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

by

D. Kargbo[1], D. Strongin[2], H. Rostami[3], J. Delilac[4], Z. Hassan[5], S. Chatterjee[6], D. Hausner[7], S. Nguyen[8], and A. Aly[9]

1. Adjunct Associate Professor, Dept. of Civil & Environmental Engineering, College of Engineering, Temple University, & Soil Scientist, US EPA Region 3
2. Professor, Dept. of Chemistry, College of Science & Technology, Temple University
3. Assistant Professor, Philadelphia University
4. Associate Professor, Dept. of Electrical & Computer Engineering, College of Engineering, Temple University
5. Professor, Dept. of Physics, College of Science & Technology, Temple University
6. Graduate Research Assistant, College of Engineering, Temple University (PhD Candidate)
7. Graduate Research Assistant, Chemistry Dept., College of Science & Technology, Temple University
8. Graduate Research Assistant, Dept. of Electrical & Computer Engineering, College of Engineering, Temple University
9. Graduate Research Assistant, Dept. of Physics, College of Science & Technology, Temple University

NANO

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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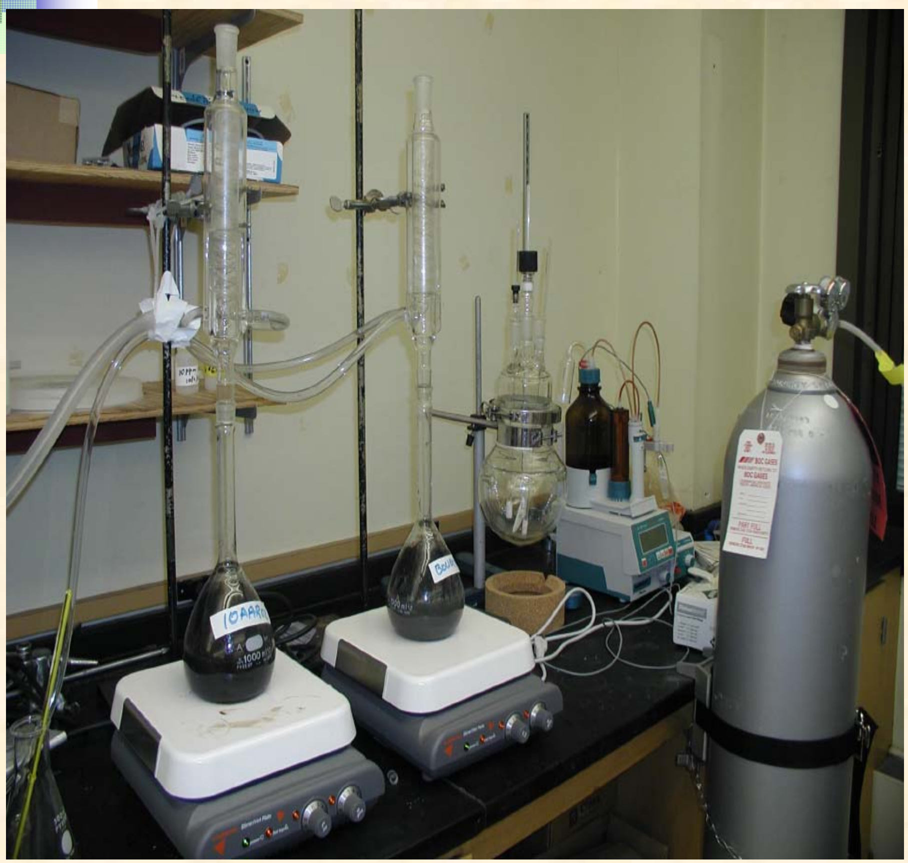
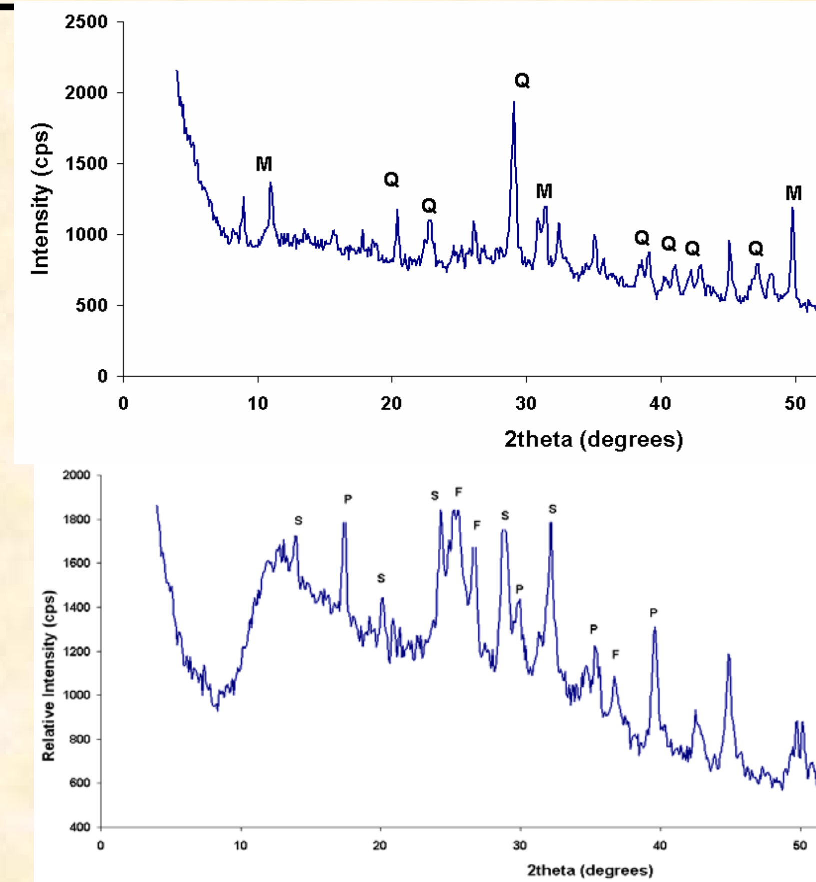
ZEOLITE SYNTHESIS



