

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

by

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Metal Sequestration by Nanoparticles

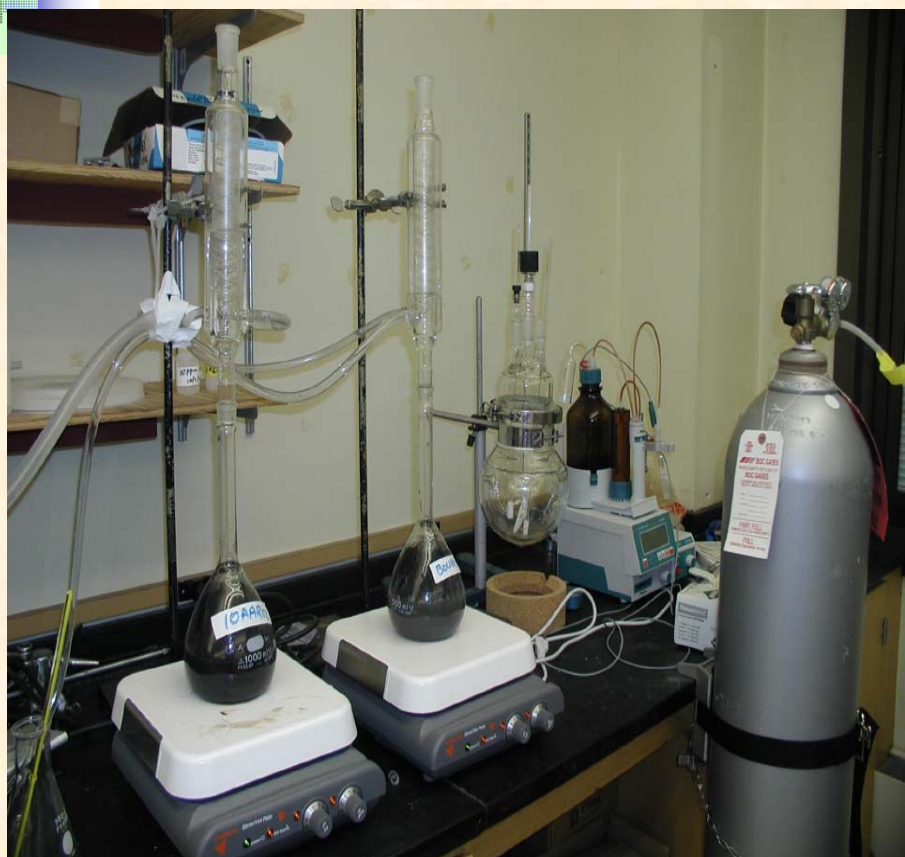
Goal: Synthesis of nano-scaled particles and devices for more efficient and cost effective environmental applications

Particles: Zeolites and Iron Oxy-hydroxide Nanoparticles

Why use zeolites for metal sequestration?

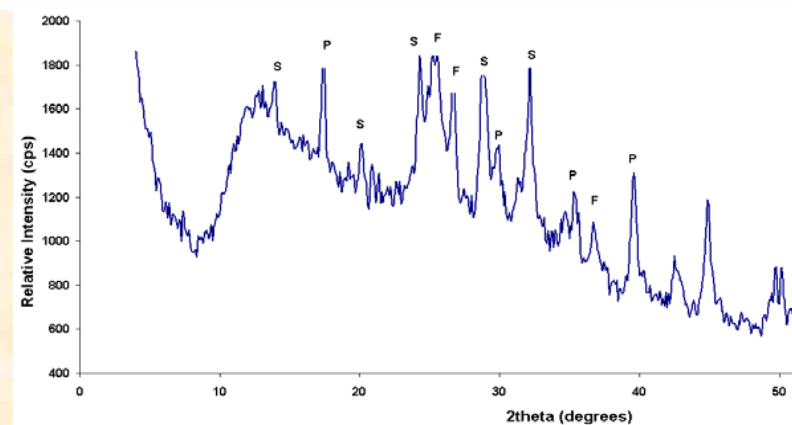
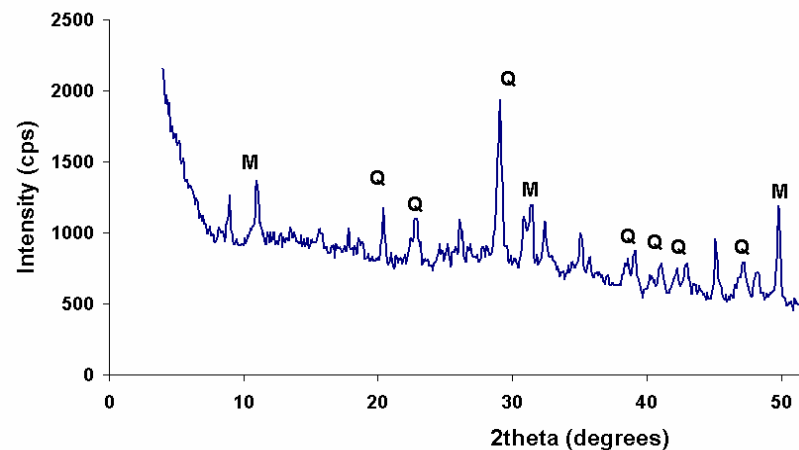
- Nano-sized channel system of zeolites
 - 0.4 to 1.4 nm
- Provides size- & shape-selective matrix for absorbed molecules
- Maintains a high surface-to-mass ratio

