A Bioengineering Approach to Environmental Remediation

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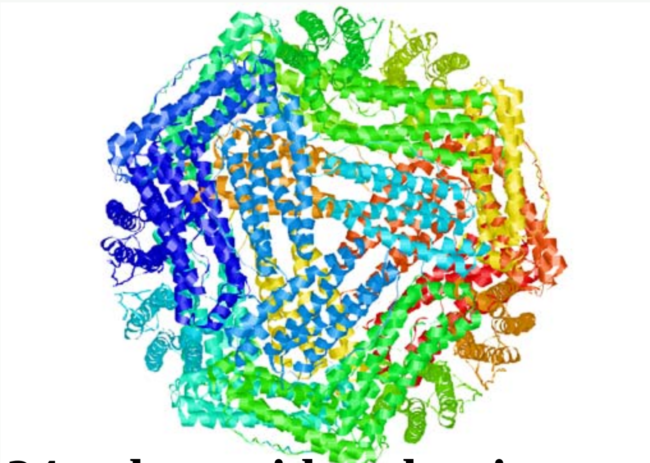
Acknowledgments

Hazel-Ann Hosein - Temple Univ.
Mark Allen - Montana State Univ.
Dan Ensign - Montana State Univ.

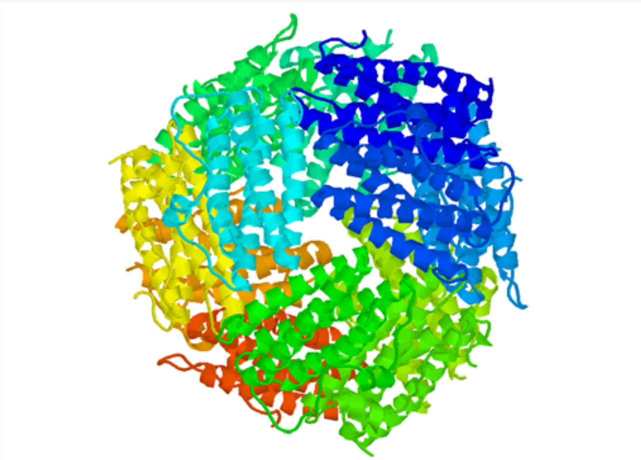
Horse Spleen Ferritin (HSF)



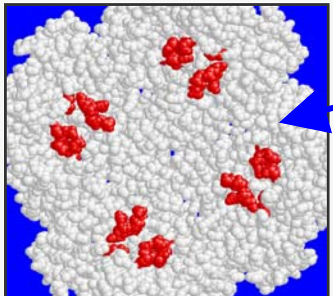
- **<u>24</u> polypeptide subunits**
- **Spherical protein cage (<u>120 Å dia.</u>)**
- **Cavity (<u>80 Å dia.</u>)**
- **Accommodates up to <u>4500 Fe atoms</u>**

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>**



Glutamate (COO^-)

12 distinct sites
10 Glu residues (at each site)

