# Nanotechnology and the Environment: Nano-scale Research at Temple University

by

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# Metal Sequestration by Nanoparticles

Goal: Synthesis of nano-scaled particles and devices for more efficient and cost effective environmental applications

Particles: Zeolites and Iron Oxy-hydroxide Nanoparticles

Why use zeolites for metal sequestration?

- Nano-sized channel system of zeolites
  - 0.4 to 1.4 nm
- Provides size- & shape-selective matrix for absorbed molecules
- Maintains a high surface-to-mass ratio

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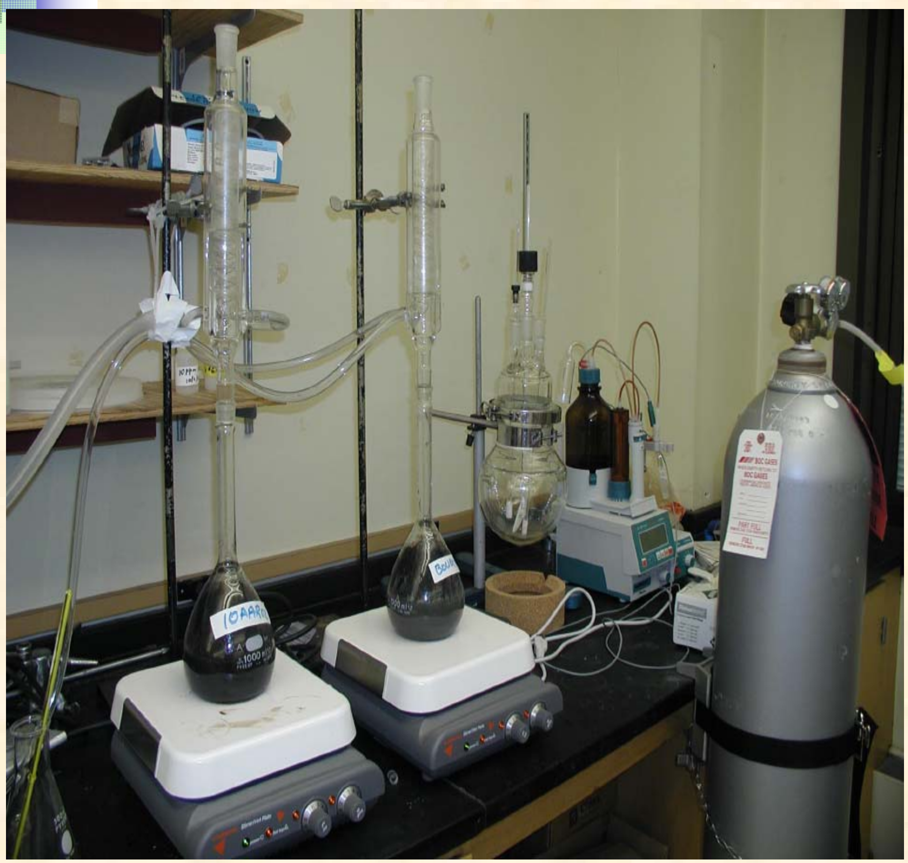
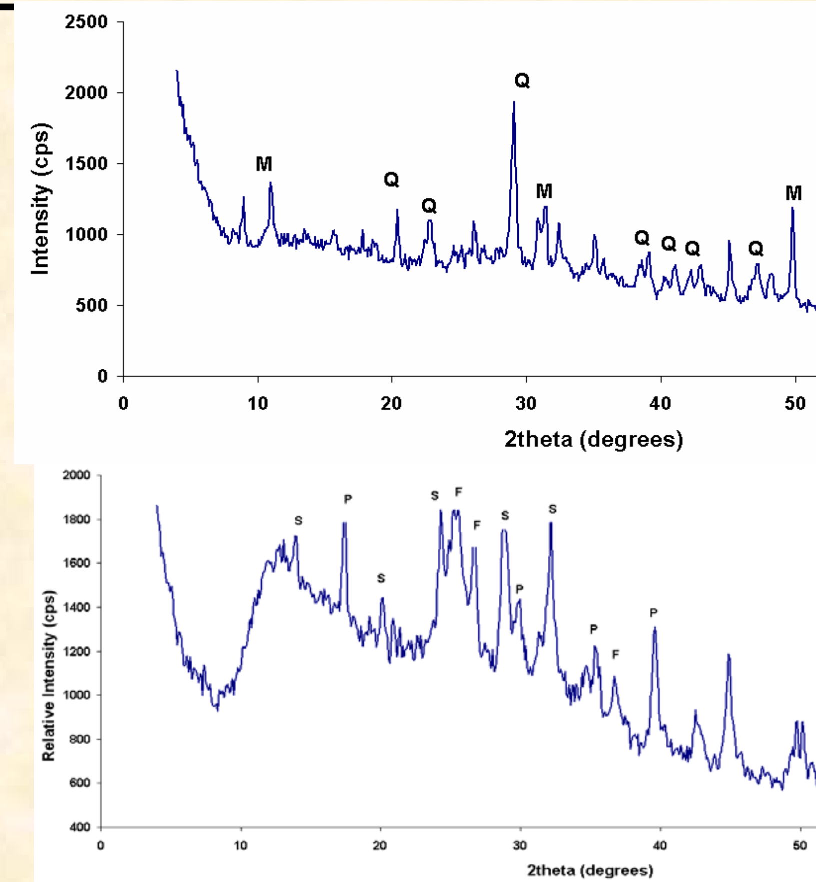
# ZEOLITE SYNTHESIS