ZEOLITE SYNTHESIS



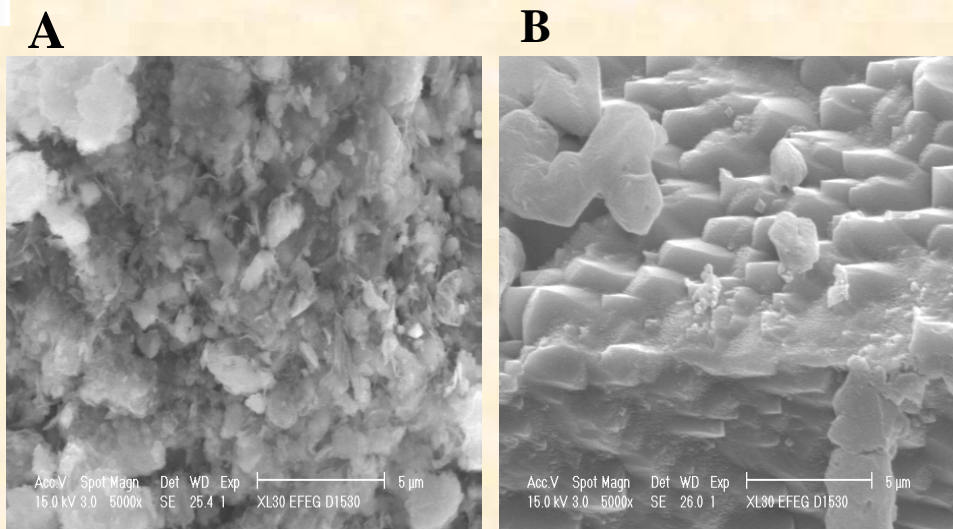
The reflux method of generating zeolites from ash.
Kargbo, 2004 (by permission)

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

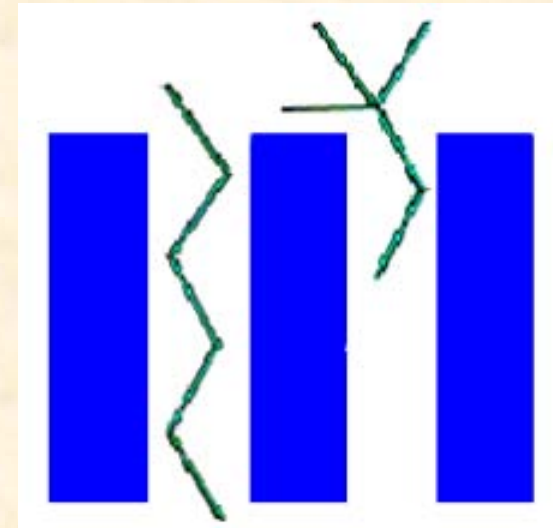
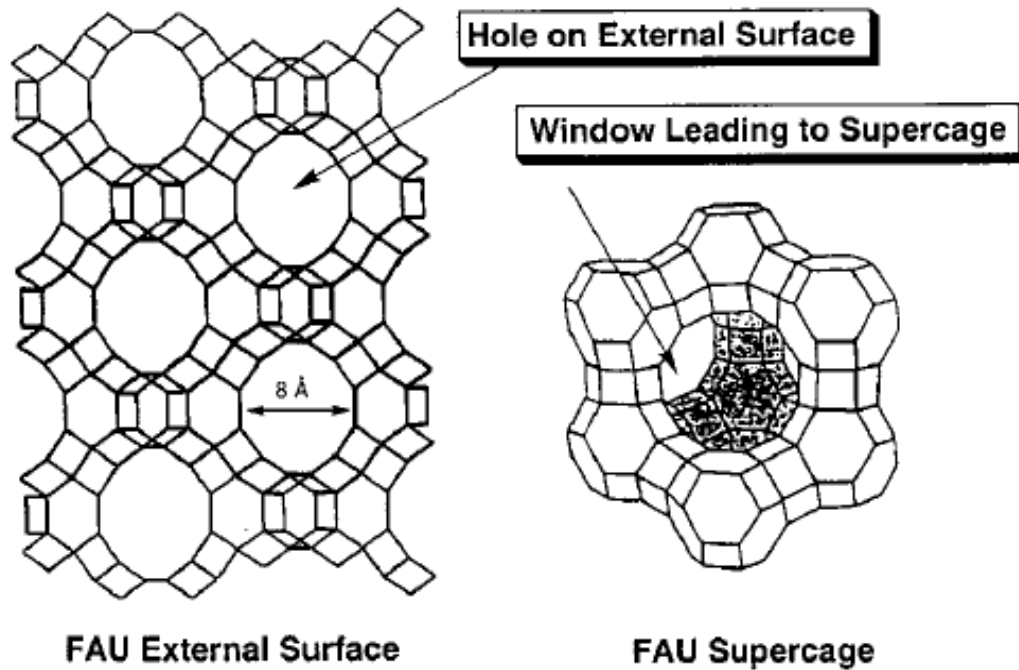
Zeolites Verification and Preparation for PRB



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 ₂ O ₃	27.5	19.4	23.4
Fe ₂ O 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
Source 1	192	176
Source 2	0.1	0.1
Source 3	0.1	0.2

