2Ag \rightleftharpoons NH_4^+ + 2Ag^+ + H_2O$$

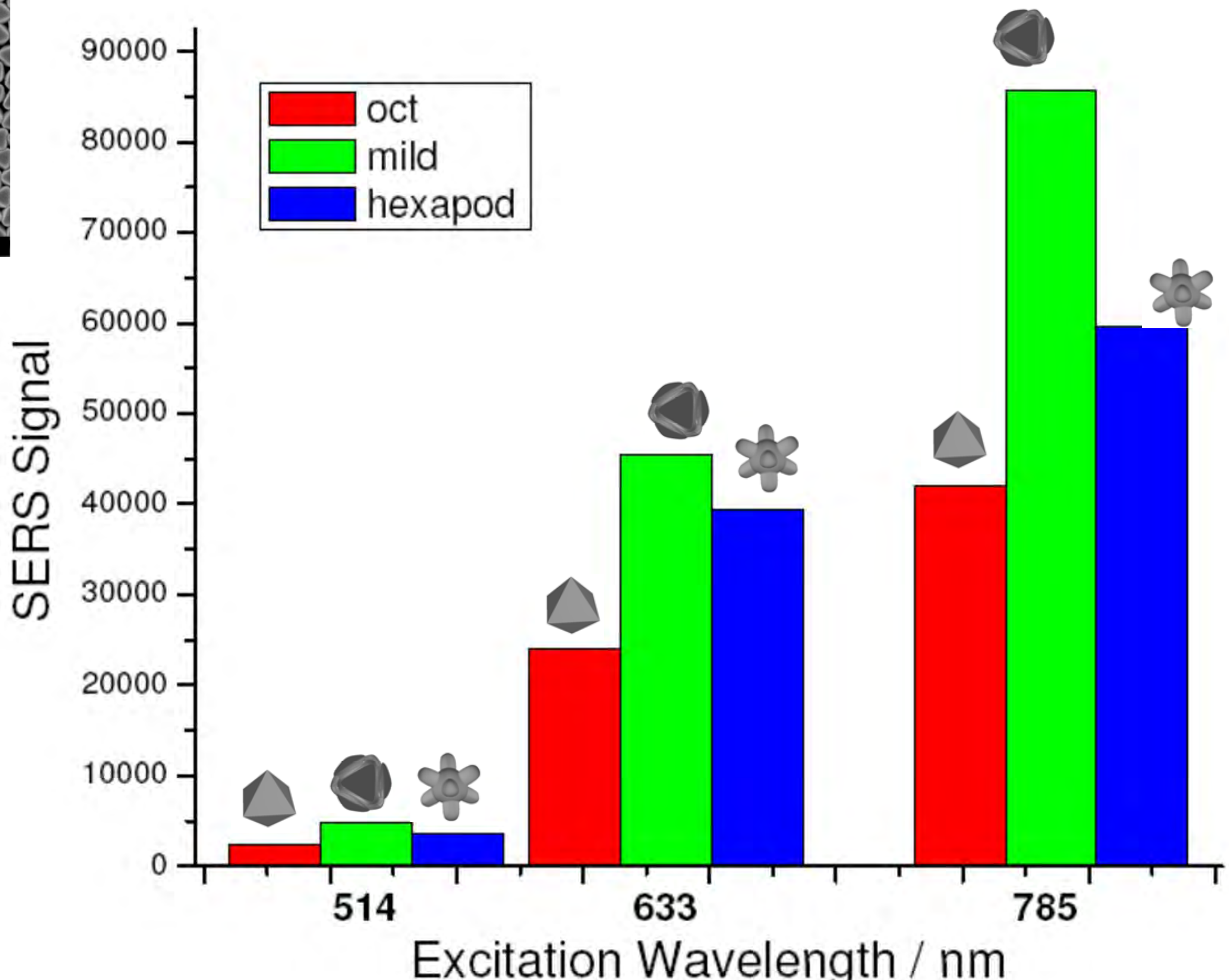


Improved Sensing

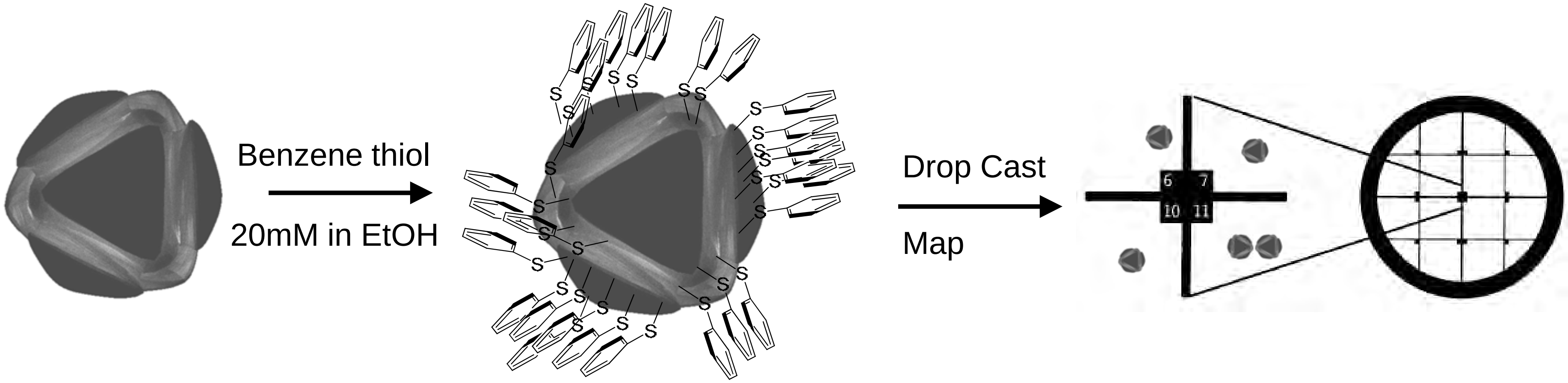


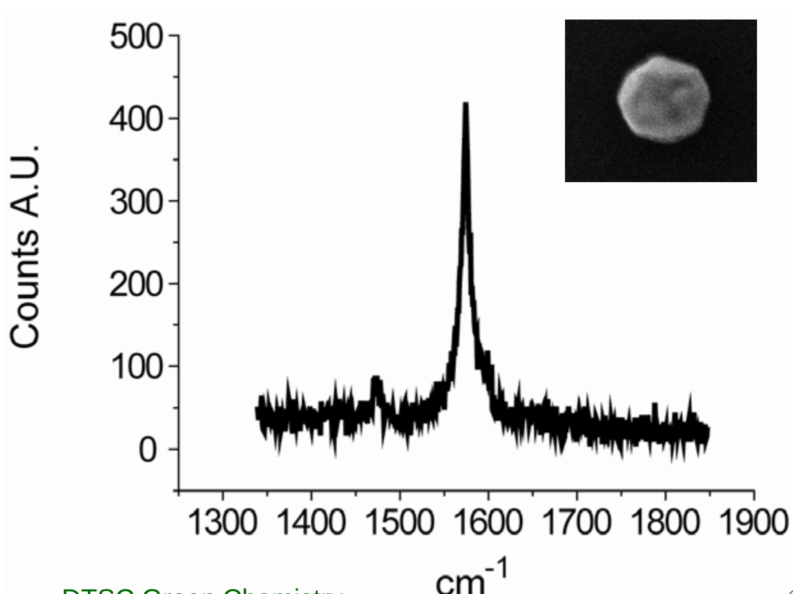


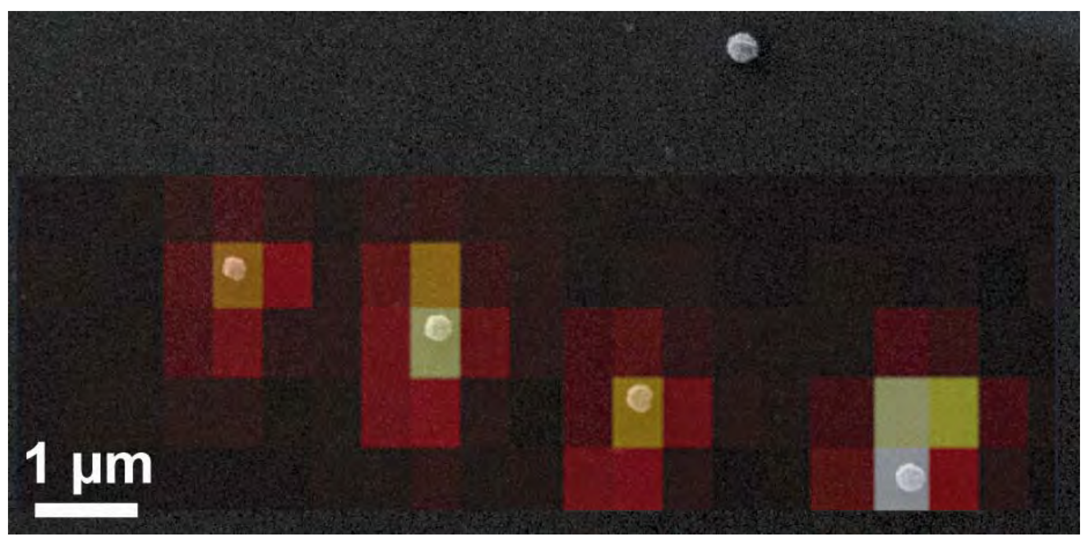




Sensing on a single Nanoparticle