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

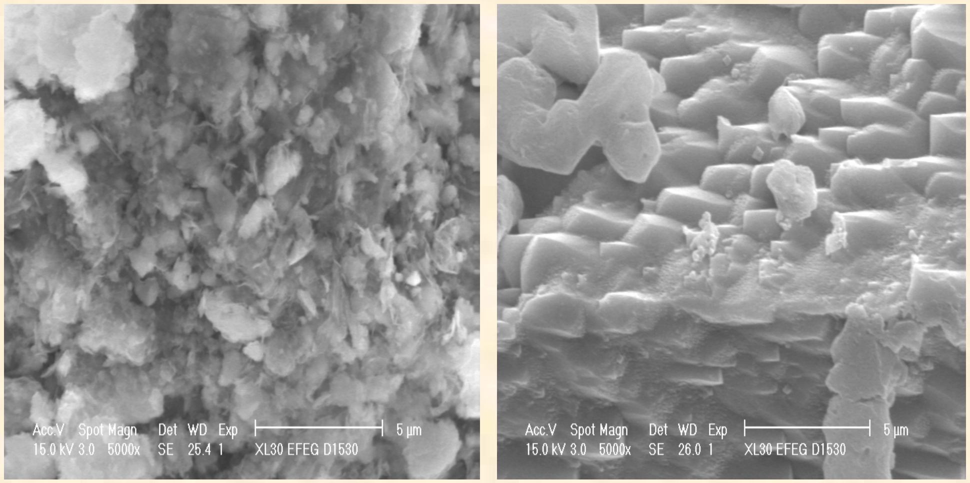
ASH (Waste ash/Coal fly ash) + 3M NaOH + Heat



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

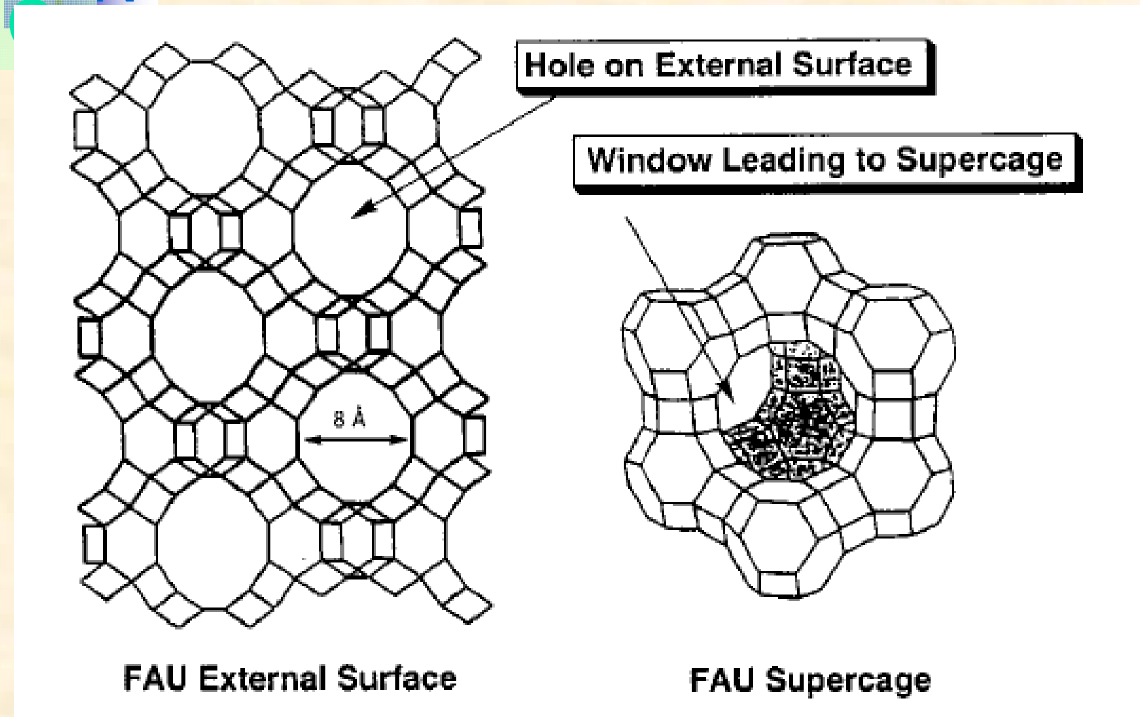
A B

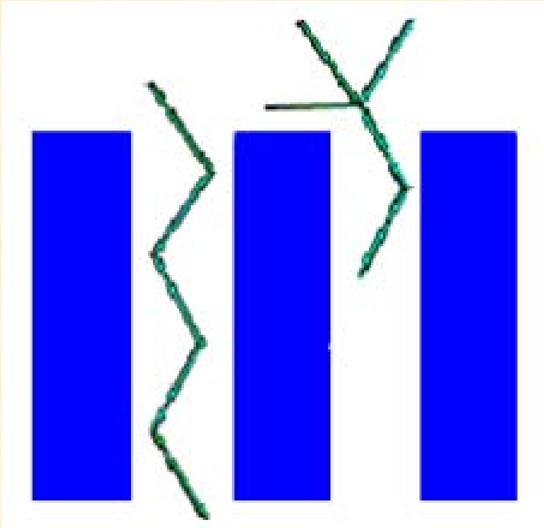


Scanning electron microscope images of MSWC ash. A= Untreated sample; B= Sample fused in NaOH. XRD verified presence of zeolite Na-P1 and faugasite ***(Kargbo, 2004, by permission)***.