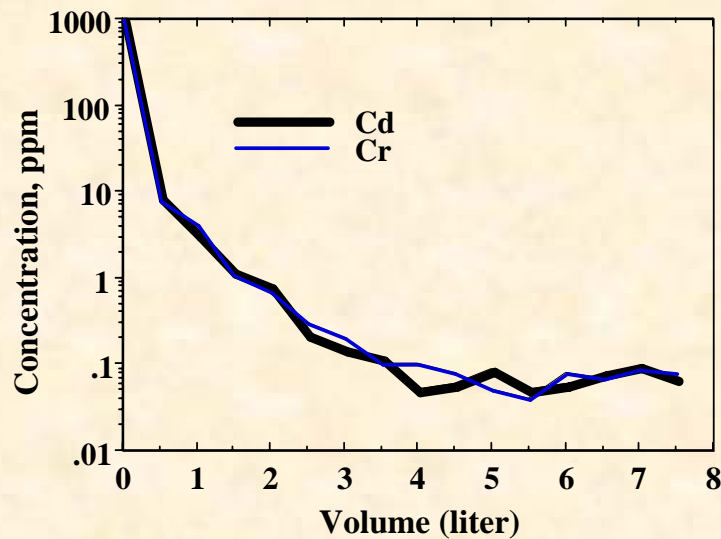
Resulting Solution Concentration (ppm)

- 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

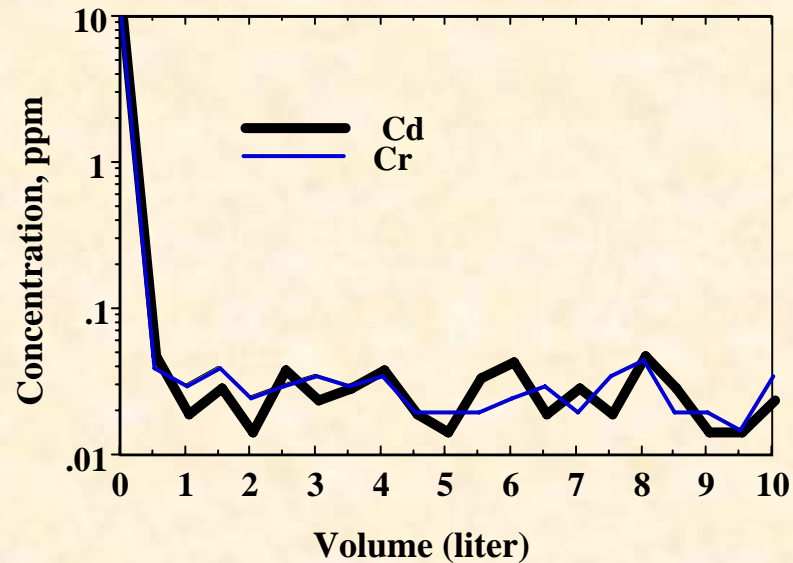
Column Testing (1)

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



Column Testing (2)

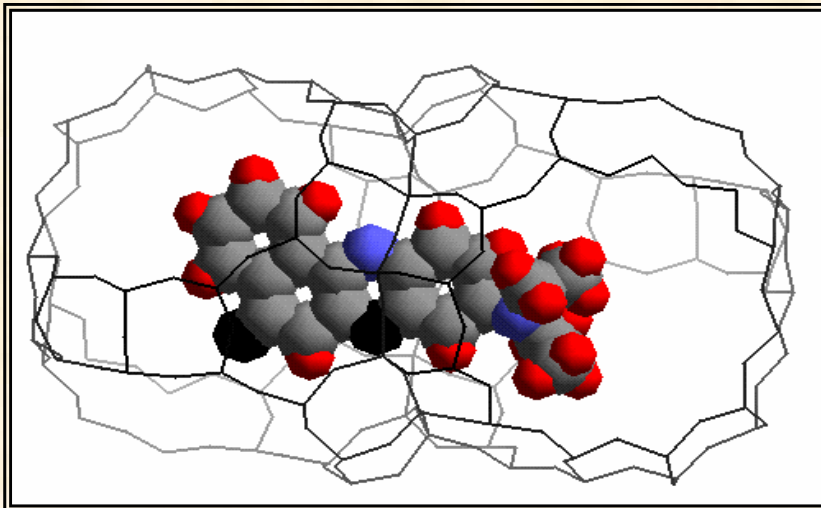
Results of 10 ppm Cd and 10 ppm Cr, passed through 200 gm of barrier materials



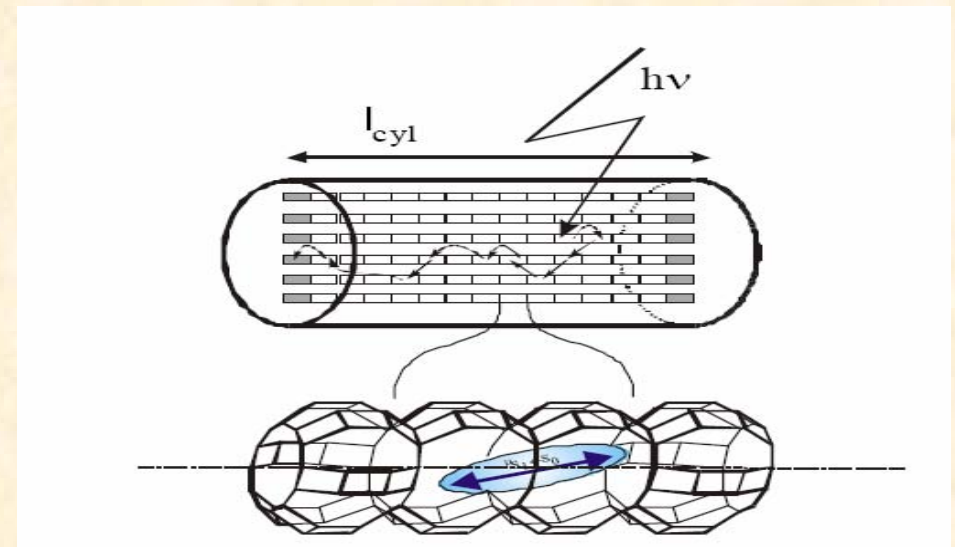
Hence, CAFA-PRB containing zeolites has ability to remove Cr and Cd very effectively.