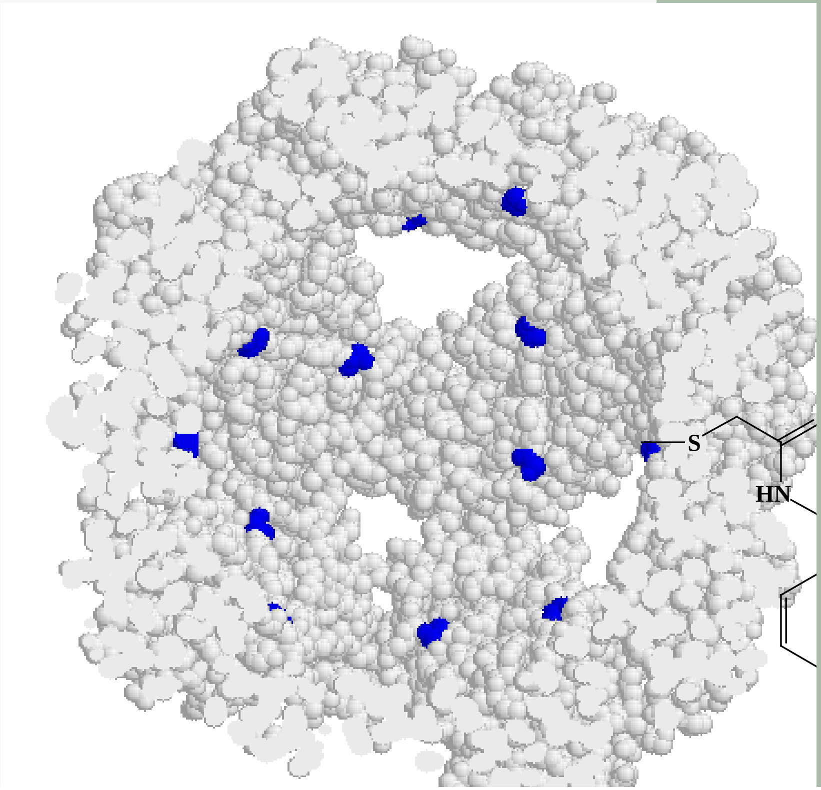
Small Heat Shock Protein Cage

From the thermophile

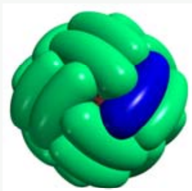
Cloned Mutant used

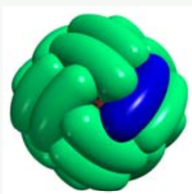
24 subunit cage with large 3nm

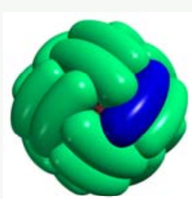
Diameter pores

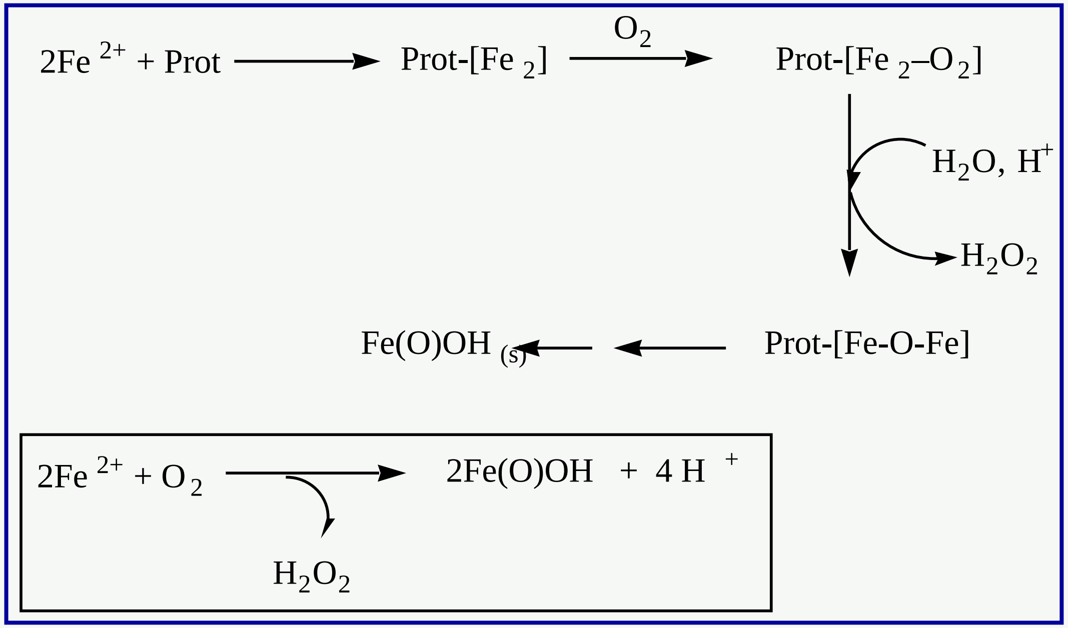


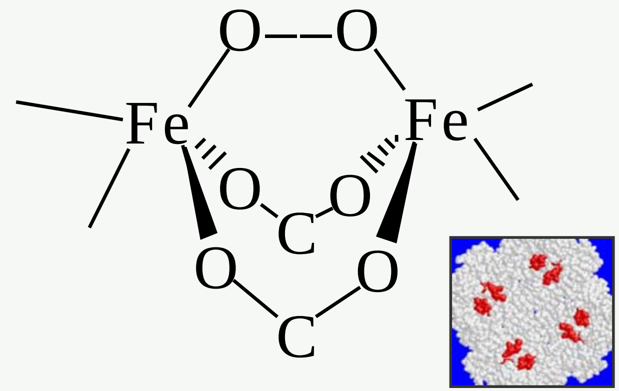
Goals of EPA - Funded Research


Ferritin as a (photo)catalyst