- **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).

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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

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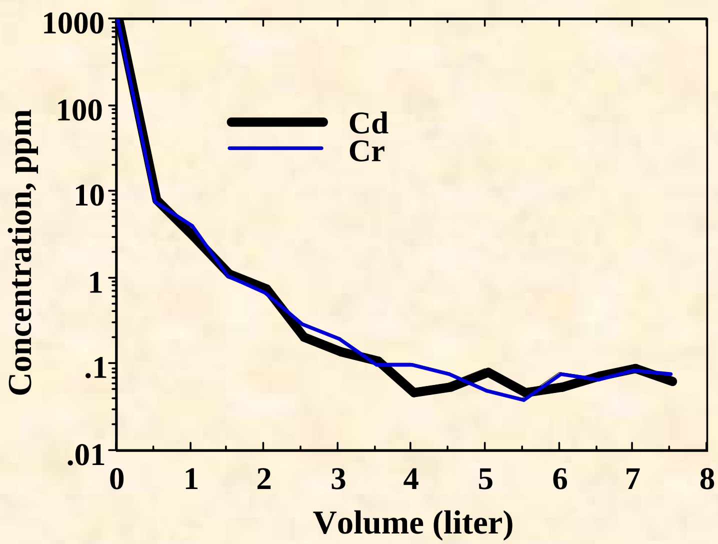
Toxic Metal Sequestration by Zeolites

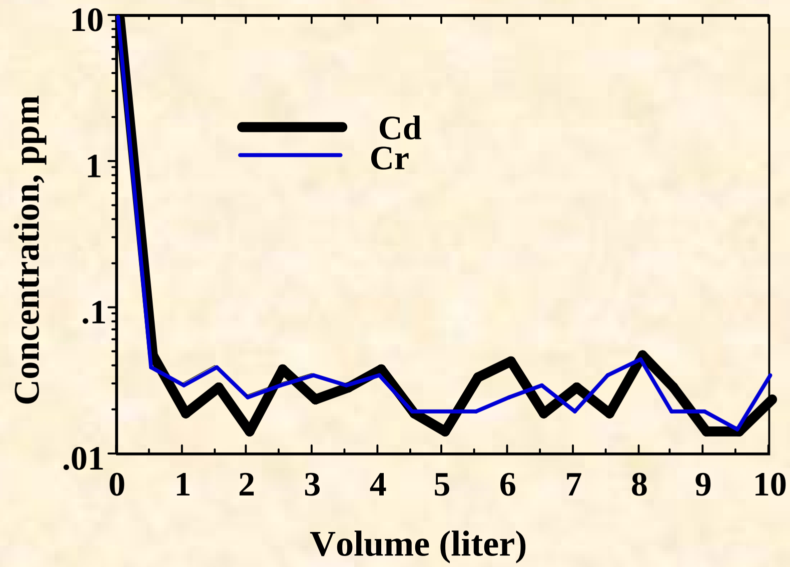
Column Testing (1)

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.

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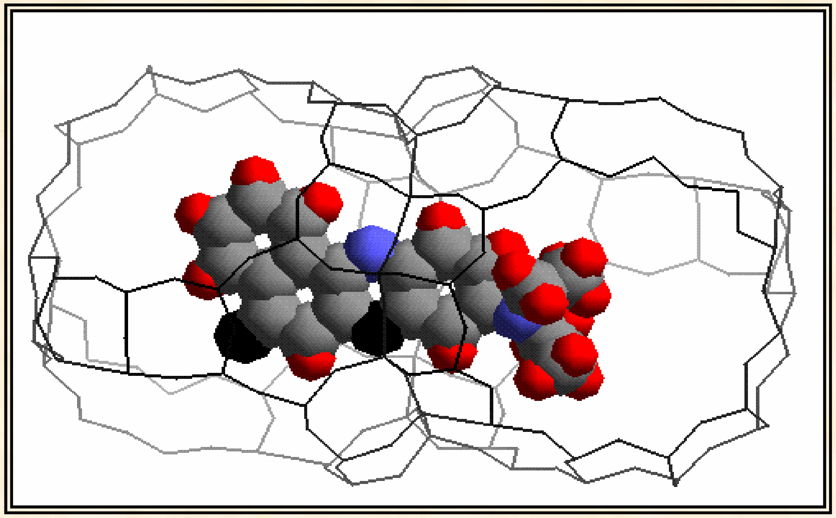
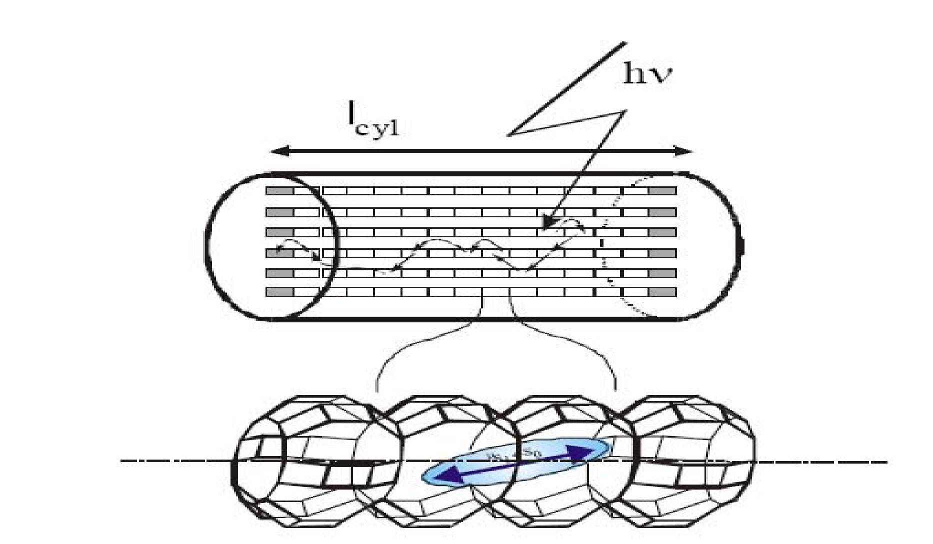
Other Ongoing Contaminant Remediation Research Using zeolites