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 presence 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

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 - ✓ Ben Franklin Partners/Consortium for Sustainable Design & Research
 - ✓ Dr. David Kargbo, Project PI
 - ✓ Dr. Hosein Rostami (Philadelphia Univ), Project Co-PI
 - ✓ 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 agglomeration 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:

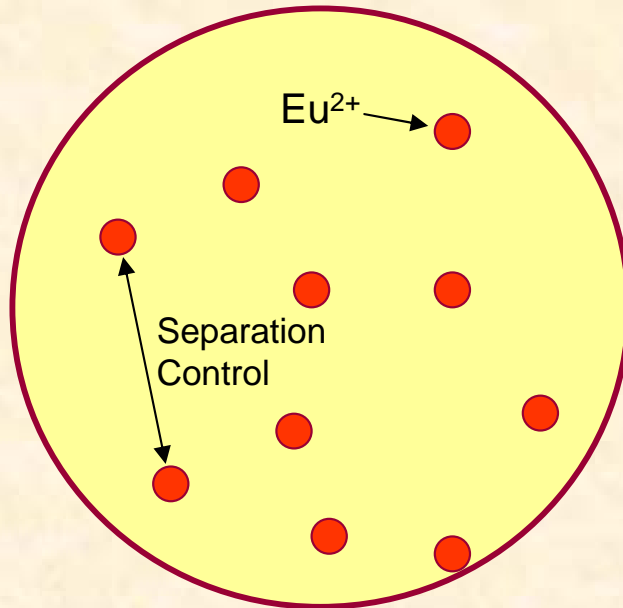
A versatile method of fabricating nano-particles of metals, insulators and semiconductors

Doping with Different Active Atoms
Control over the Chemistry During the Fabrication