Ferritin as a Template for The growth of oxide and Metallic nanoparticles


Functionalization of the ferritin shell





Ferroxidase catalysed

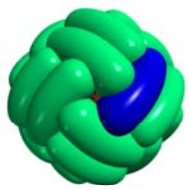
(important early on in the mineralization process)

Hwang, J., Krebs, C., Huynh, B. H., Edmondson, D. E., Theil, E. C. & Penner-Hahn, J. E. (2000). *Science* **287**, 122

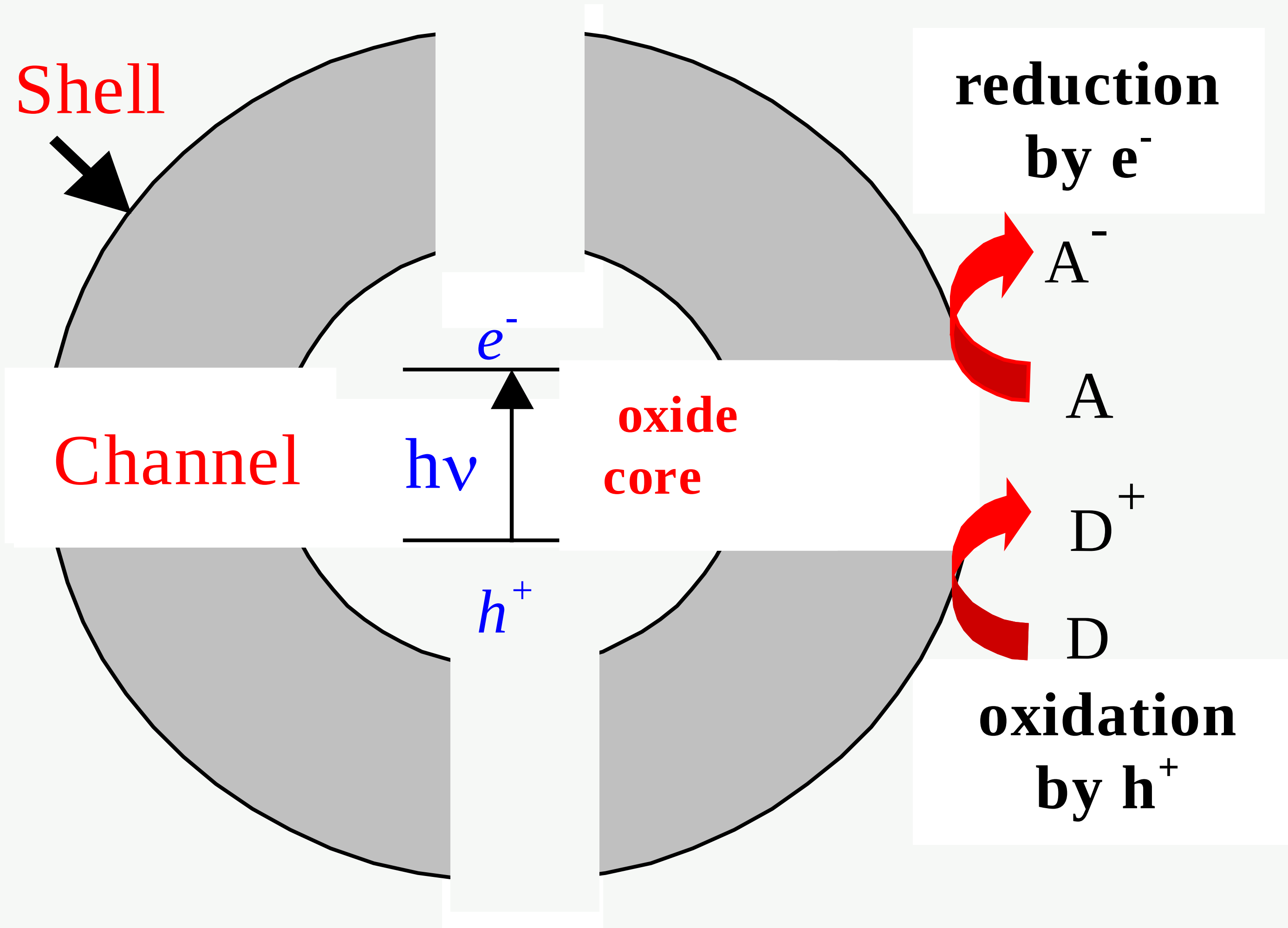
$$4Fe^{2+} + O_2 \longrightarrow 4Fe(O)OH + 2H_2O + 8H^+$$