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.

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Acknowledgement

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  - ✓ Ben Franklin Partners/Consortium for Sustainable Design & Research
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    - ✓ 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 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

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Atomic Tailoring of Nanosensors

We have demonstrated:

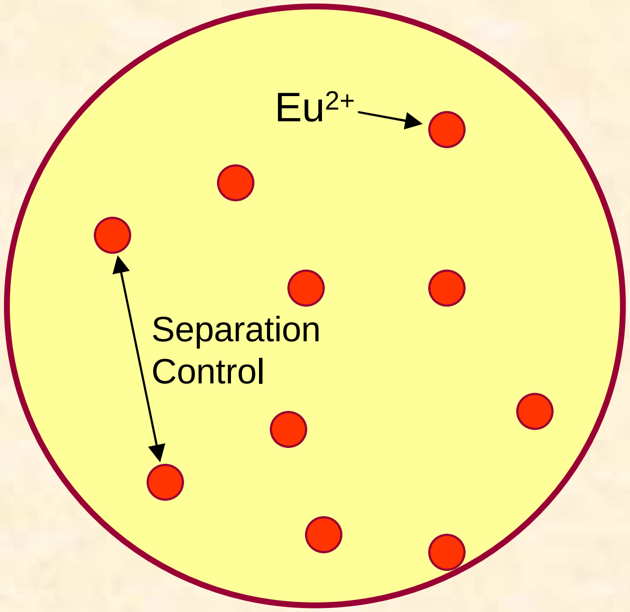
Pulsed Laser Deposition:
A versatile method of fabricating nano-particles of metals, insulators and semiconductors

Doping with Different Active Atoms

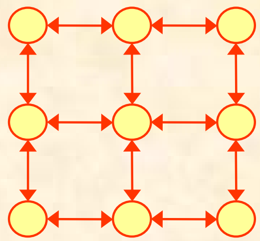
Control over the Chemistry During the Fabrication