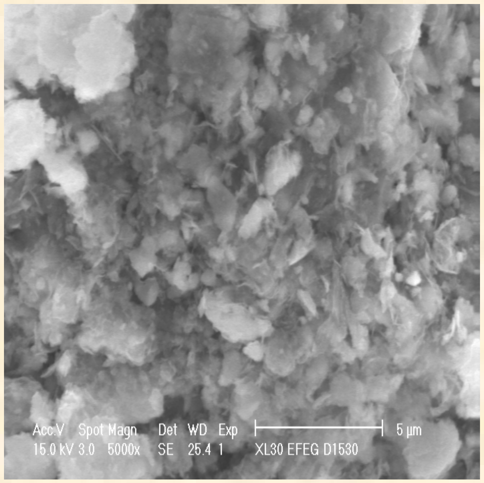




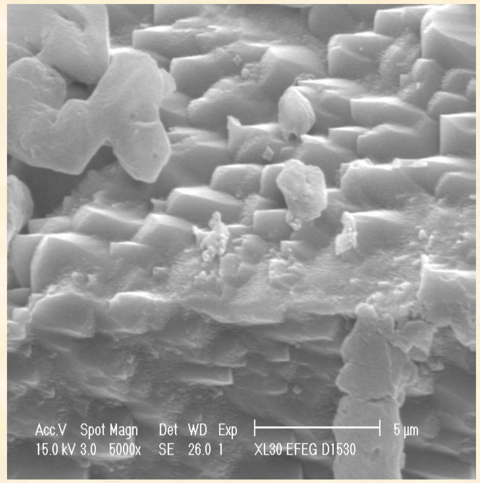

| | |
|---|---|
| The reflux method of generating zeolites from ash.<br>*Kargbo, 2004 (by permission)*<br><br>ASH (Waste ash/Coal fly ash) + 3M NaOH + Heat | X-ray diffraction patterns for untreated (top) and treated (bottom) MSWC ash. M=Mullite; Q=Quartz; P=Zeolite Na-PI; F=Faugasite; S=Sodalite Octahydrate |

# Zeolites Verification and Preparation for PRB

A



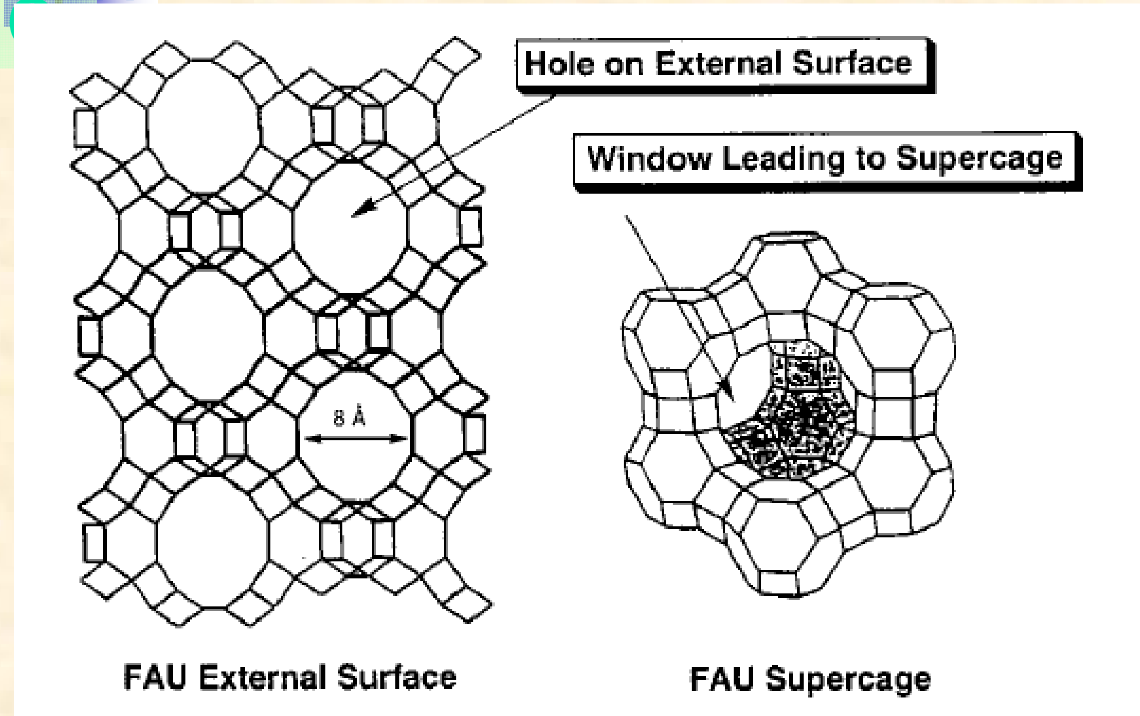

B

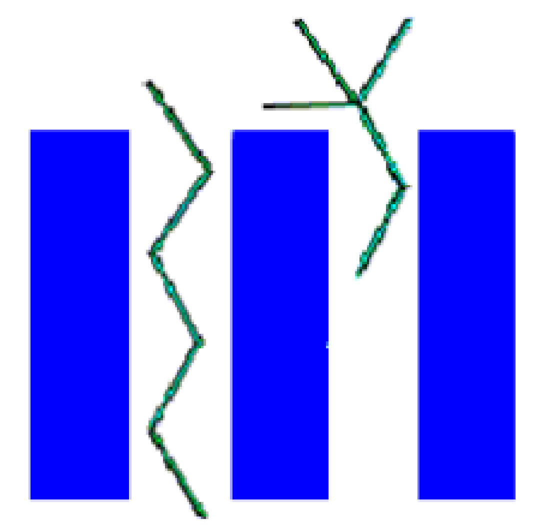



Scanning electron microscope images of MSWC ash. A= Untreated sample; B= Sample fused in NaOH. XRD verified presence of zeolite Na-P1 and faugasite ***(Kargbo, 2004, by permission)***.

- **Both MSWC ash and coal fly ash generated zeolites of similar composition**
- **For preparation of material for PRB applications, ash was chemically activated to form a:**
  - **chemically activated fly ash (CAFA) barrier material**

# Toxic Metal Sequestration by Ash-based Zeolites



**Void space structure of faujasite zeolite:**
- **Interconnecting 3-D network**

**Network possesses:**
- **8-Å pore openings on external surface.**
- **13-Å internal supercages connected by 8-Å pores.**

Diagram of faugasite structure (left), and the channel and cage system of zeolites demonstrating size- & shape-selective properties for absorption of molecules (right).