Mineral catalysed

(autocatalytic Fe(II) oxidation
and hydrolysis



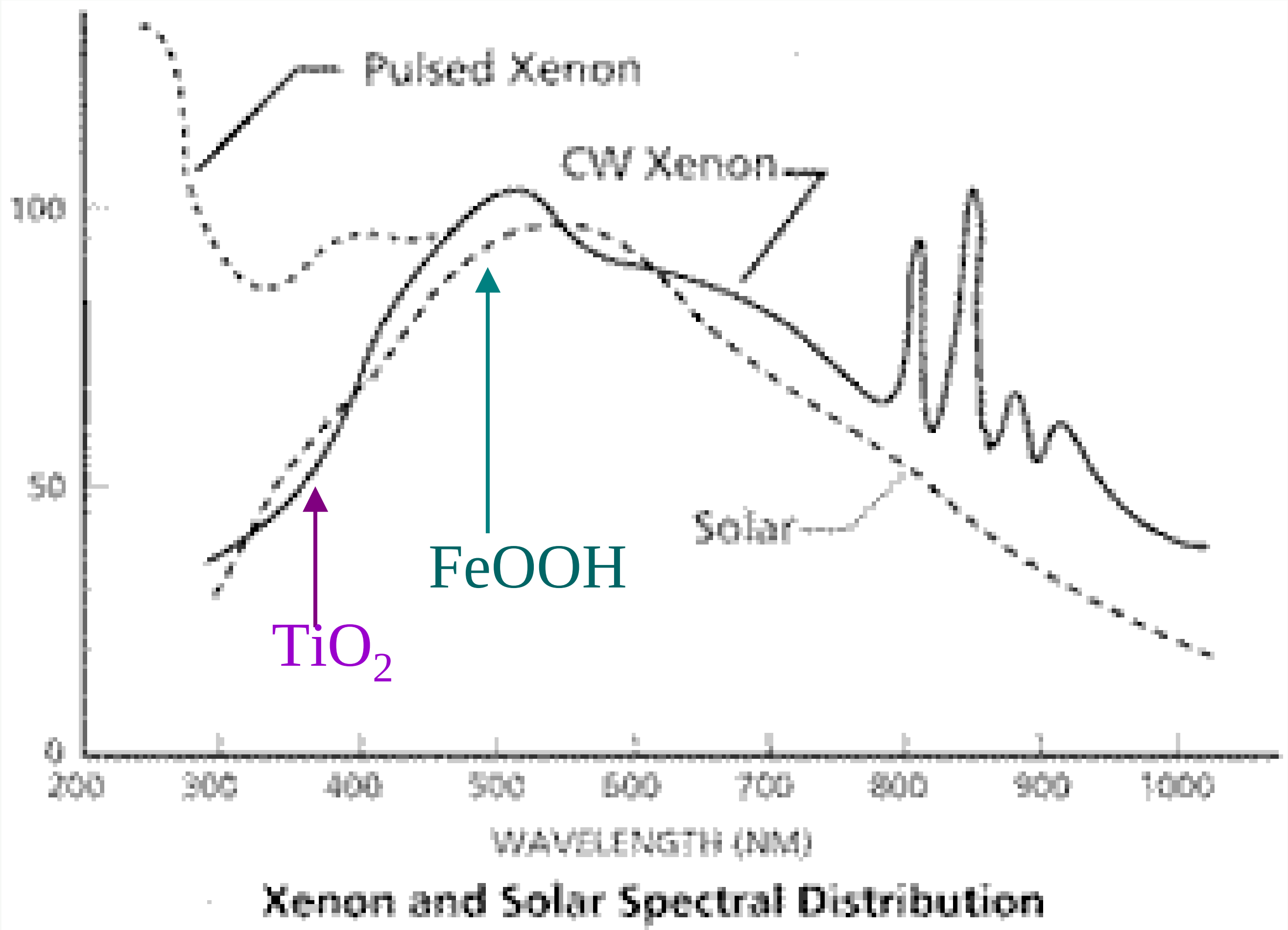
Ferritin as a Photocatalyst



TiO_2 vs. Ferric oxides

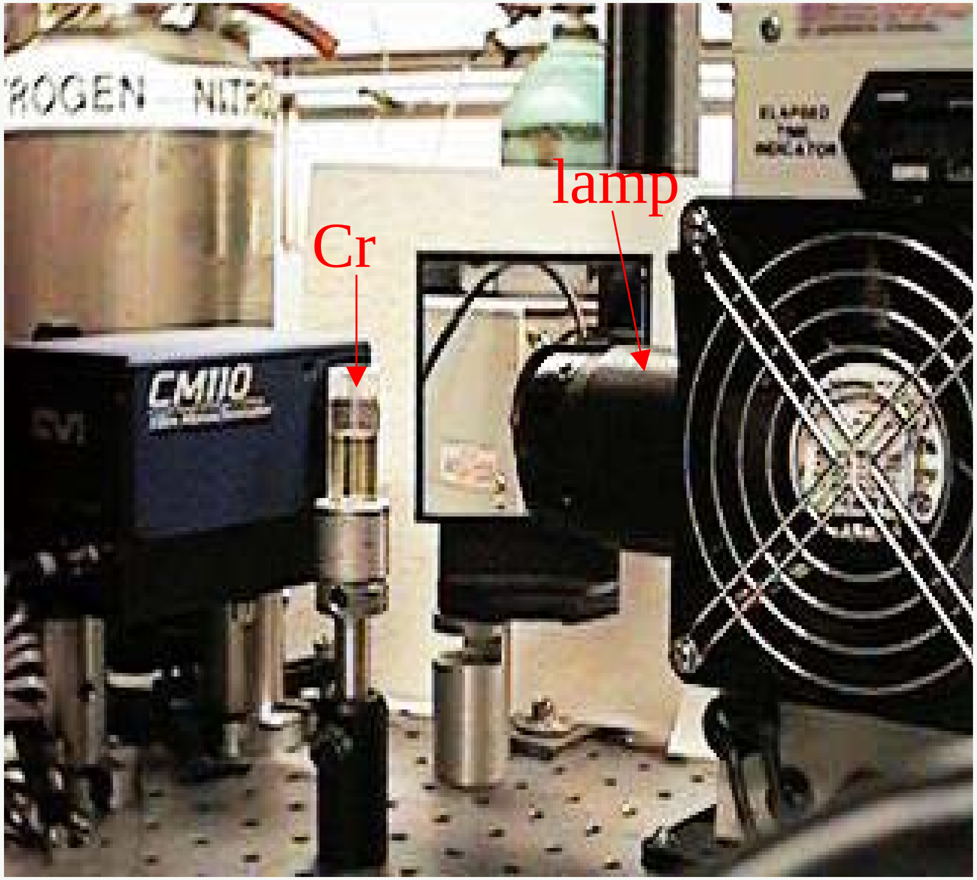
- TiO_2
  - Bandgap=3.2 eV
  - uv lamps needed to maximize photochemistry
  - very high stability
- Ferric oxides (e.g., FeOOH
  - Bandgap=2.2 - 2.8eV
  - <u>can utilize a significant part of solar spectrum</u>
  - low stability - photocorrosion

Xenon vs. Solar spectrum



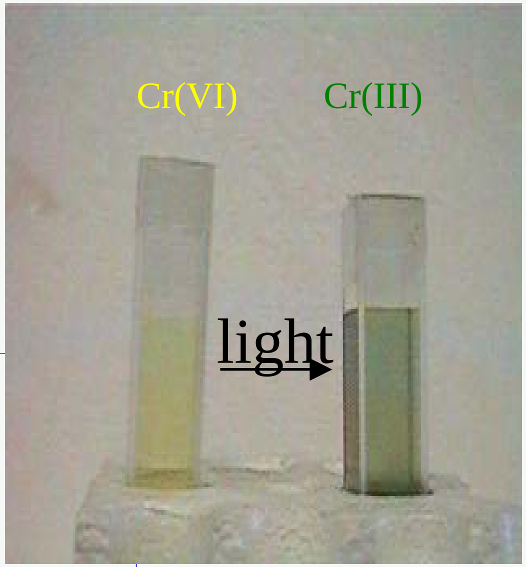
Xenon: The Full Spectrum vs. Deuterium Plus Tungsten *by Robert A. Capobianco,*
http://opto.perkinelmer.com/library/papers/tp9.asp