Glassy or Crystalline Particles to Control Surface Reactivity

Atomic Tailoring



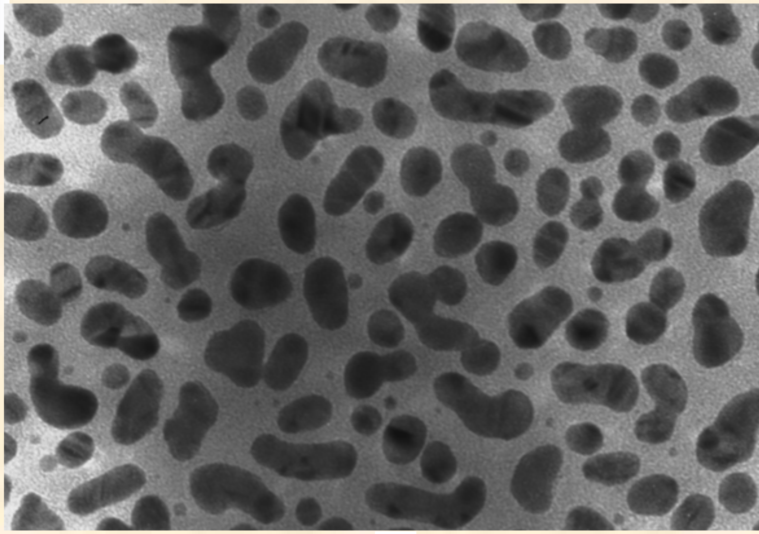
…or Array of Nano-Sensors



- 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

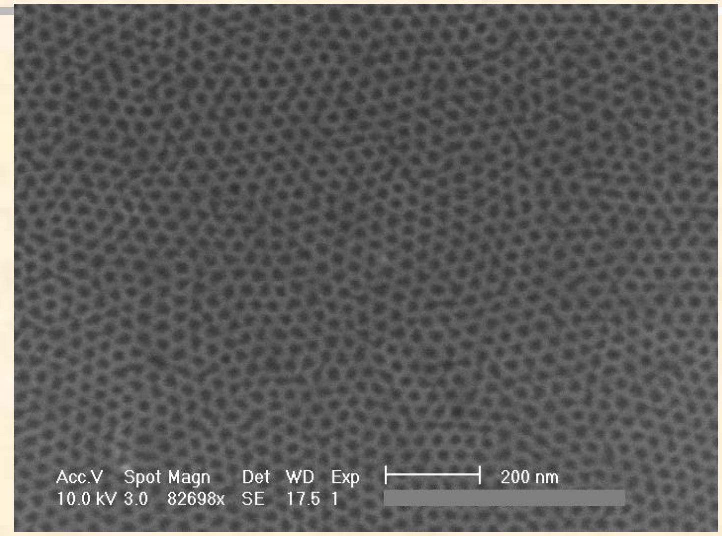
Experimental Results

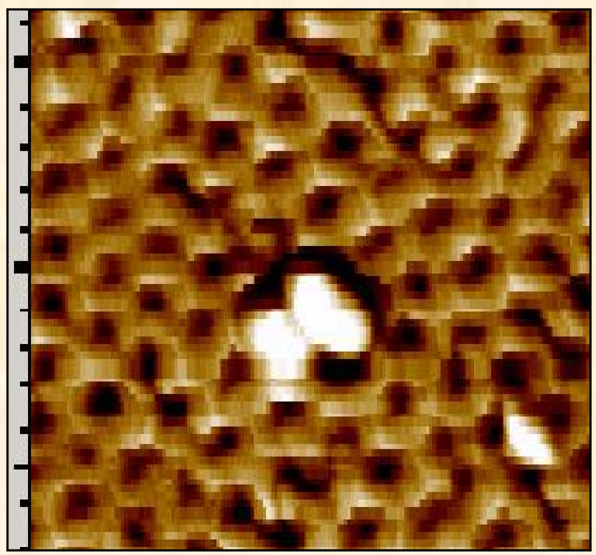
Nanoparticles of MgS Tailored with Eu^{2+} and Eu^{3+}



— 10nm

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





100 nm

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

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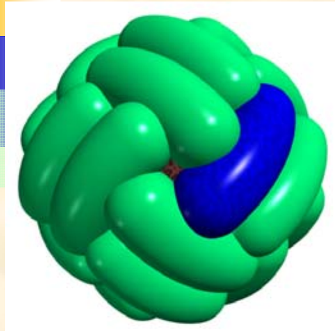
Acknowledgement

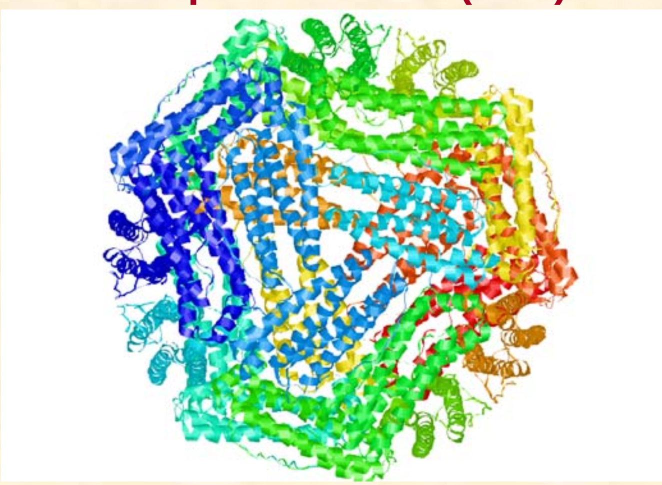
- Research funded by grant from NSF:
  - ✓Project PI: Dr. Zameer Hasan

Size-Reactivity Relationship of Iron Oxyhydroxide Nanoparticles Assembled within Ferritin



Ferritin

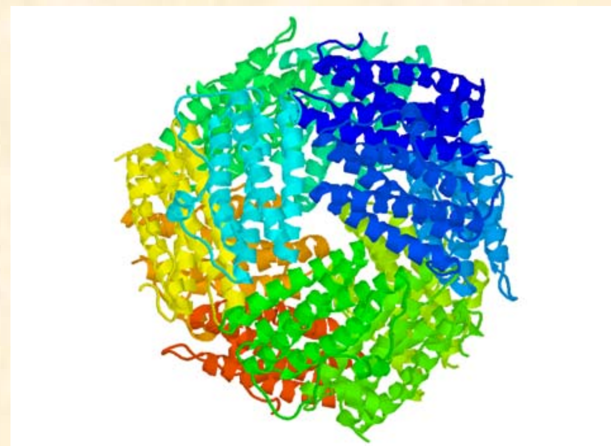
Horse Spleen Ferritin (HSF)



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

Stores Fe as hydrated Fe_2O_3 (rust)

Listeria Innocua
Ferritin-like Protein (LFLP)