# Toxic Metal Sequestration by Zeolites

## Batch Testing & Results: Cr & Cd

Ash composition by source

| | Source 1 | Source 2 | Source 3 |
|---|---|---|---|
| $SiO_2$ | 61.1 | 63.2 | 53.8 |
| $Al_2O_3$ | 27.5 | 19.4 | 23.4 |
| $Fe_2O_3$ | 4.5 | 5.4 | 6.0 |
| CaO | 1.7 | 4.3 | 8.9 |
| MgO | 0.9 | 1.3 | 1.9 |
| Alkali | 0.9 | 1.1 | 1.0 |
| $SO_3$ | 0.3 | 1.4 | 0.9 |
| LOI | 2.7 | 2.1 | 0.6 |

Cr and Cd Sequestration Results

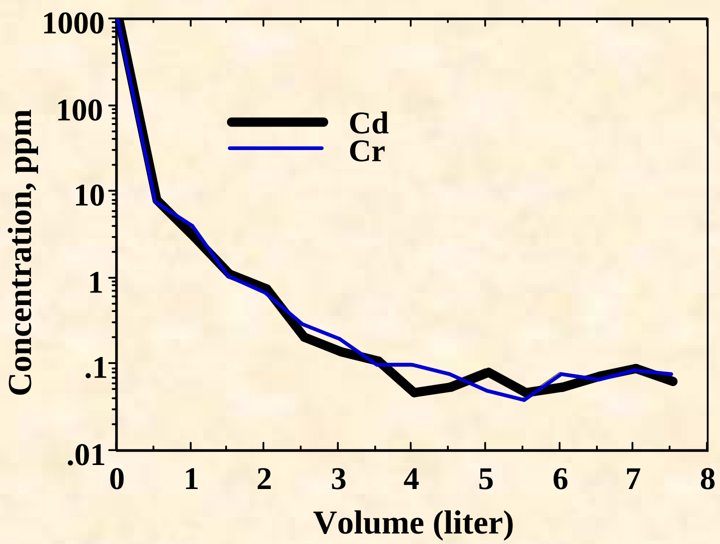
| CAFA-PRB Source | 1000 ppm Cr | 1000 ppm Cd |
|---|---|---|
| | Resulting Solution Concentration (ppm) | |
| Source 1 | 192 | 176 |
| Source 2 | 0.1 | 0.1 |
| Source 3 | 0.1 | 0.2 |

- CAFA-PRB material from each source produced and crushed into pelletized form.
- Ten grams barrier materials added to 500 mL of 1,000 ppm sol of Cr and Cd
- Source 1 removal ability < source 2 and 3
- Sources 2 and 3 have similar removal efficiency
- Source 2 selected for column test

# Toxic Metal Sequestration by Zeolites

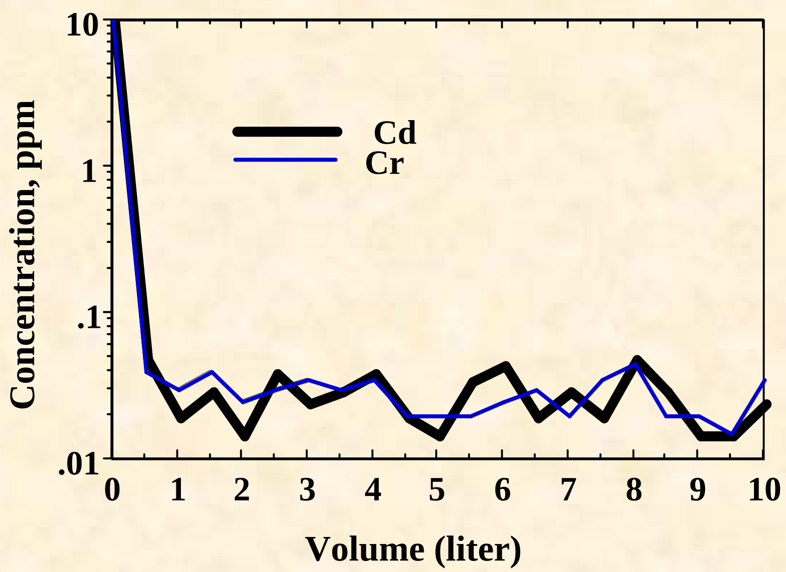
**Column Testing (1)**

Results of 1000 ppm Cd, and1000 ppm Cr, passed through 200 g of barrier materials




**Column Testing (2)**

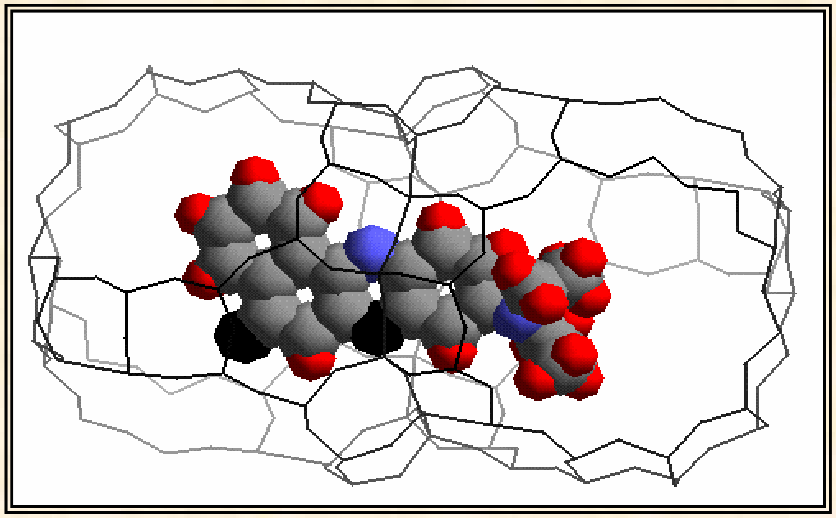
Results of 10 ppm Cd and 10 ppm Cr, passed through 200 gm of barrier materials