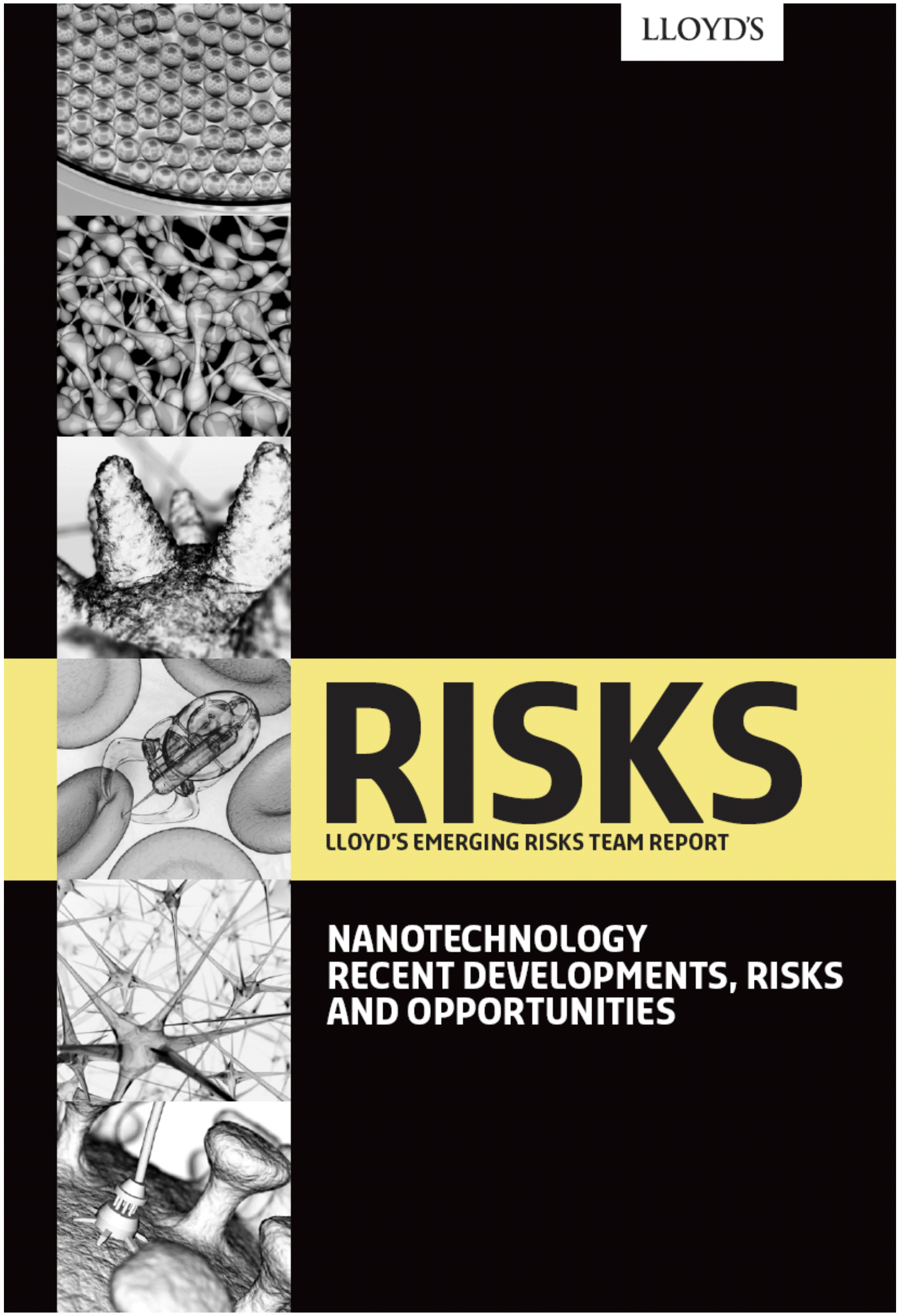


What Makes This Green Chemistry?

1. **Continual Improvement**
2. **Safer Starting Materials**
3. **Tool for continuous monitoring**
4. **Efficient Material utilization**

Benefits

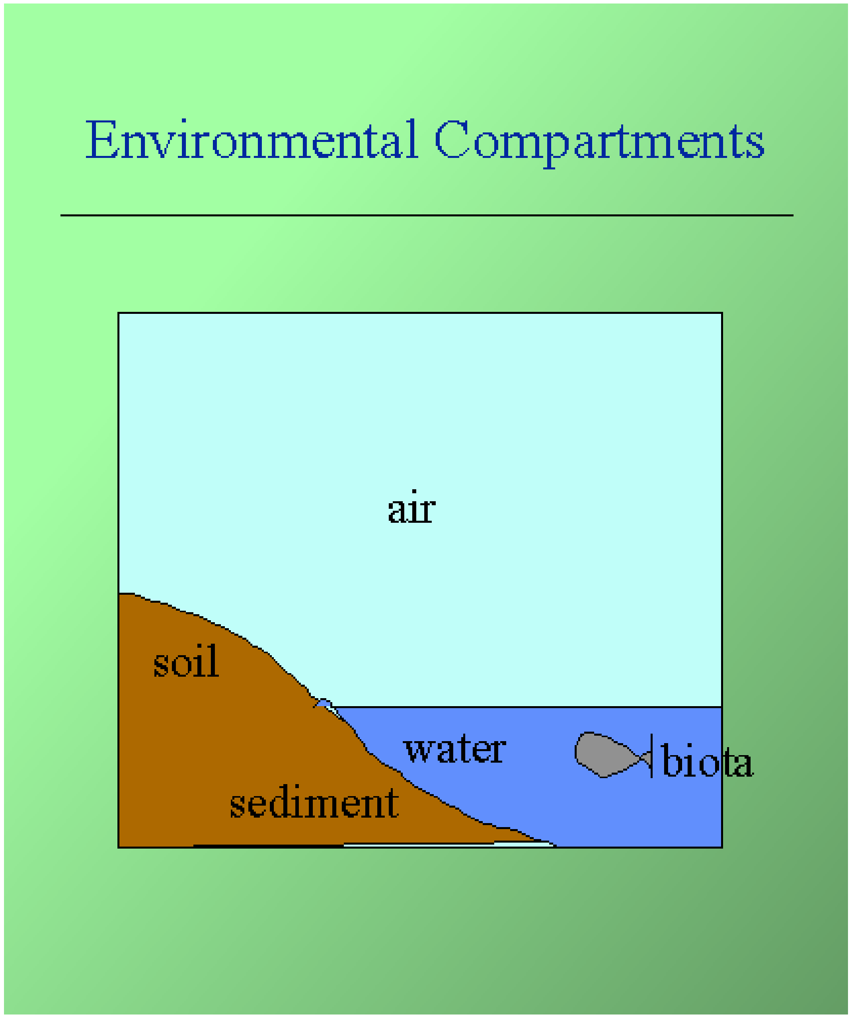
1	**Innovation**	• New understanding of basic science.
2	**Efficiency**	• Decrease Waste • Decrease use of Hazardous Substances
3	**Enhanced Reputation**	• Publications in JACS and Angwandte



Implications of Nanotechnology

1. Large market
2. New properties
3. Unknown impacts on health
4. Unknown impacts on the environment
5. Lack of regulation