Glassy or Crystalline Particles to Control Surface Reactivity

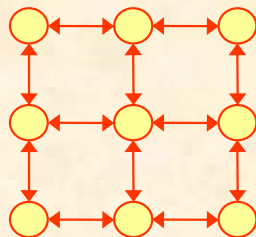


Atomic Tailoring



- 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

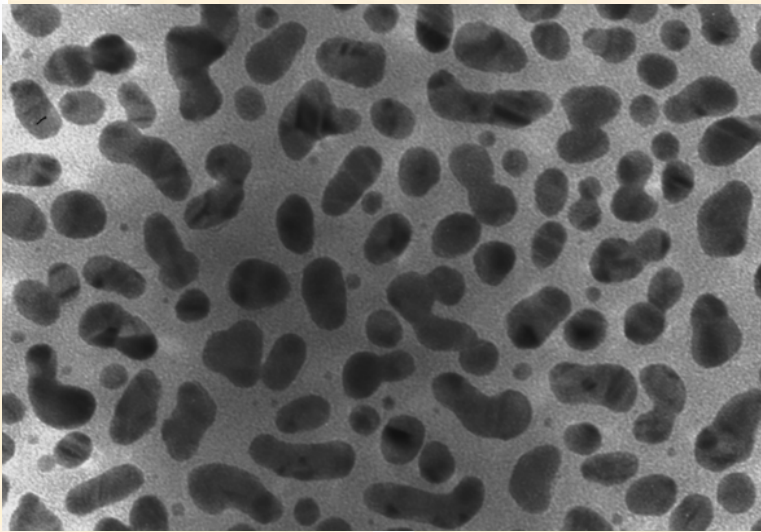
...or Array of Nano-Sensors



Experimental Results

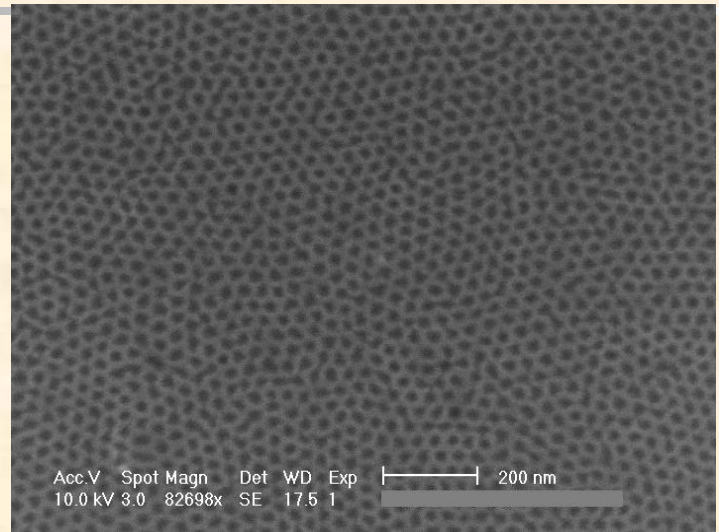


Nanoparticles of MgS Tailored with Eu^{2+} and Eu^{3+}

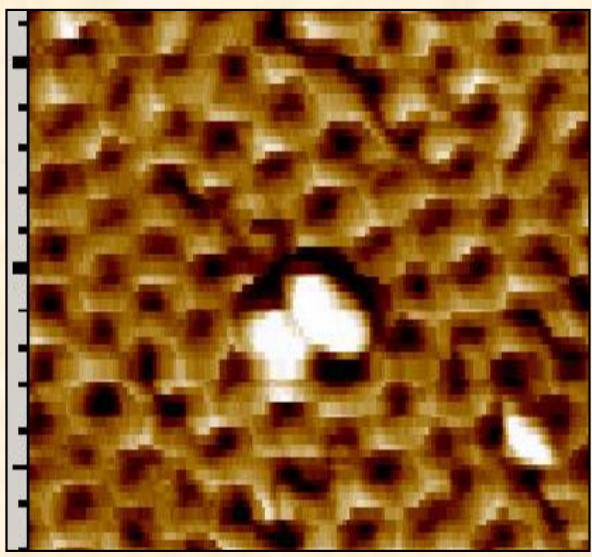


— 10nm

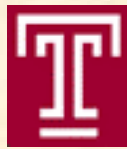
Nano-indentations on Si Surface (Coll: Princeton U.)



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



100 nm

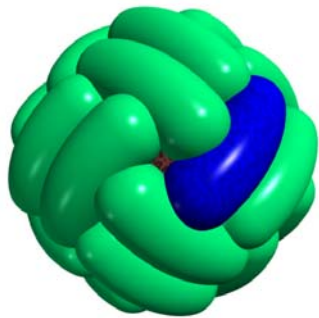




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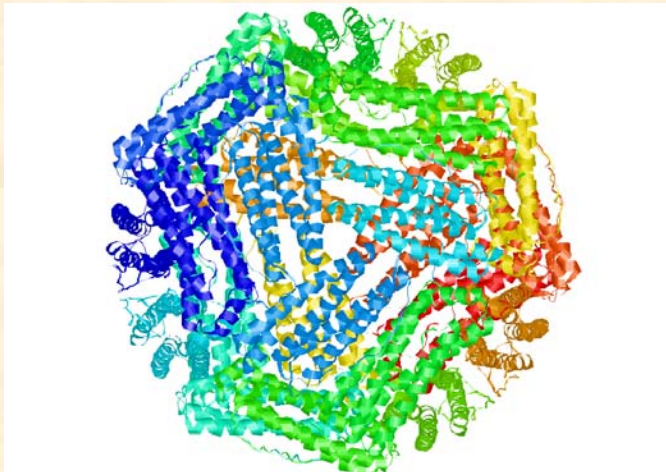
- Research funded by grant from NSF:
 - ✓ Project PI: Dr. Zameer Hasan

Size-Reactivity Relationship of Iron Oxyhydroxide Nanoparticles Assembled within Ferritin



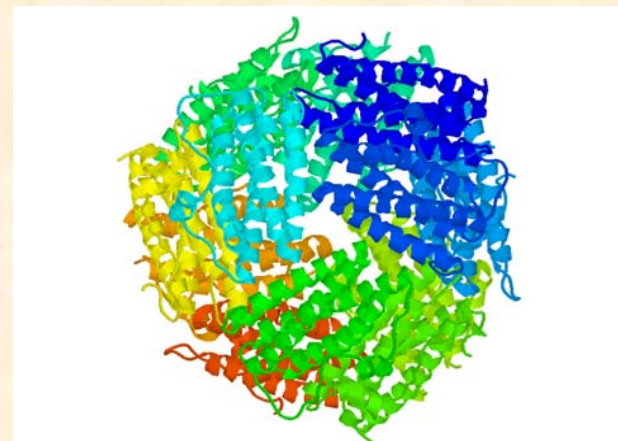
Ferritin

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 (56 Å dia.)
- Accommodates up to 500 Fe atoms