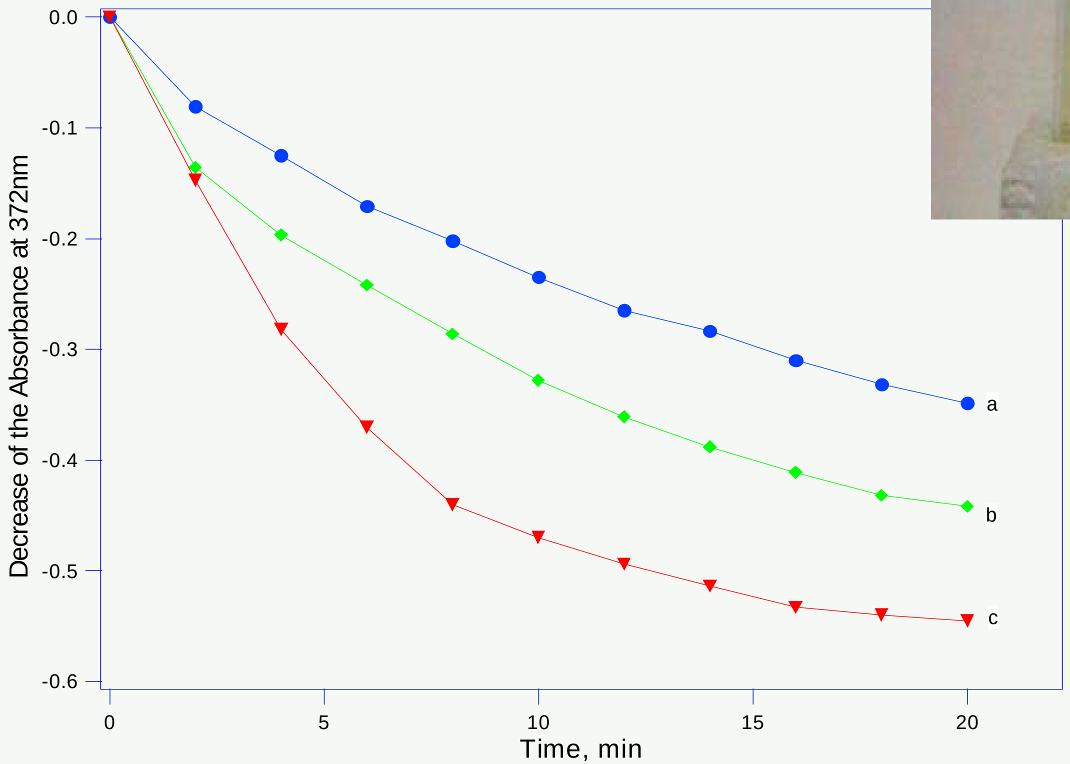
Experimental



Can we tailor a nanoparticle system having a bandgap
In the visible with high stability for application in
environmental remediation?

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+}\ 7H_2O$$





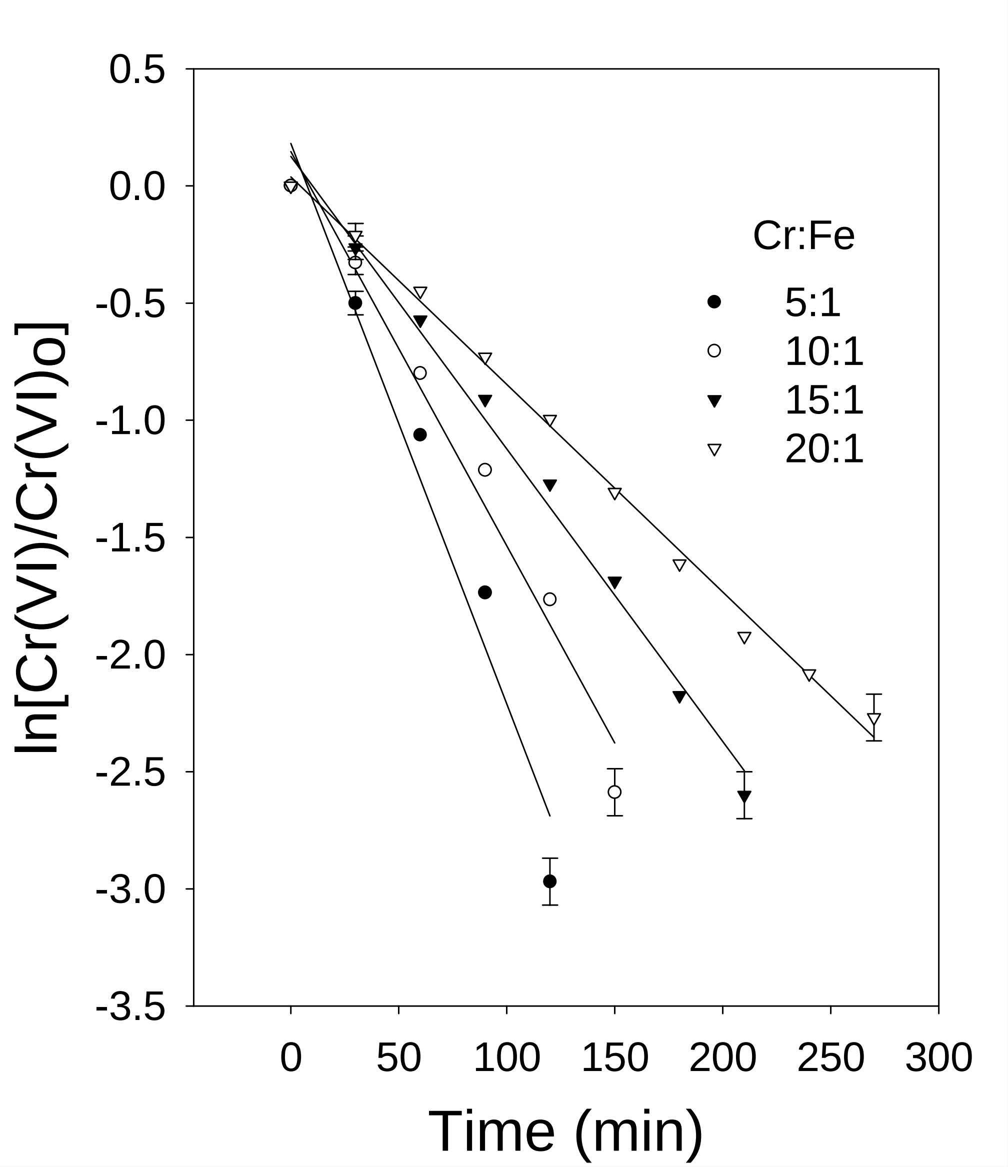
The decrease of the absorbance at 372 nm. The final concentration of the species: $Na_2Cr_2O_7$: $5x10^{-6}$M; tartrate: $3x10^{-2}$M; Ferritins: 0.25mg/ml; Buffer: 0.1M. Tris, pH8.5. a, CoOOH-Fn; b, MnOOH-Fn; c, FeOOH-Fn.