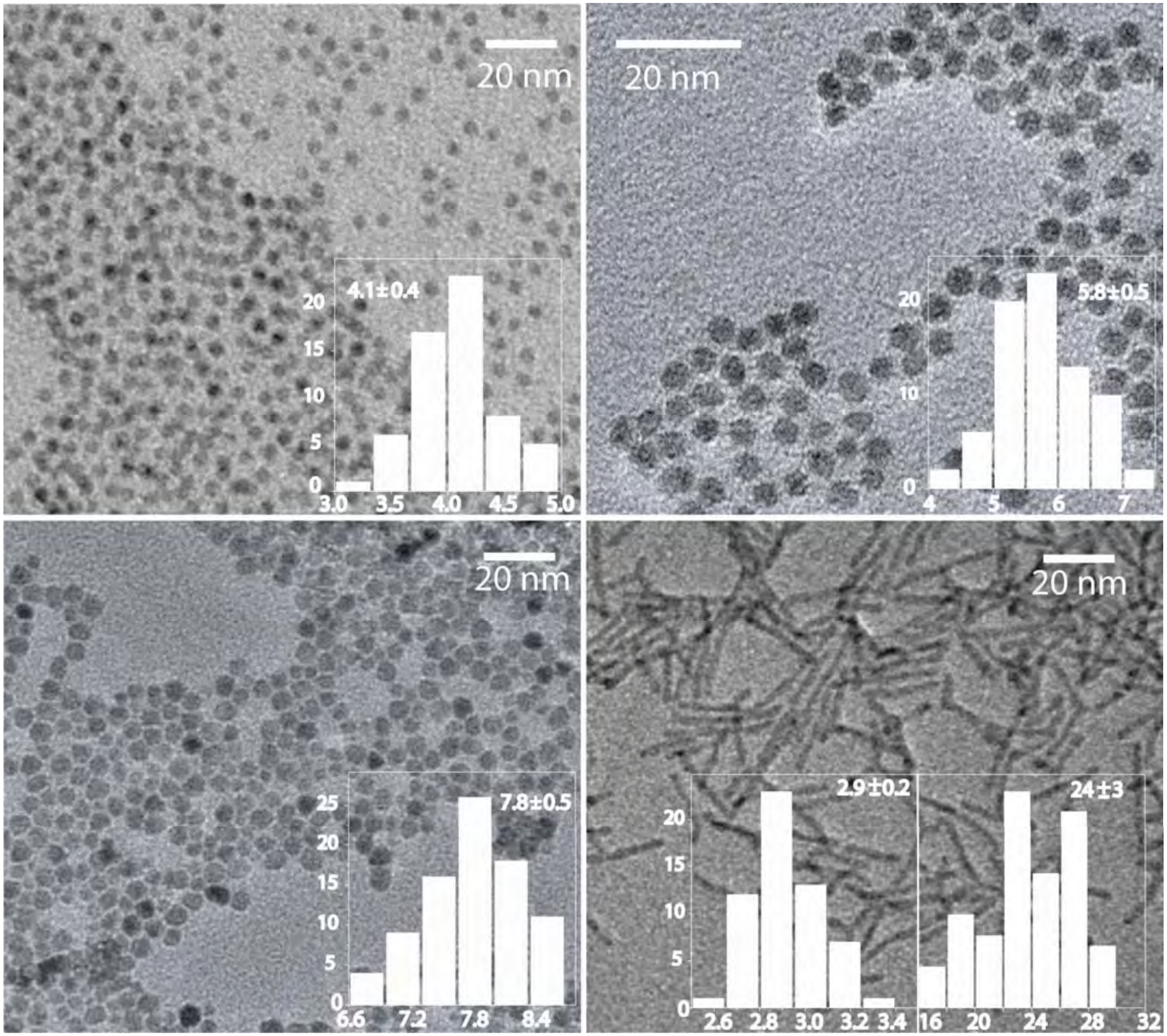
Fate of Nanoparticles



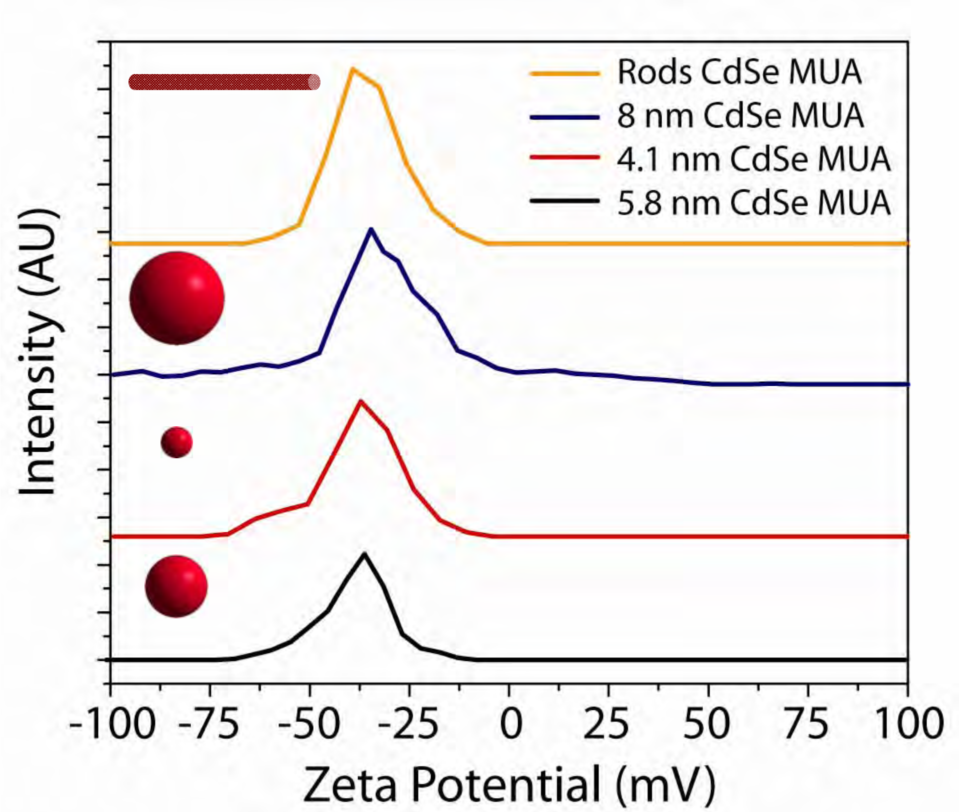
Nanoparticle Characteristics

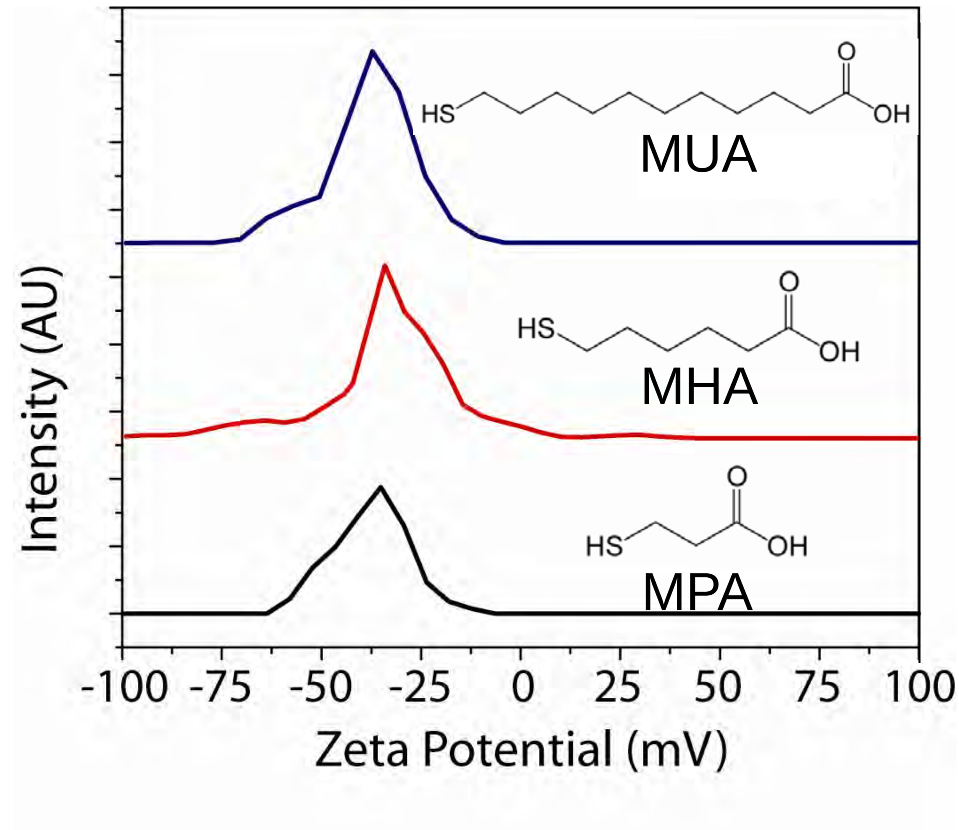
- •Size between 1-100 nm
- •Molecular weights very high
  - •100,000 – 1,000,000 g/mol
- •Vapor pressure not relevant
  - •Aerosols need to be characterized.
- •Water/soil partitioning will depend on surface coatings
- •Water transport depends on stability of nanoparticle suspensions