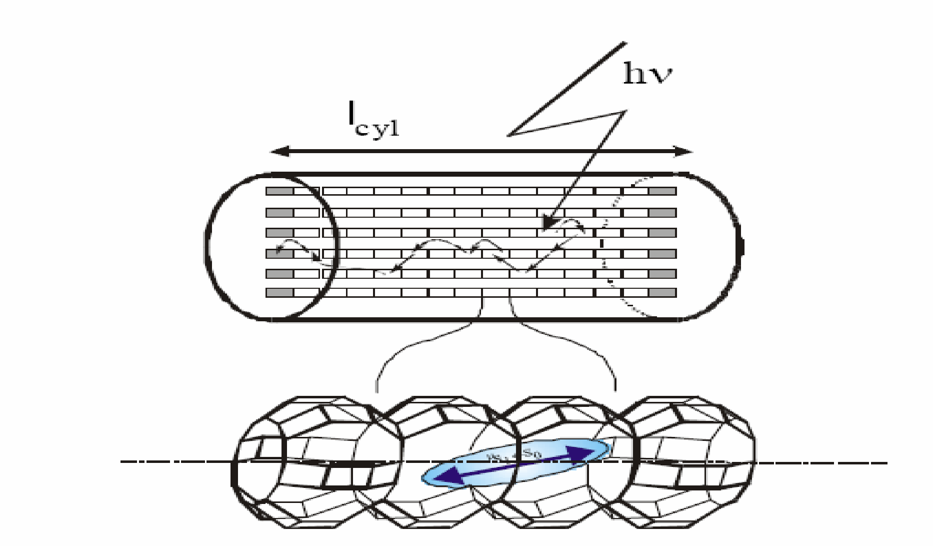



Hence, CAFA-PRB containing zeolites has ability to remove Cr and Cd very effectively.

# Other Ongoing Contaminant Remediation Research Using zeolites

## Sequestration of toxic gases






- **Nile Red synthesized in zeolite cages**
- **Reaction involves 1-naphthol and nitrosodiethylaminophenol in acetic acid in presense of zeolite**
- **Nile red formed encapsulated in the supercages.**

Representation of a cylindrical nanocrystal consisting of organized dye molecules acting as donors (empty rectangles), and a trap at the front and the back of each channel, indicated by the shaded rectangles.

# Acknowledgement

- Research funded by grant from:
  - ✓ Ben Franklin Partners/Consortium for Sustainable Design & Research
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    - ✓ Dr. Joan Delalic, Project Co-PI
    - ✓ Dr. Zameer Hasan, Project Co-PI

# Nanoparticle Fabrication for Environmental Applications

**Atomic Tailoring**

Sample problems with current nanoparticle application

- Particle agglomoration of nanoparticles (e.g., NZVI) in field applications
- Understanding reasons for enhanced reactivity (beyond the increased surface area)
- Inability to control chemical properties of produced nanoparticles for site-specific applications

# Atomic Tailoring of Nanosensors

**We have demonstrated:**

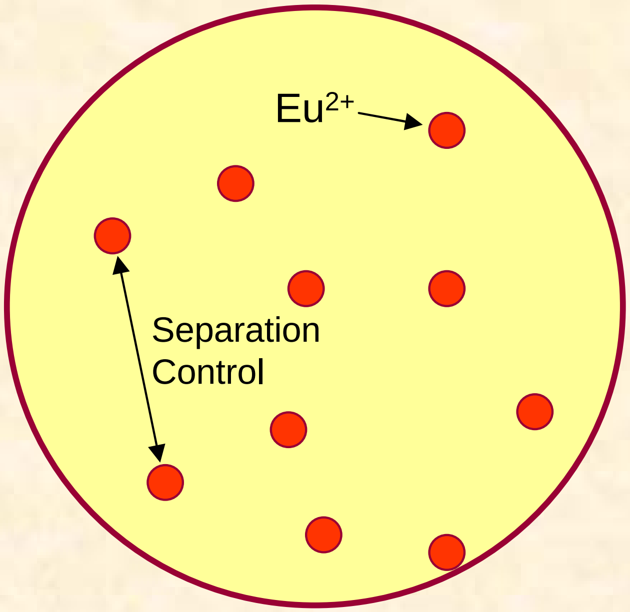
**Pulsed Laser Deposition:**
A versatile method of fabricating nano-particles of metals, insulators and semiconductors

Doping with Different Active Atoms

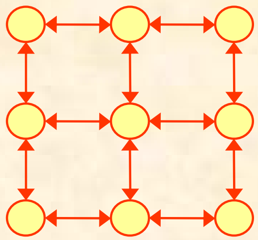
Control over the Chemistry During the Fabrication

Glassy or Crystalline Particles to Control Surface Reactivity

# Atomic Tailoring



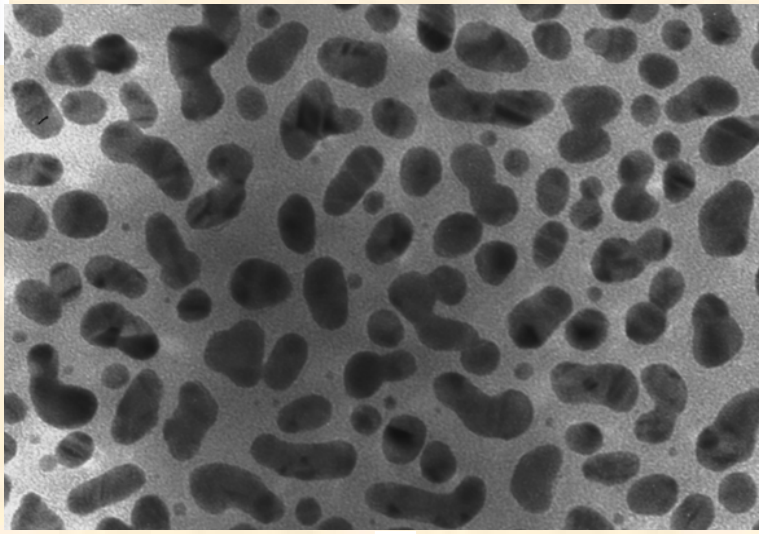

**…or Array of Nano-Sensors**



- Control size of nanoparticles
- Control active ions in them
- Control the separation between the ions
- Nanopatterned Surface controlling the separation between the nanoparticles with nanometer precision