Stability of catalytic ferritin particles

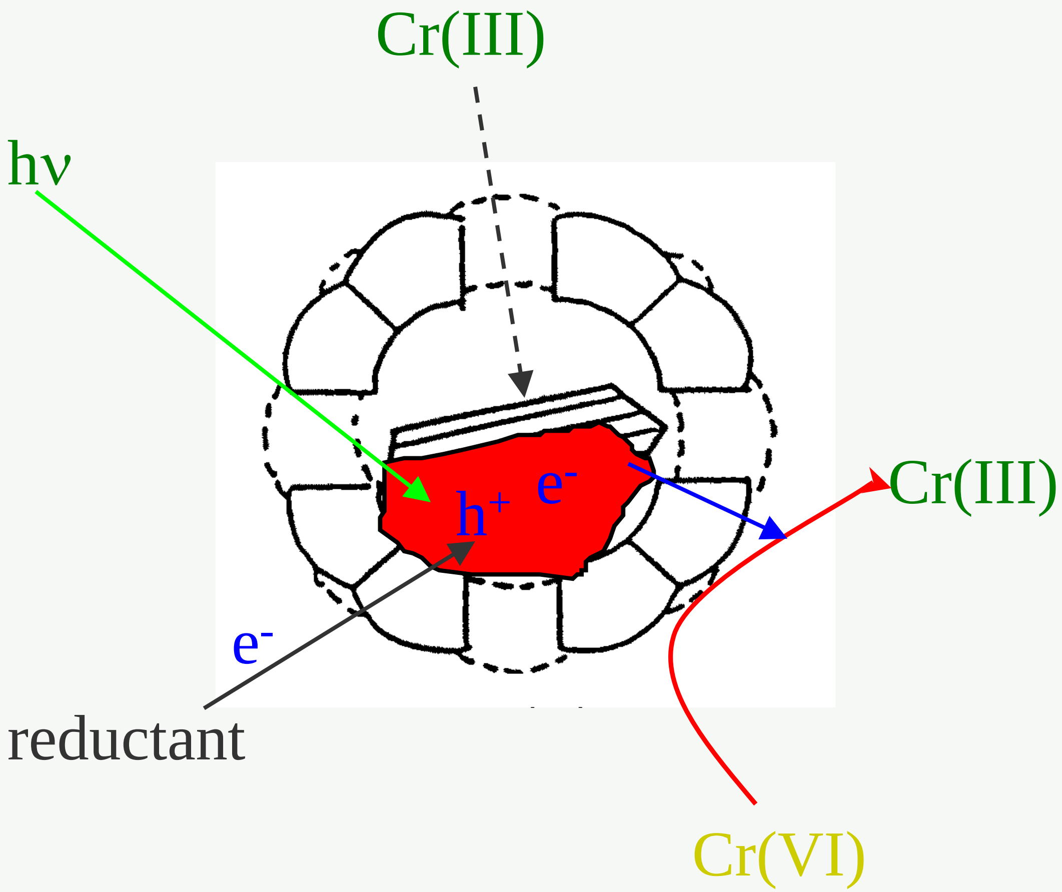
$Cr_2O_7^{2-}$ (4.0x10^{-4} M)

Reductant – tartrate (3.2x10^{-3} M)