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

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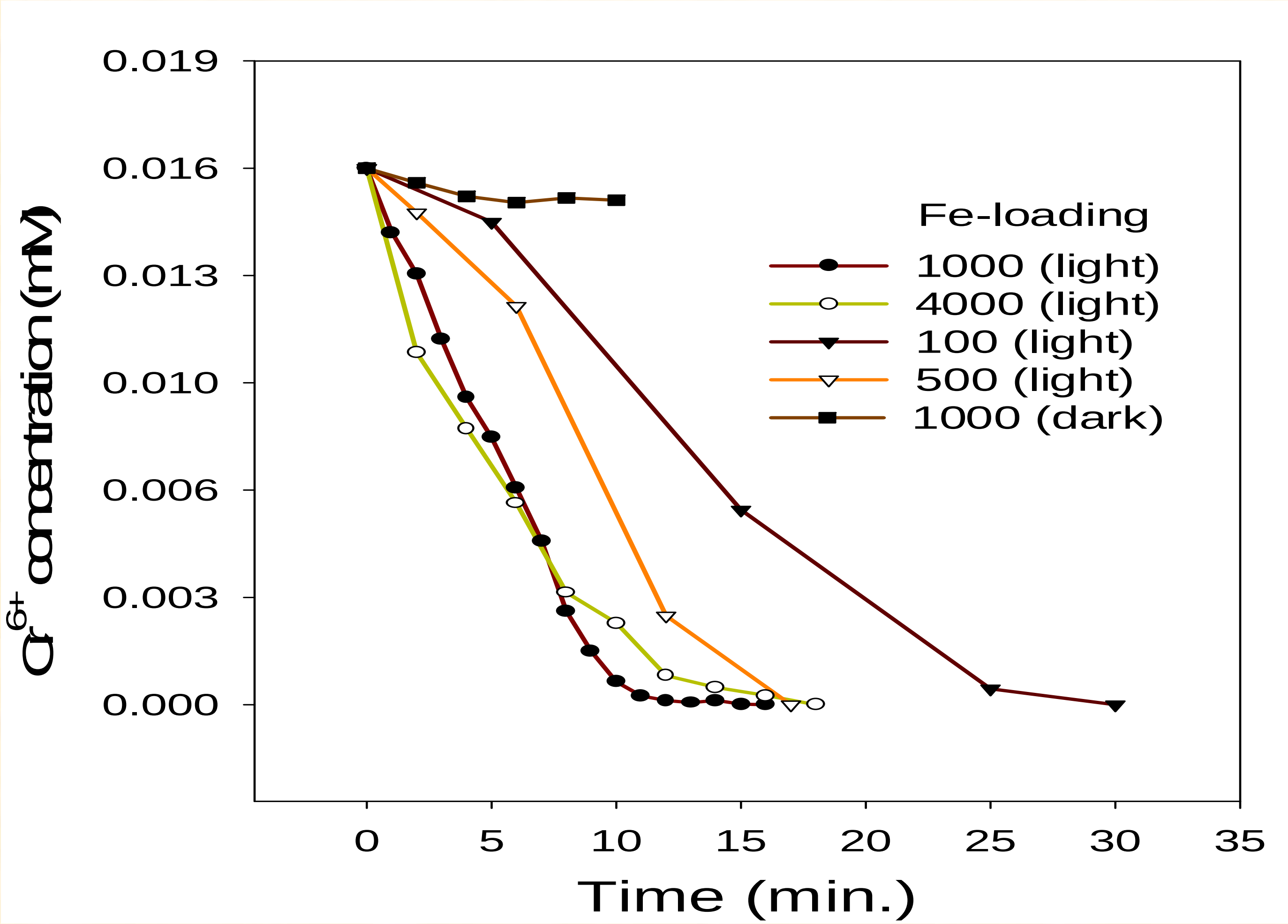
$Cr_2O_7^{2-}$ (4.0×10^{-4} M)

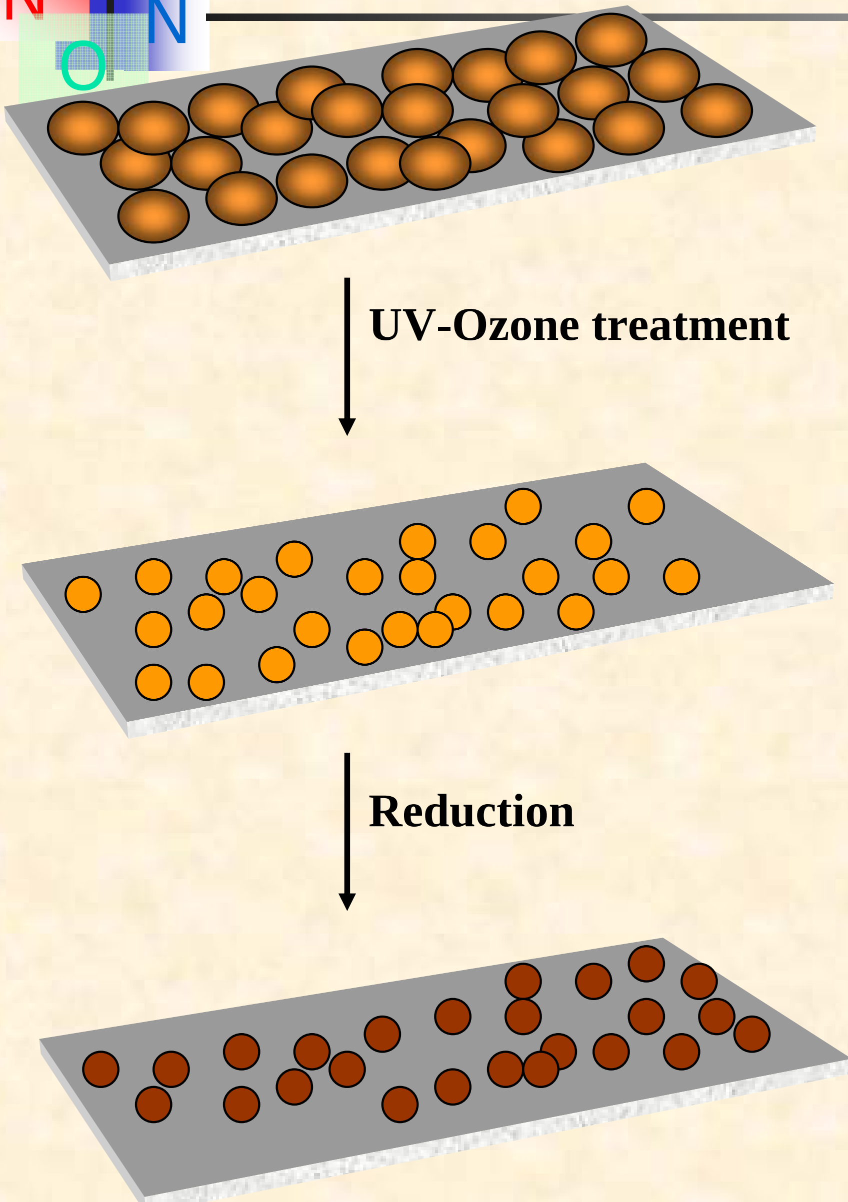
Reductant – tartrate (3.2×10^{-3} M)

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.