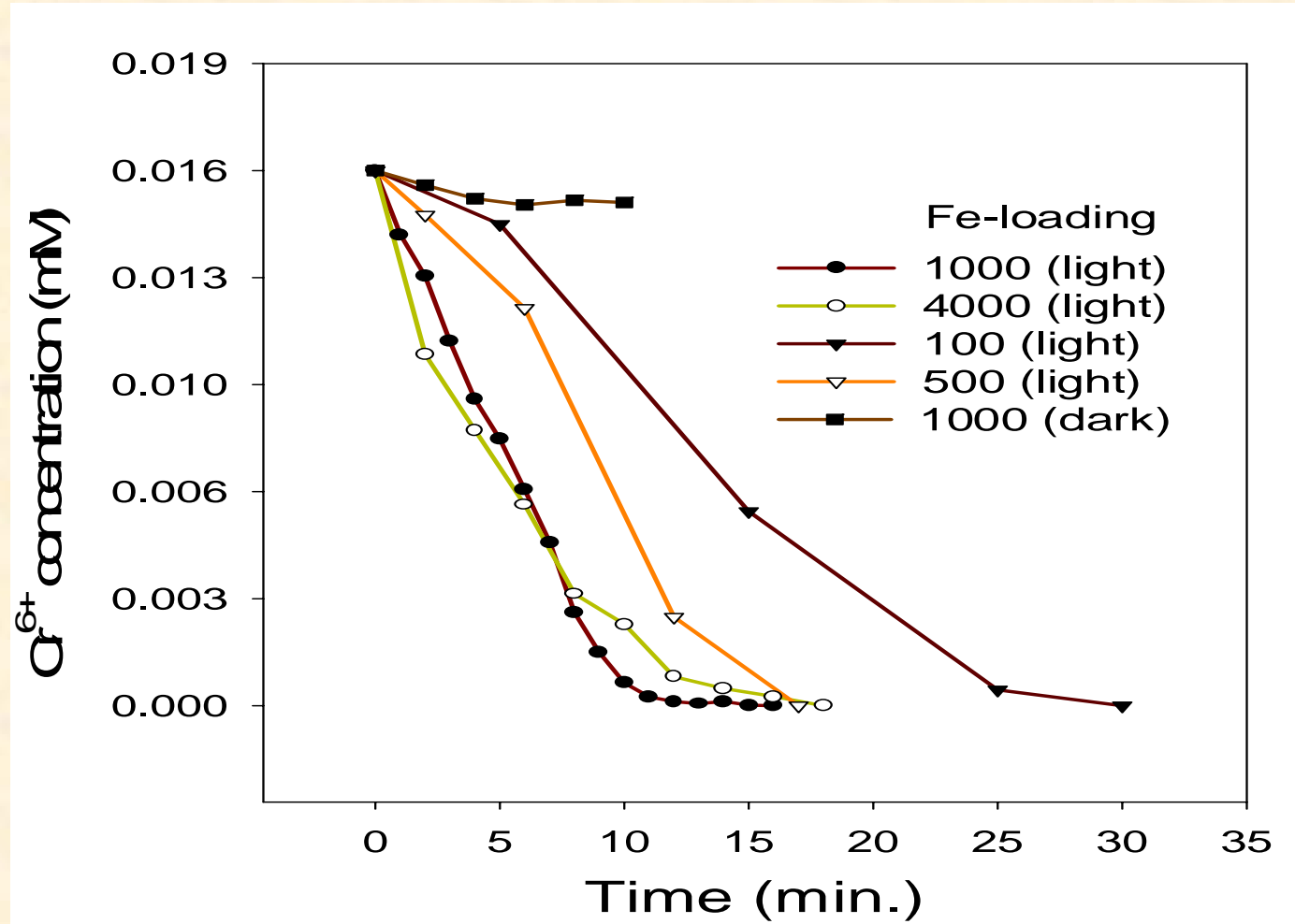


$\text{Cr}_2\text{O}_7^{2-}$ (4.0×10^{-4} M)

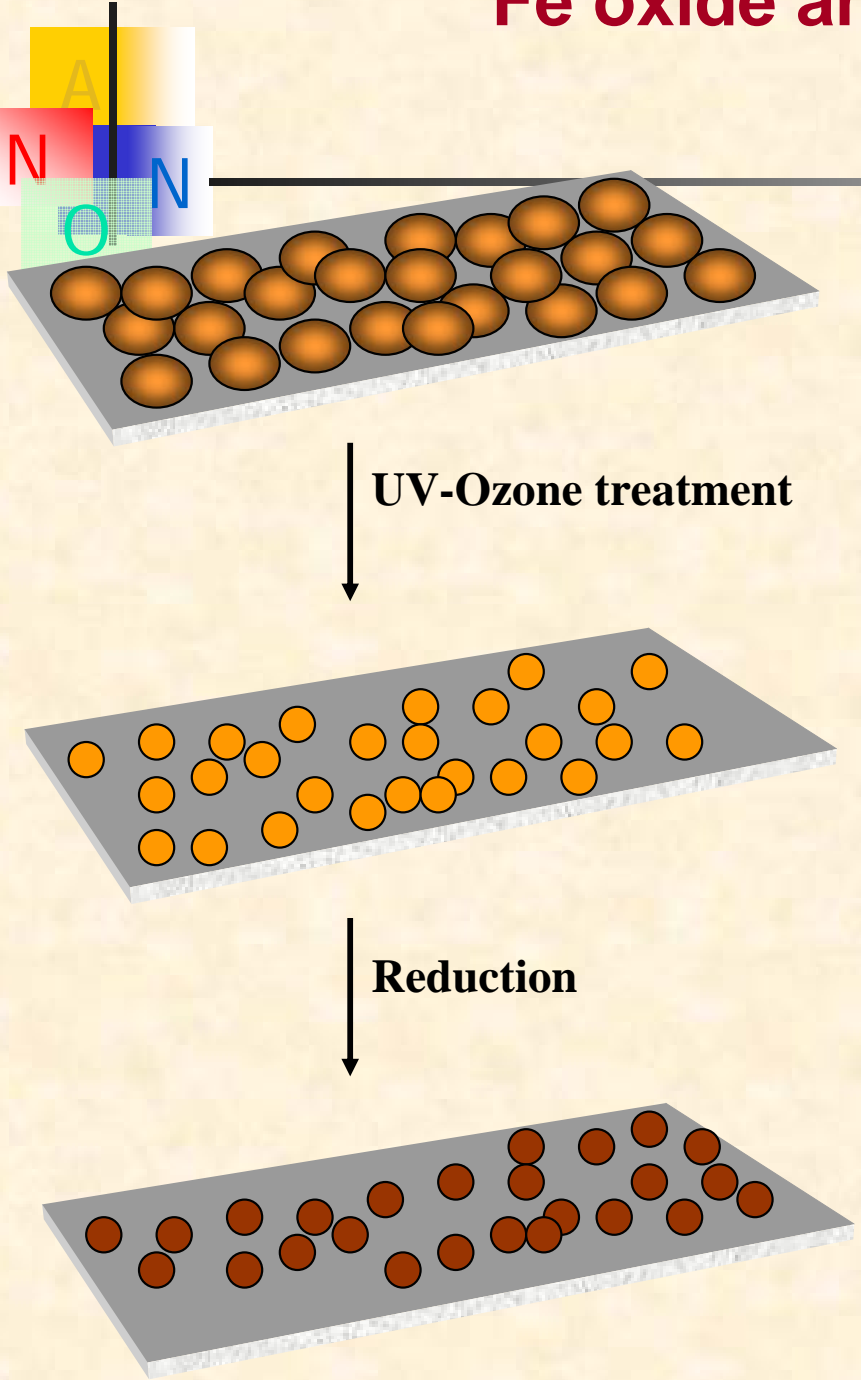
Reductant – tartrate
(3.2×10^{-3} M)