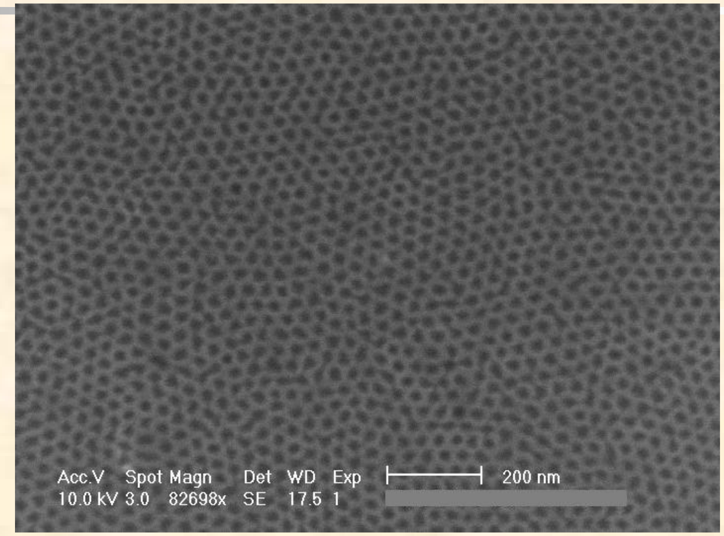
# Experimental Results

Nanoparticles of MgS Tailored with $Eu^{2+}$ and $Eu^{3+}$

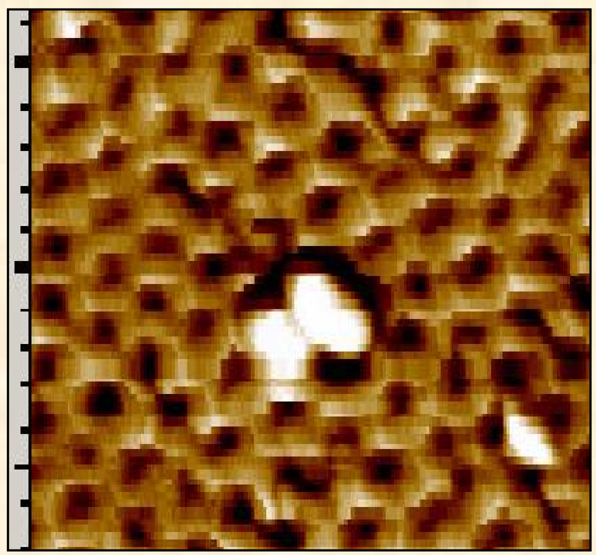


10nm

Nano-indentations on Si Surface (Coll: Princeton U.)




AFM IMAGE Nanoparticles of MgS Selectively Lodged in Nano-indentations on Si

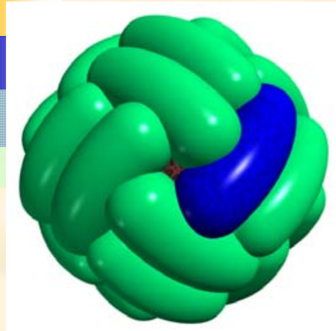


100 nm

## Acknowledgement

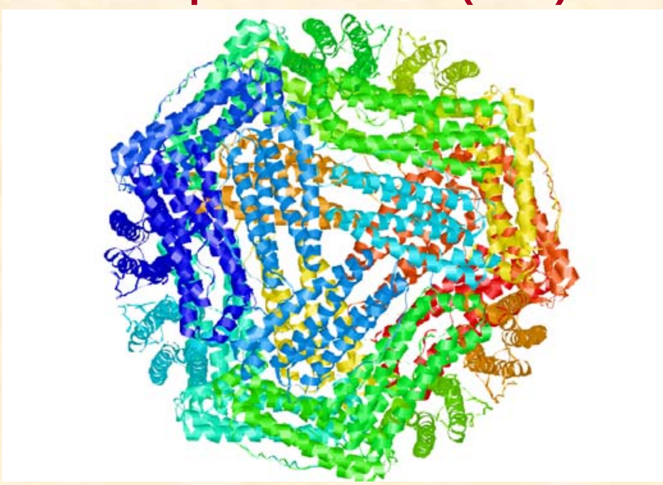

- Research funded by grant from NSF:
  - ✓Project PI: Dr. Zameer Hasan

# Size-Reactivity Relationship of Iron Oxyhydroxide Nanoparticles Assembled within Ferritin



Ferritin

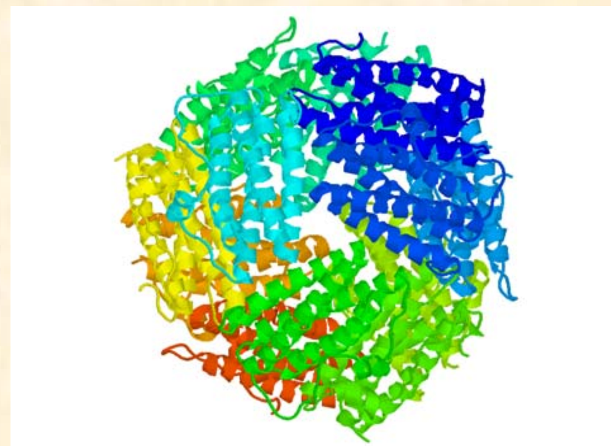
**Horse Spleen Ferritin (HSF)**



- 24 polypeptide subunits
- Spherical protein cage (120 Å dia.)
- Cavity (80 Å dia.)
- Accommodates up to 4500 Fe atoms

Stores Fe as hydrated $Fe_2O_3$ (rust)