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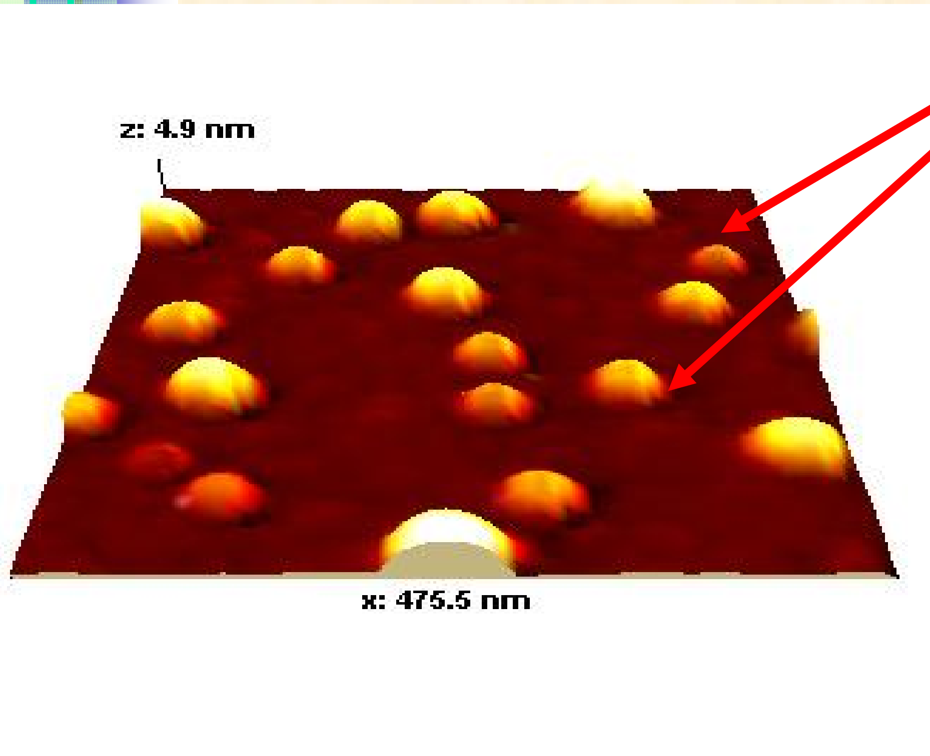
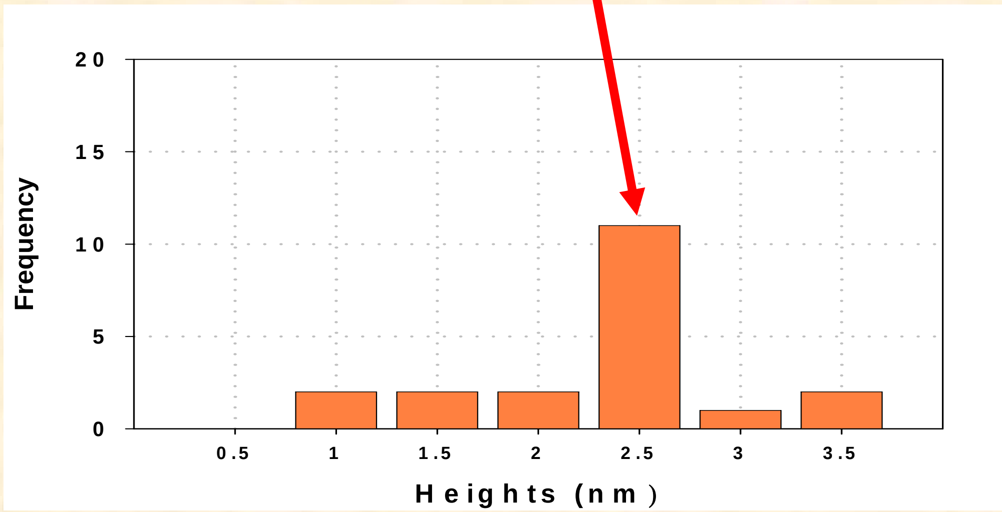
Acoustic AC mode AFM Characterization of FeOOH nanoparticles



ISOLATED NANOPARTICLES

Average Height ONLY 2.5 nm!



eOOH nanoparticles prepared by UV-one treatment of 100 Fe loaded ferritin r 60 mins at 100ºC under oxygen (<5psi)