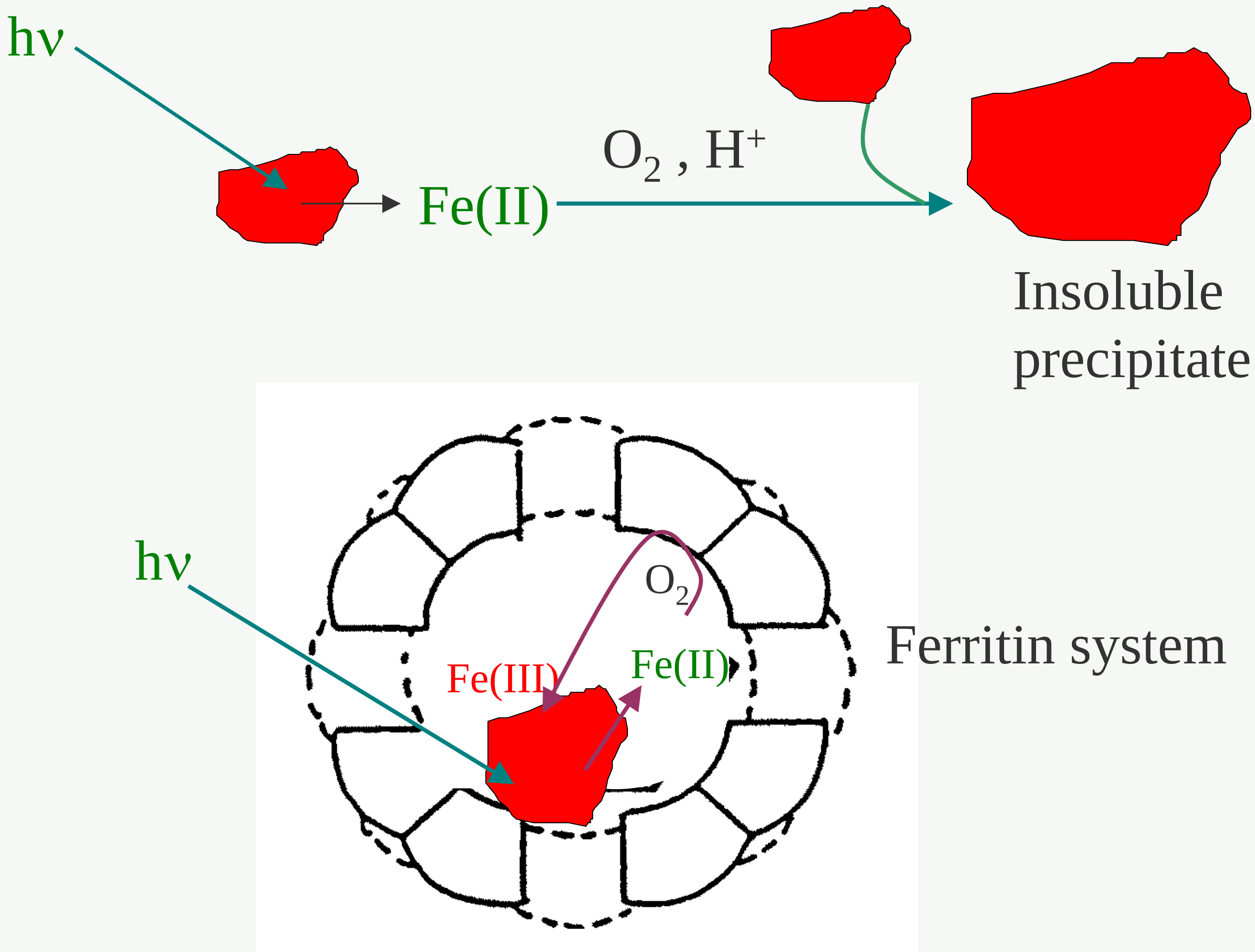
pH 7.5, tris buffer

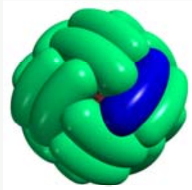


Ferritin catalyzed reduction

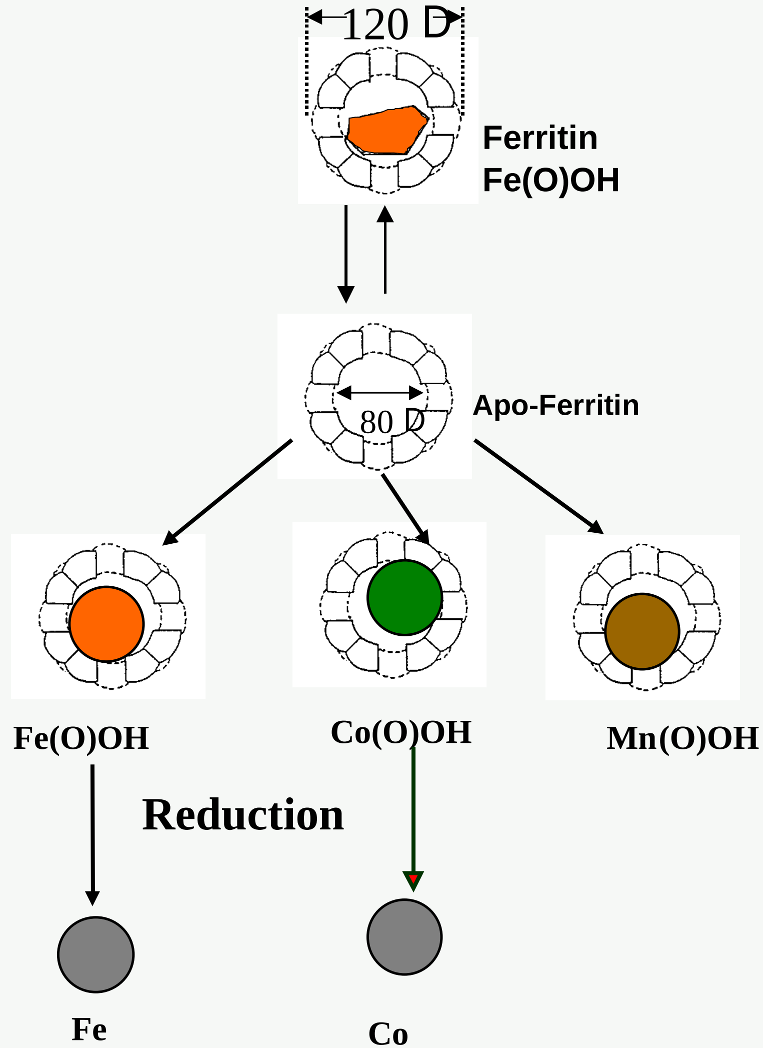


Photocorrosion and aggregation of protein free FeOOH



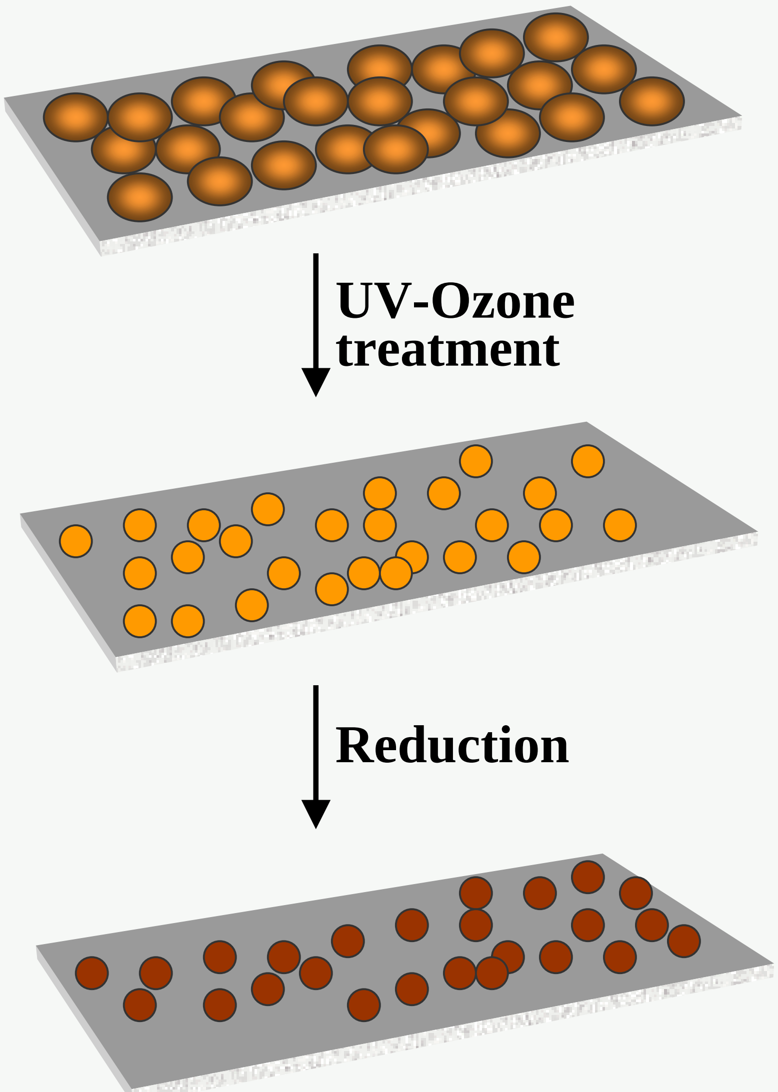


Ferritin as a Template for The growth of oxide and Metallic nanoparticles