***Listeria Innocua***
**Ferritin-like Protein (LFLP)**



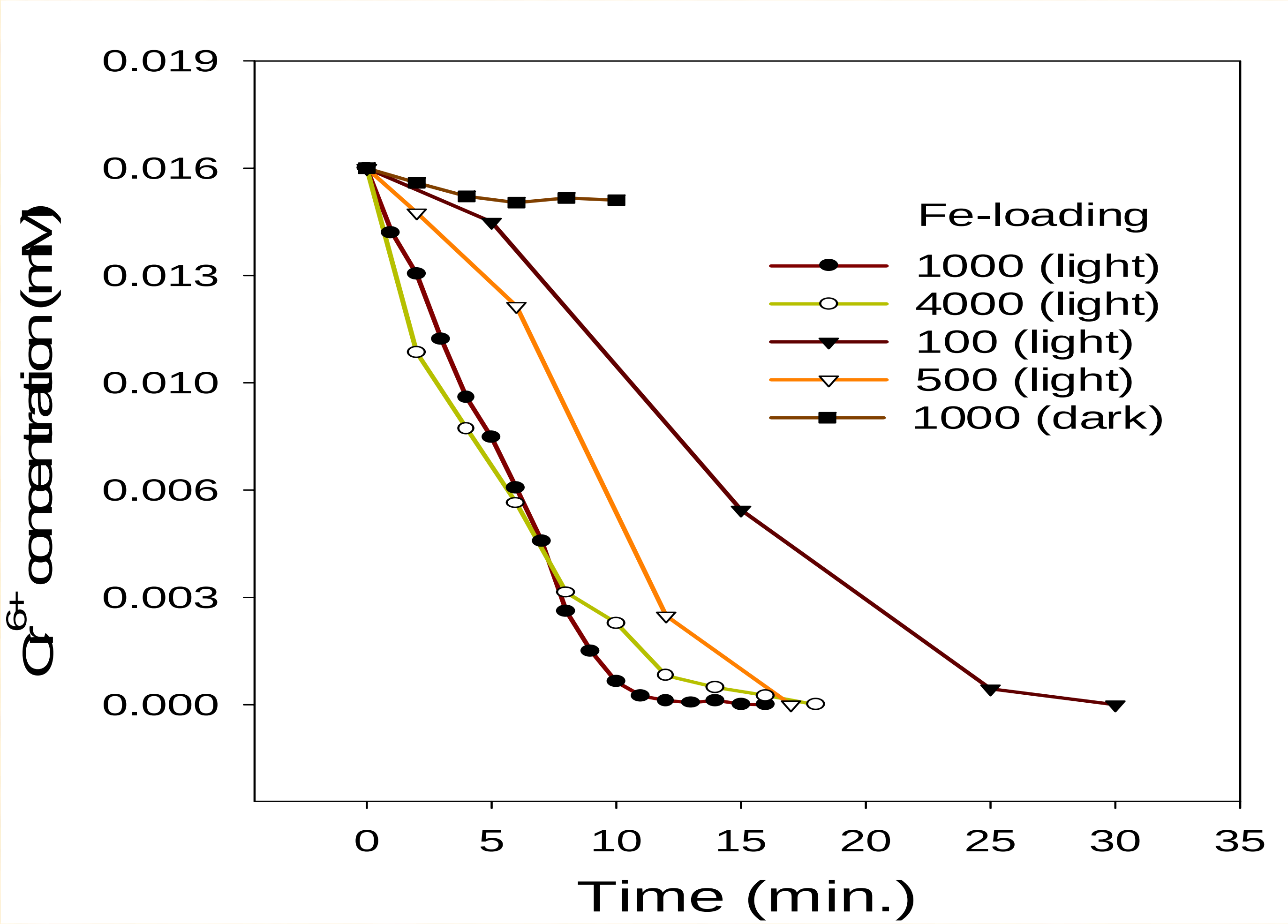
- 12 polypeptide subunits
- Spherical protein cage (90 Å dia.)
- Cavity (56Å dia.)
- Accommodates up to 500 Fe atoms

$Cr_2O_7^{2-}$ (4.0x10$^{-4}$ M)

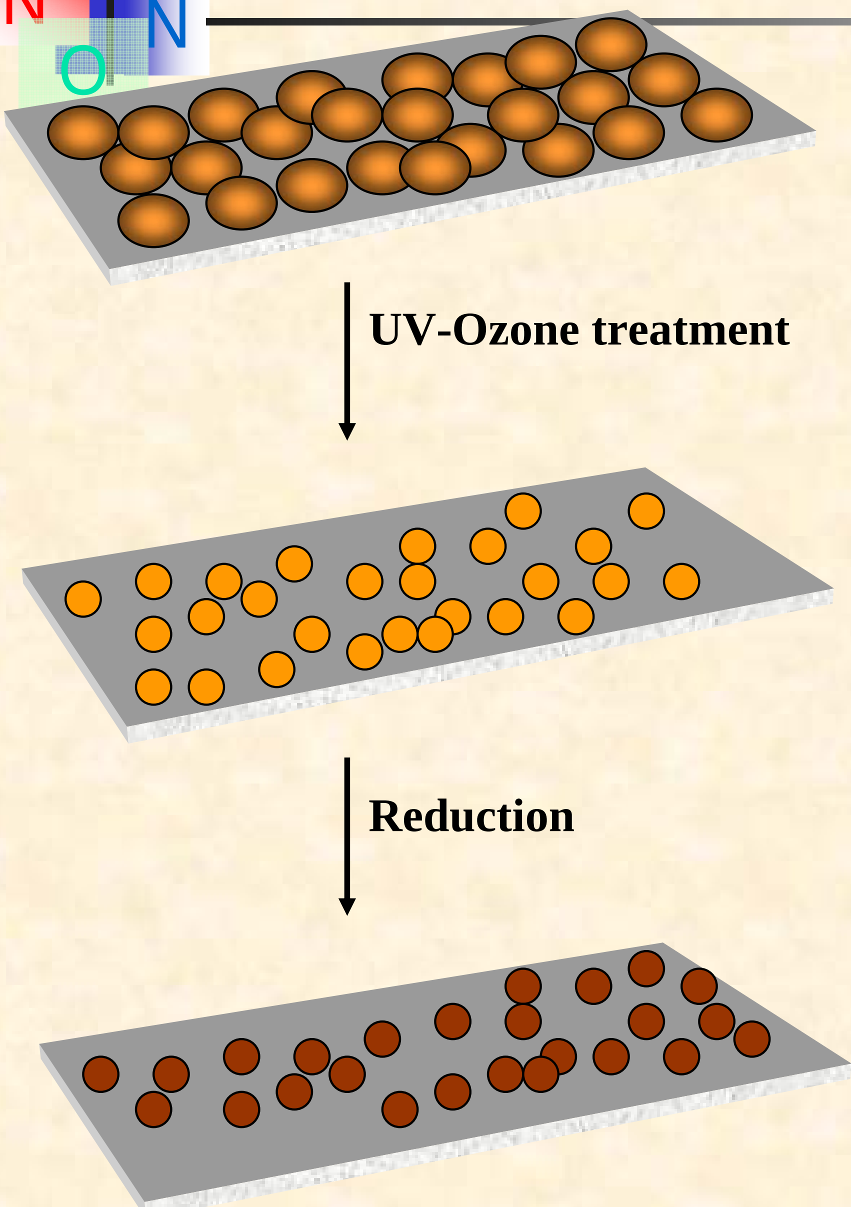
**Cr(VI) reduction in presence of Ferritin and light**