Influence of Nanoparticle Shape



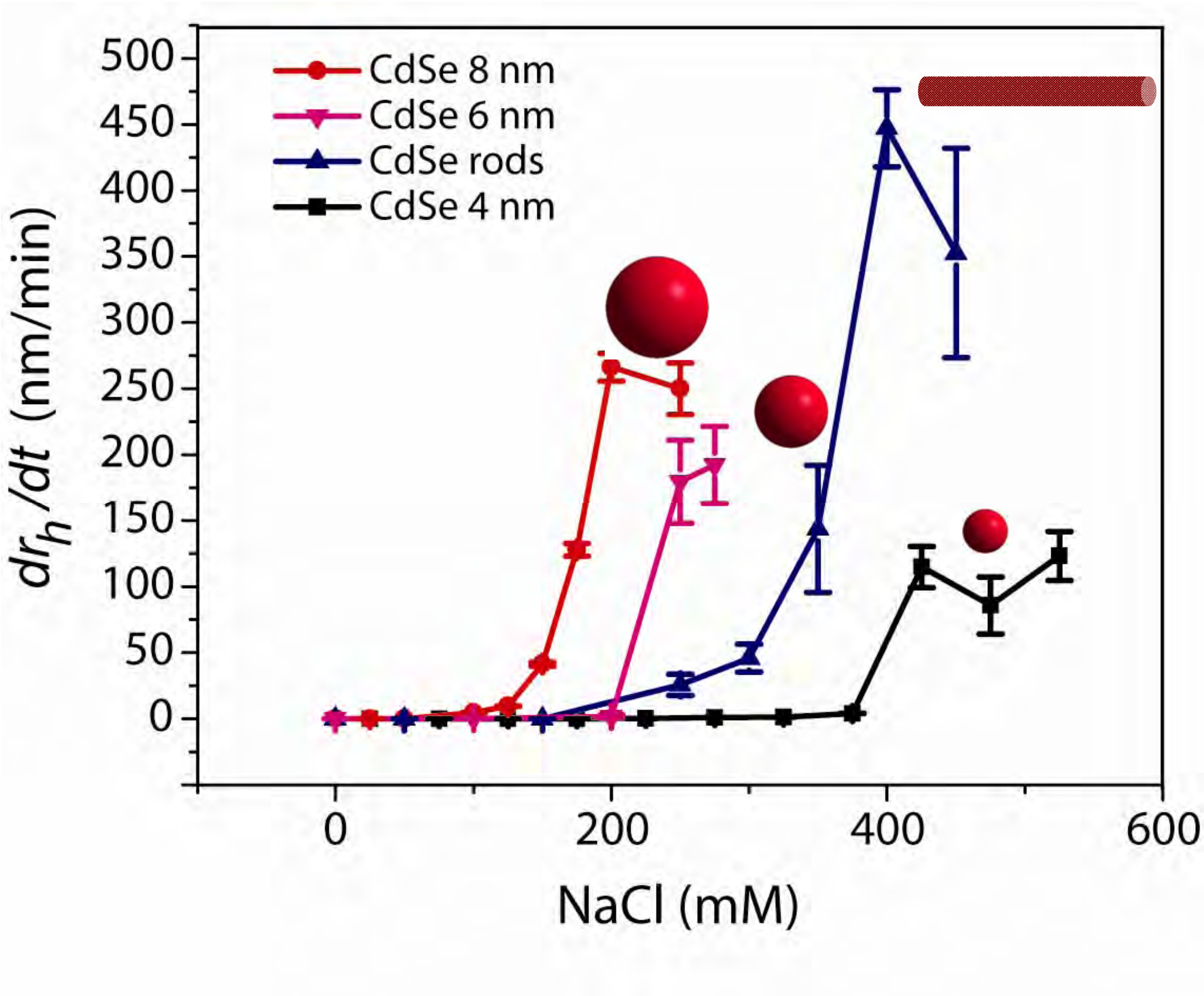
Surface Coating Characterization



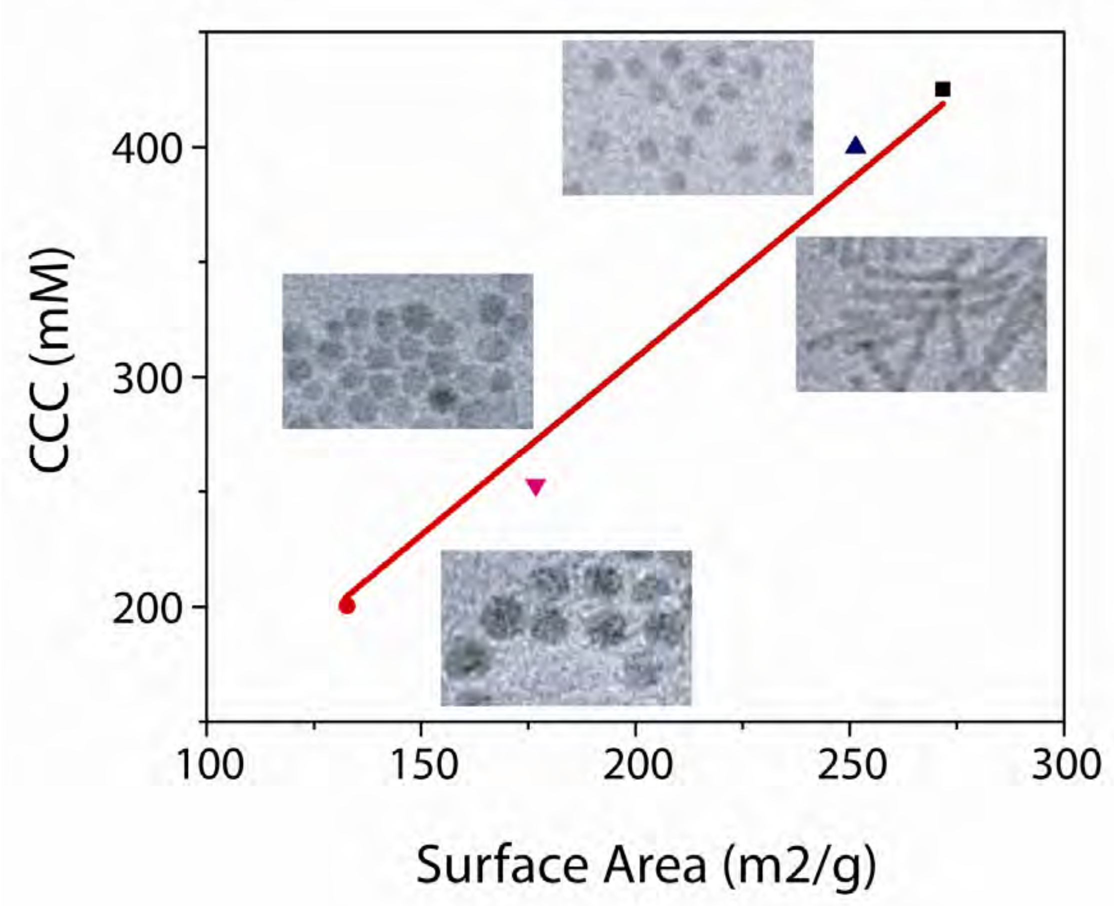


- Surface charge density is 35 (±5) mV for all particles.
- Surface charge density is 35 (±5) mV for all of the carboxylic acid ligands.