Relative height distribution of particles

AFM images of FeOOH nanoparticles

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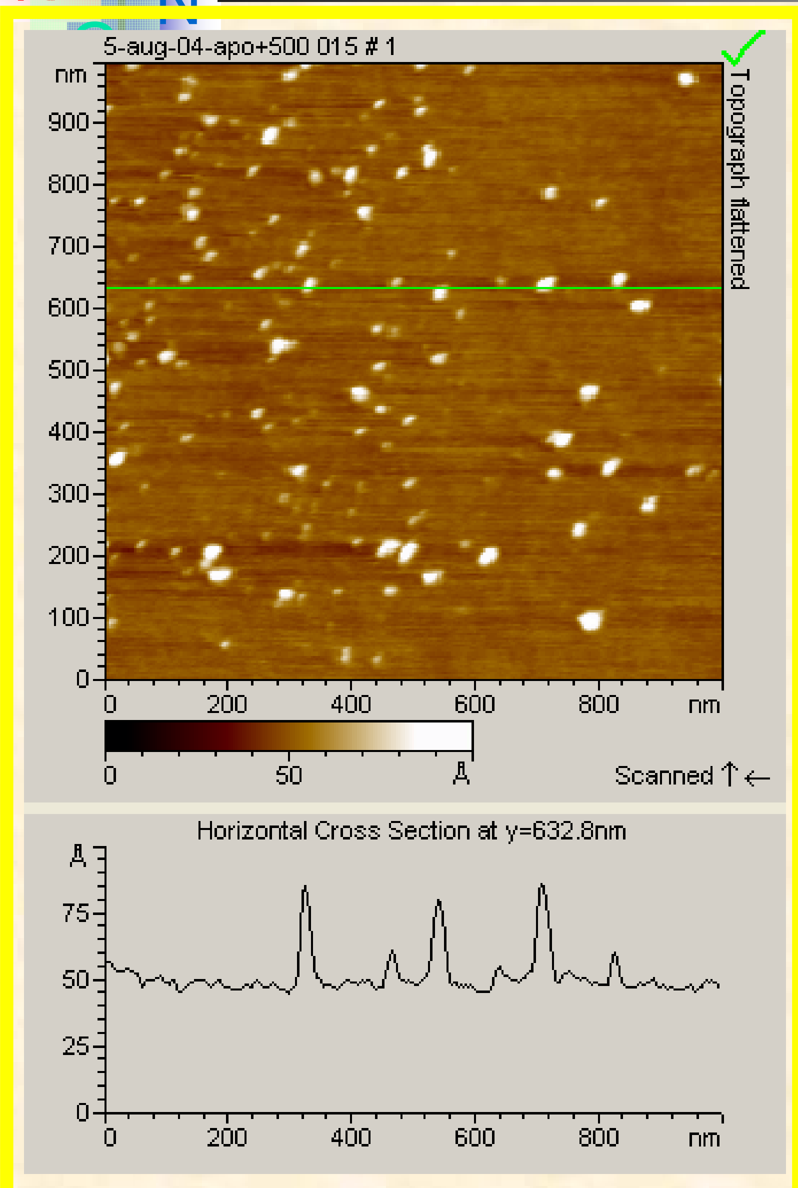
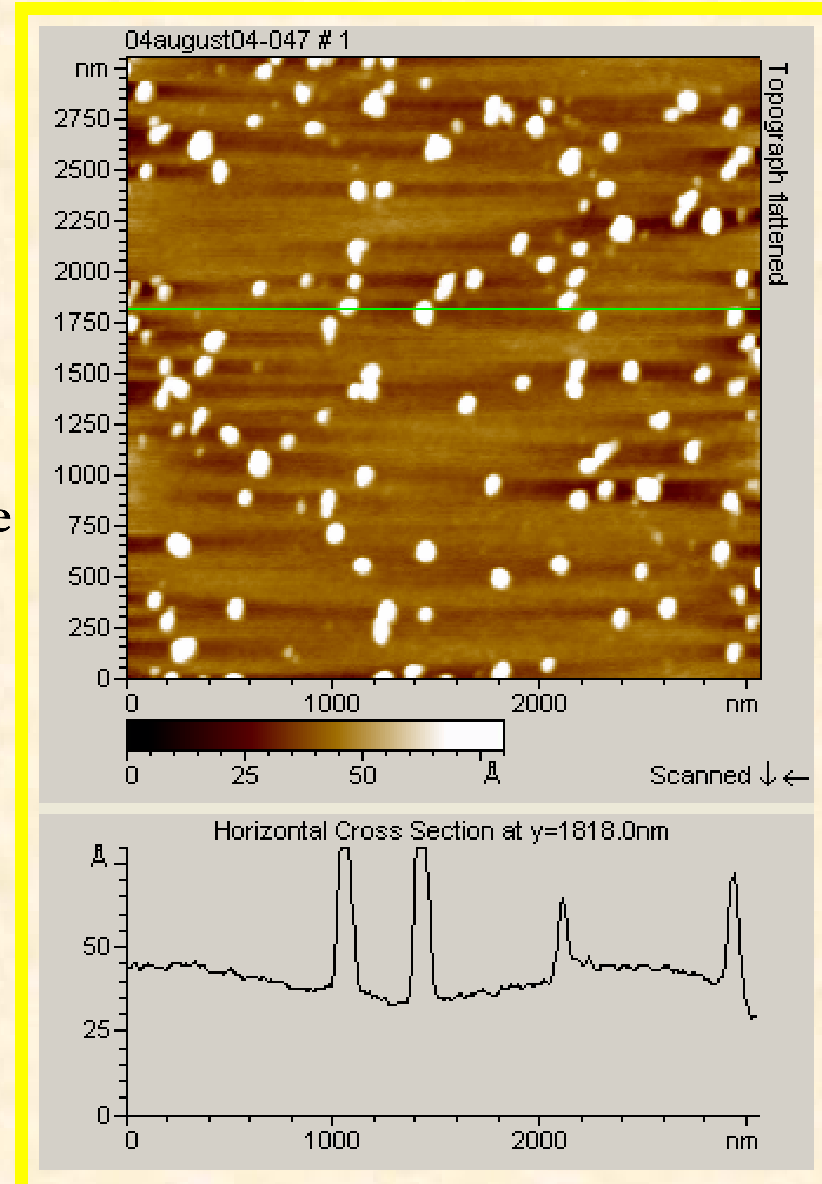
Apoferritin + 500 FeFn mixture



- 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.

Apoferritin + 2000 FeFn mixture



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  - Project PI: Daniel R. Strongin

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