**Reductant – tartrate (3.2x10$^{-3}$ M)**

**pH 7.5, tris buffer**



# General synthetic scheme for Fe oxide and metal production

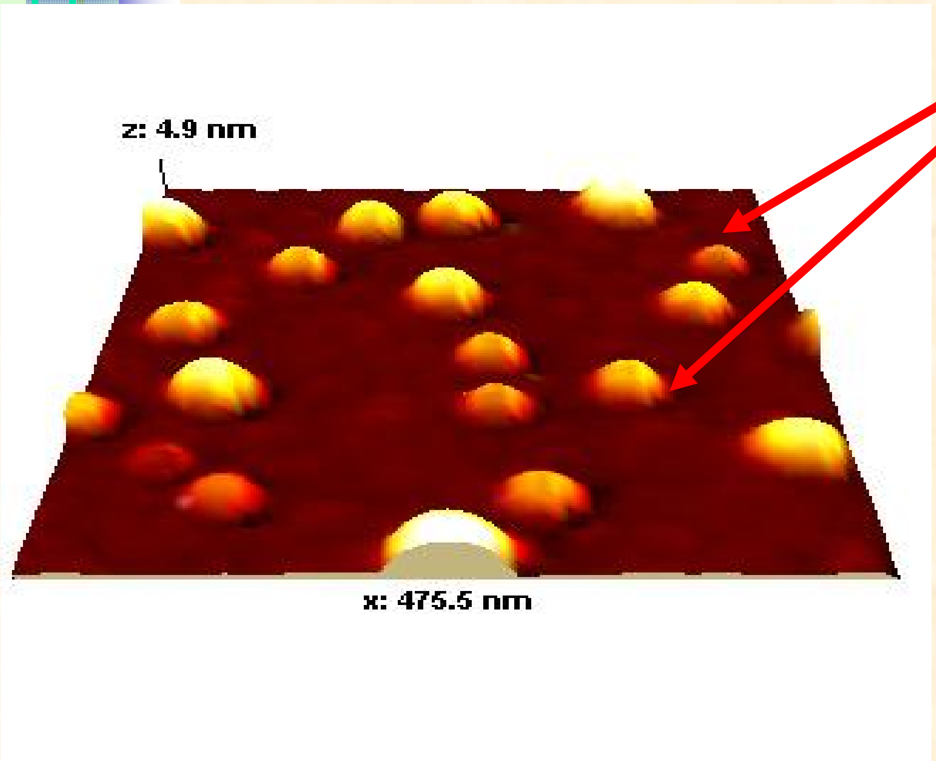




**The PSD-UV uses high intensity UV radiation to vaporize and remove the protein portion**

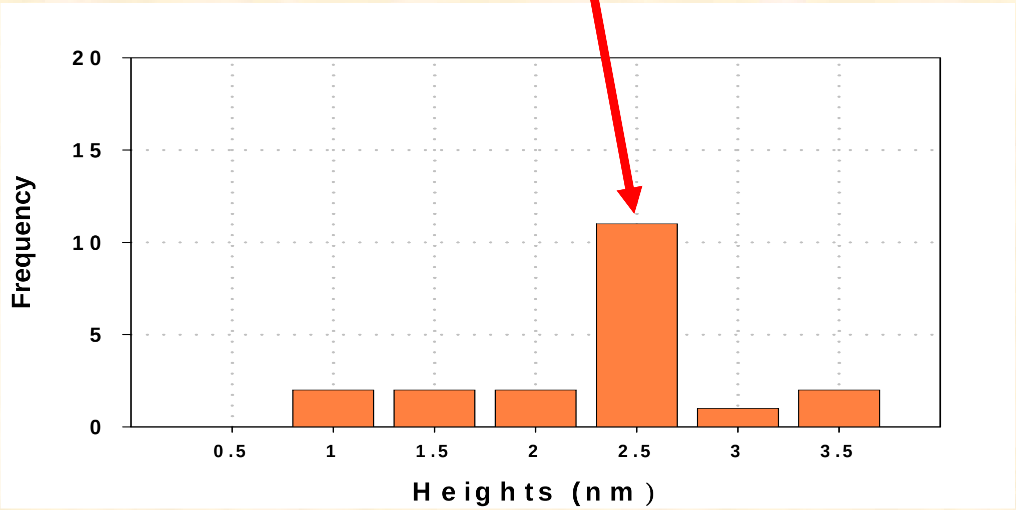
**The high pressure cell coupled to UHV chamber where reduction of metal oxide to metal occurs and accompanying transfer apparatus.**

# Acoustic AC mode AFM Characterization of FeOOH nanoparticles




**ISOLATED NANOPARTICLES**

**Average Height ONLY 2.5 nm!**




**FeOOH nanoparticles prepared by UV-ozone treatment of 100 Fe loaded ferritin for 60 mins at 100$^{o}$C under oxygen (<5psi)**