Aggregation Rates for Various Shapes

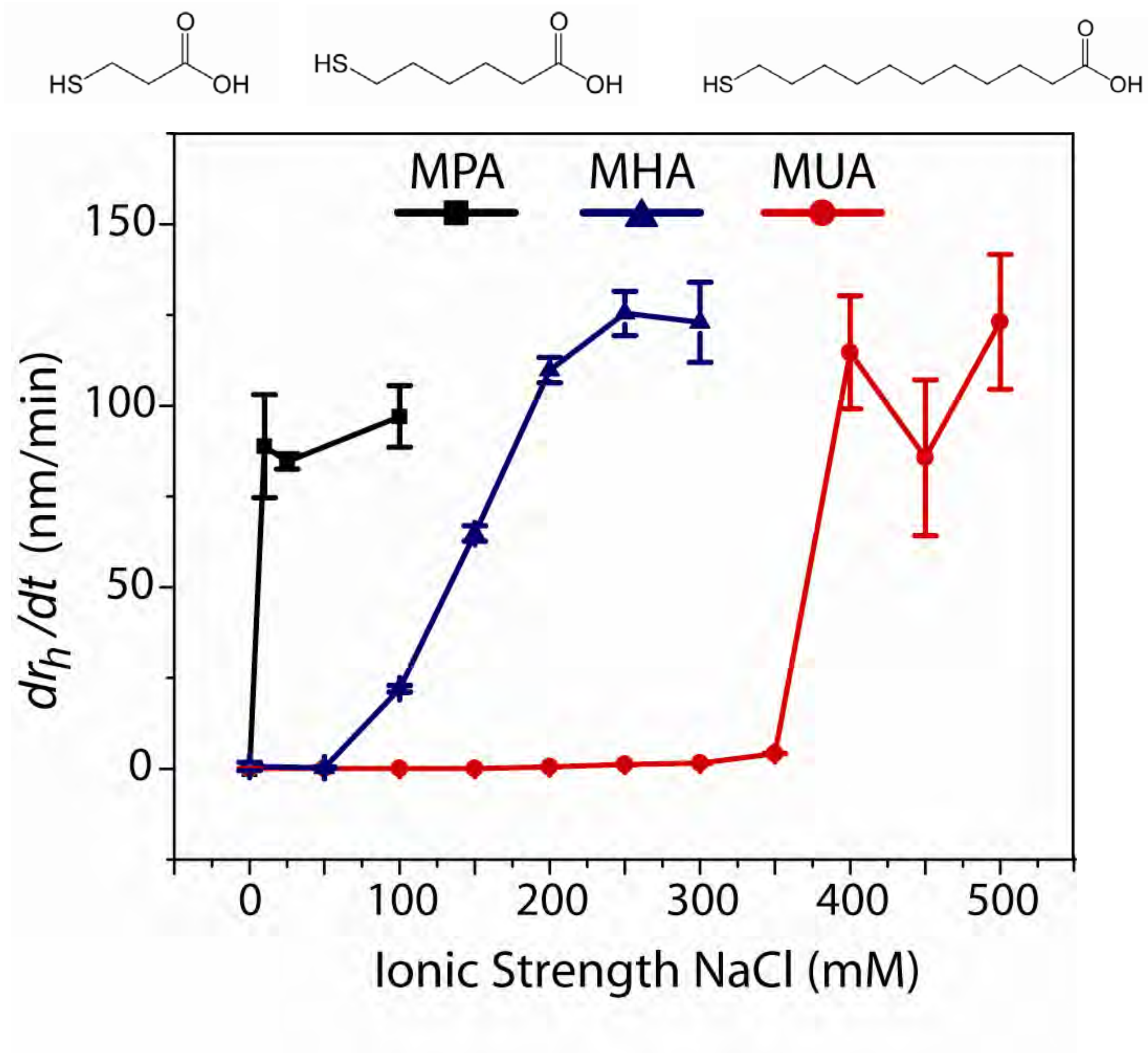


Shape and Surface Area

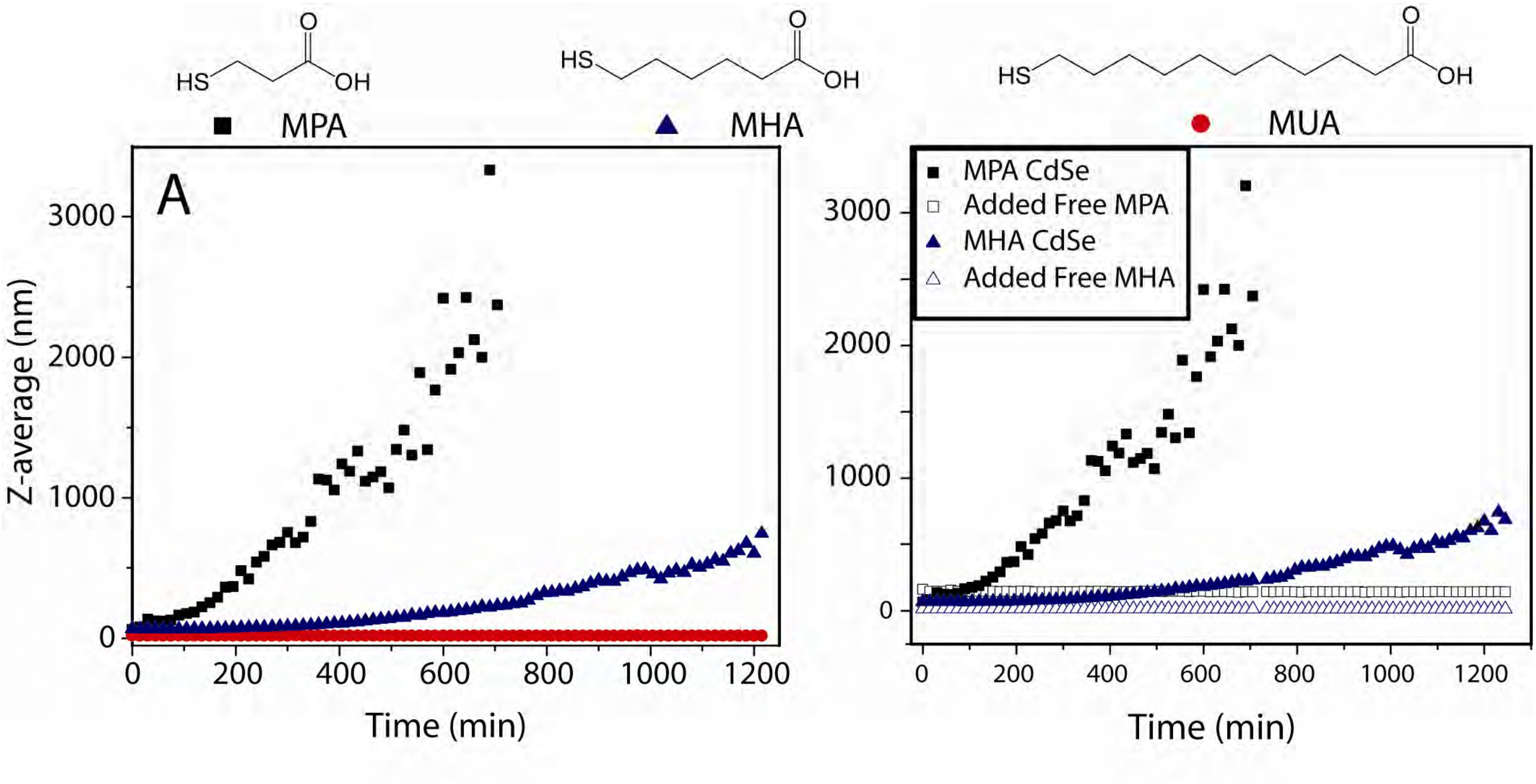


- Nanoparticle surface area is directly related to CCC.
- This predicts greater stability for 1-D and branched materials.
- Supports the primary role of electrostatic screening for NP stabilization.

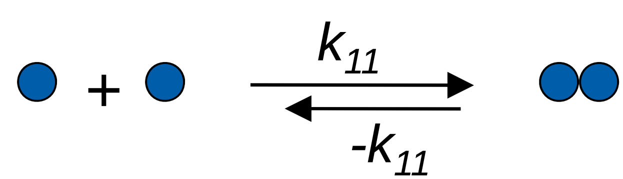
Effect of Surface Coating



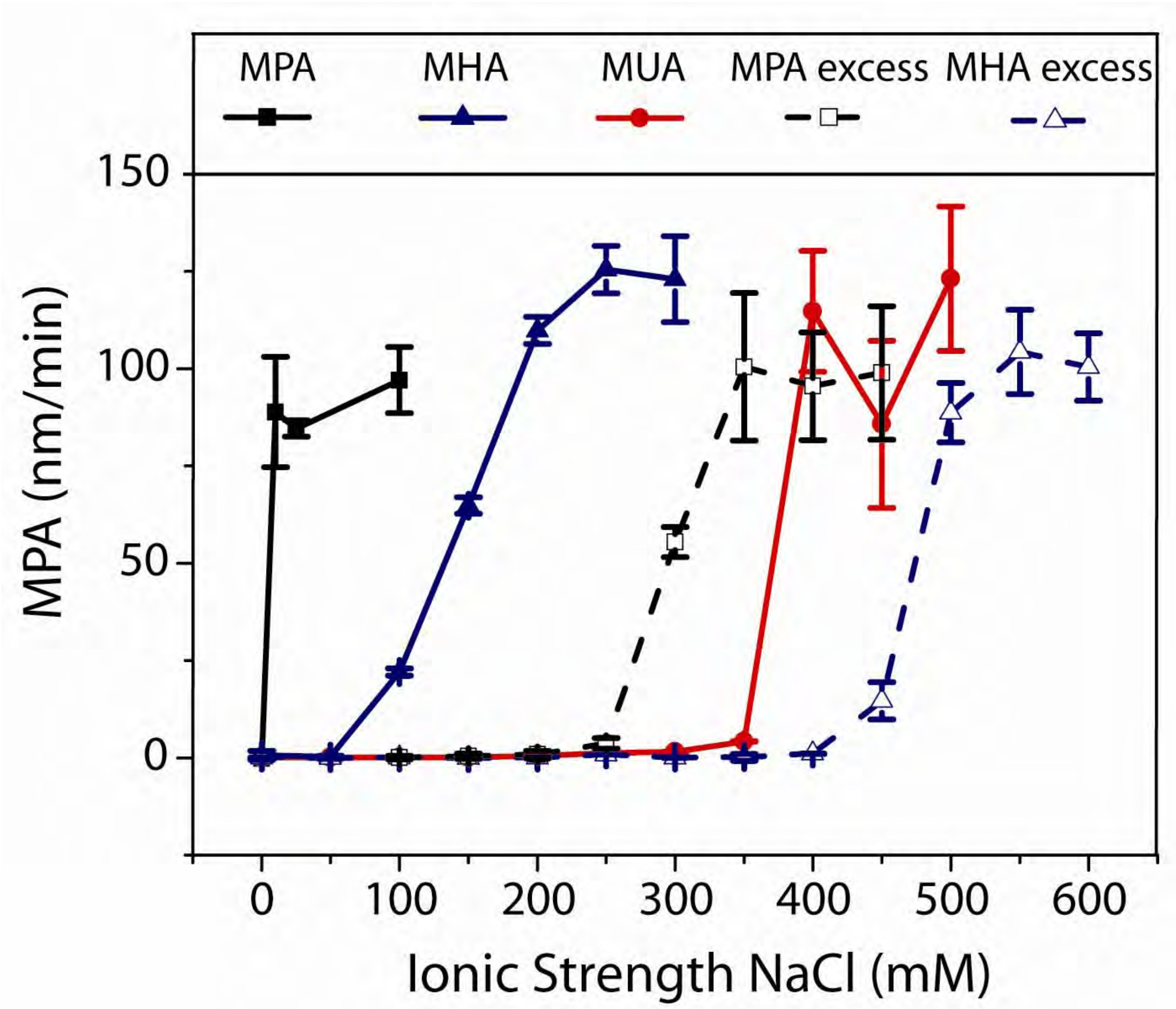
Ligand instability



- Ligand shells are dynamic
- Shorter chain ligands are less stable



Excess Ligands Stabilize Particles



- CCC can be controlled with the addition of excess ligand.

Conclusions

Shape and Size

- Surface area is the most important predictor of stability

Surface Coating

- Ligand binding is dynamic
- Longer chain ligands lend stability

What Makes This Green Chemistry?

Basic science to help

- Design for degradation
- Design safer materials

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