pH 7.5, tris buffer

Cr(VI) reduction in presence of Ferritin and light



General synthetic scheme for Fe oxide and metal production

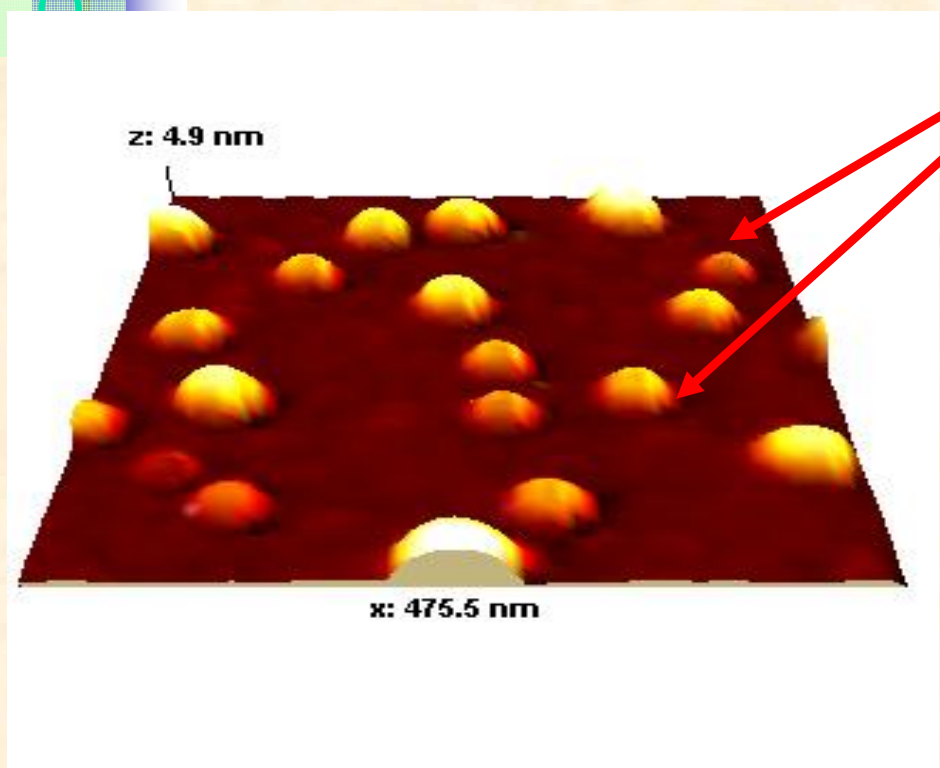
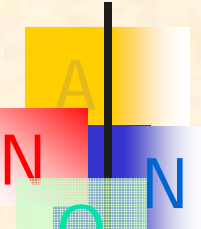


The PSD-UV uses high intensity UV radiation to vaporize and remove the protein portion

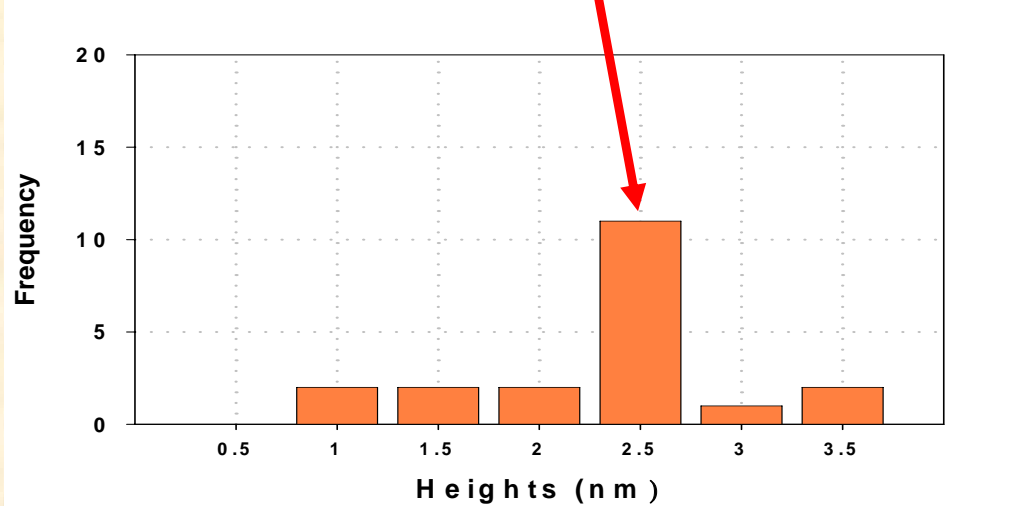


The high pressure cell coupled to UHV chamber where reduction of metal oxide to metal occurs and accompanying transfer apparatus.

Acoustic AC mode AFM Characterization of FeOOH nanoparticles



ISOLATED NANOPARTICLES
Average Height ONLY 2.5 nm!