**Relative height distribution of particles**

# AFM images of FeOOH nanoparticles

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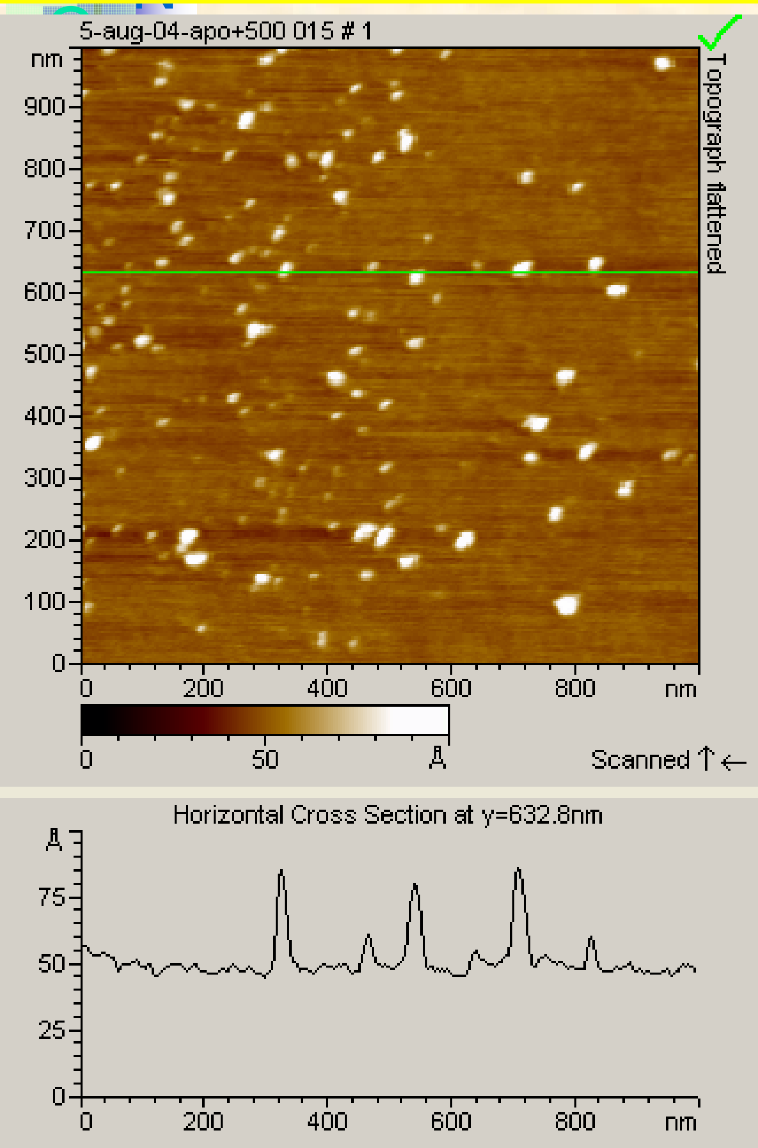
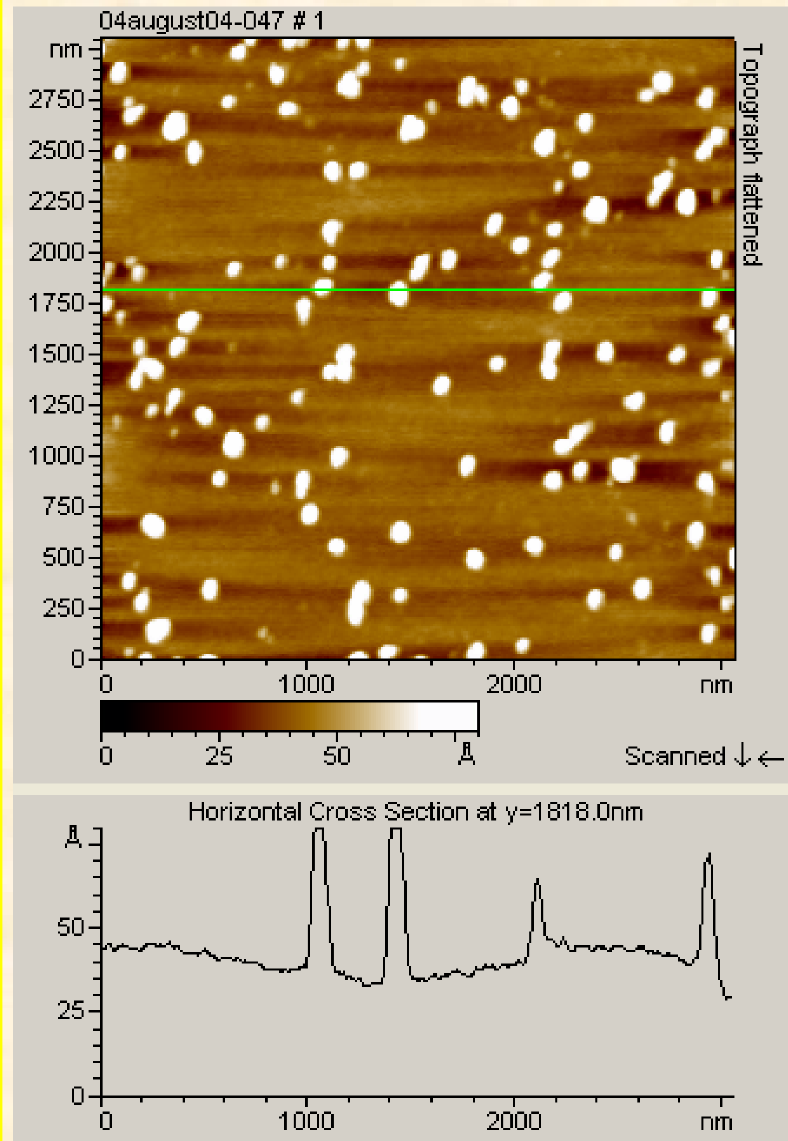
Apoferritin + 500 FeFn mixture




Apoferritin + 2000 FeFn mixture




- ISOLATED NANOPARTICLES
- Peak-to-valley height differences for the large features in the cross-section are in the:
- **2-3 nm** range for 500 Fe loaded Ferritin
- **5-6 nm** for the 2000 Fe loaded Ferritin.

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