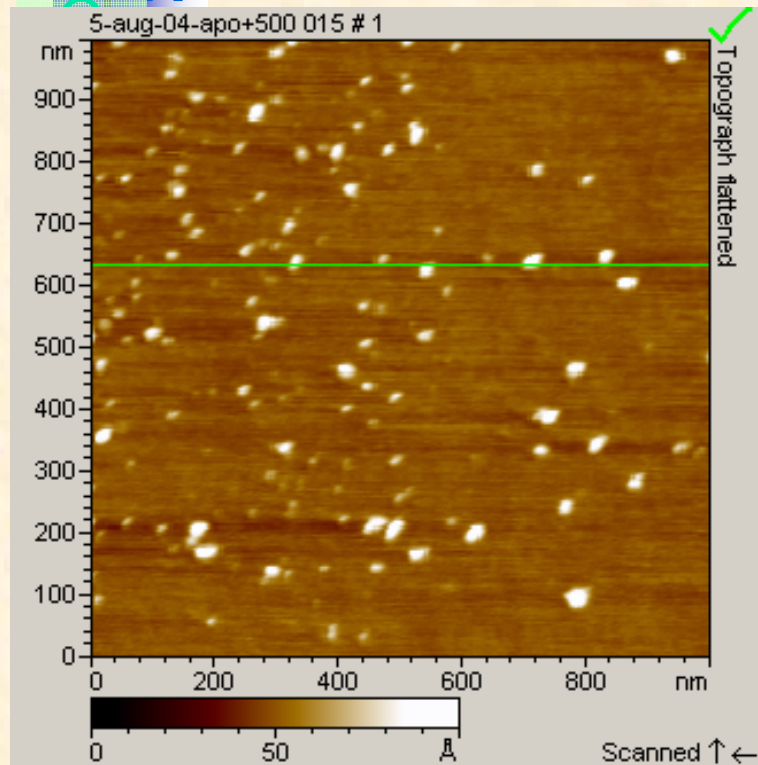
FeOOH nanoparticles prepared by UV-ozone treatment of 100 Fe loaded ferritin for 60 mins at 100°C under oxygen (<5psi)

Relative height distribution of particles

AFM images of FeOOH nanoparticles

Apo ferritin + 500

FeFn mixture



• ISOLATED NANOPARTICLES

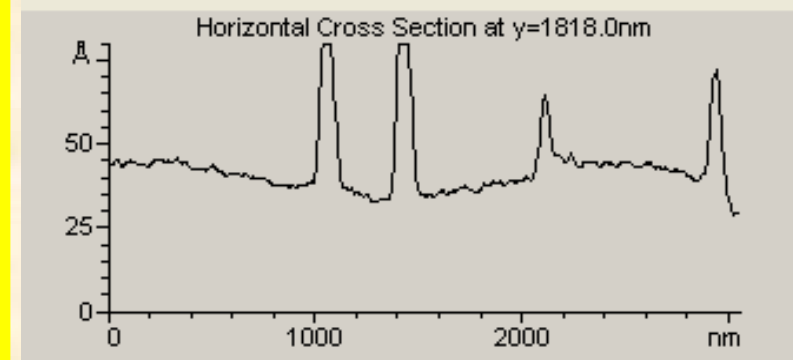
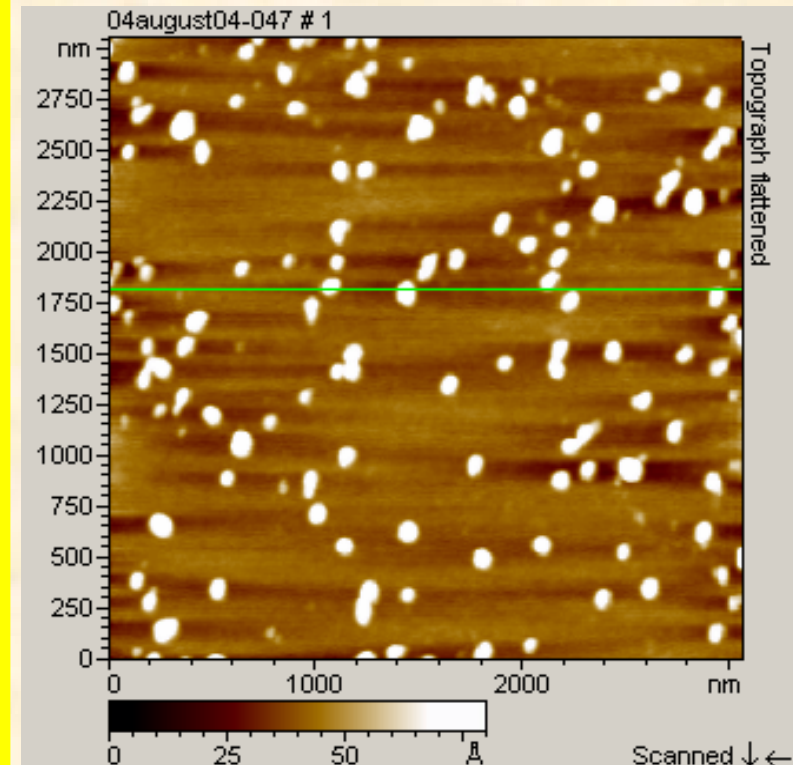
• Peak-to-valley height differences for the large features in the cross-section are in the:

• 2-3 nm range for 500 Fe loaded Ferritin

• 5-6 nm for the 2000 Fe loaded Ferritin.

Apo ferritin + 2000

FeFn mixture





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