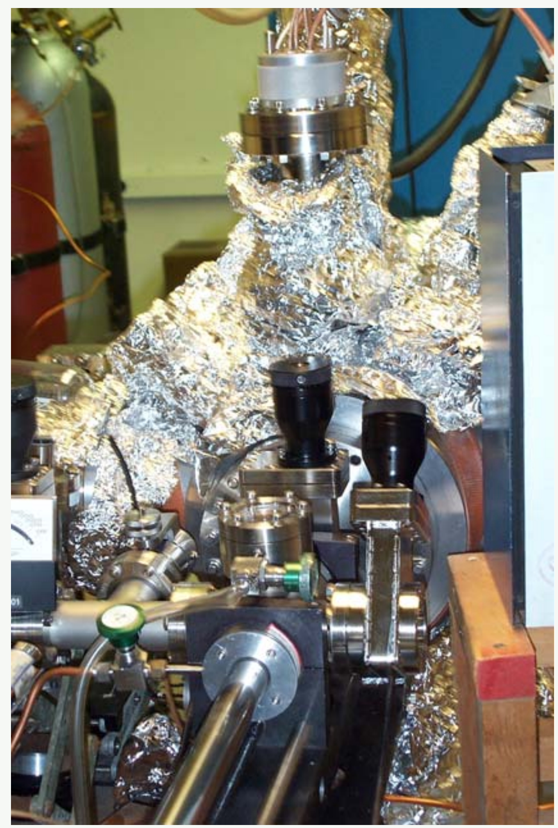


Loading of metal controls ultimate nanoparticle size

General synthetic scheme for Fe metal production

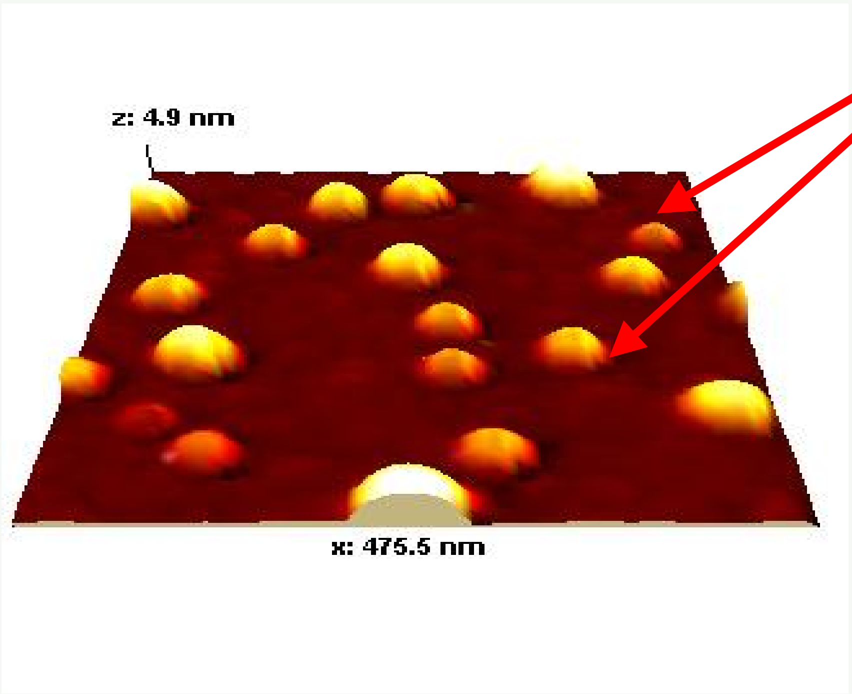


The PSD-UV uses high intensity UV radiation to vaporize and remove the protein portion



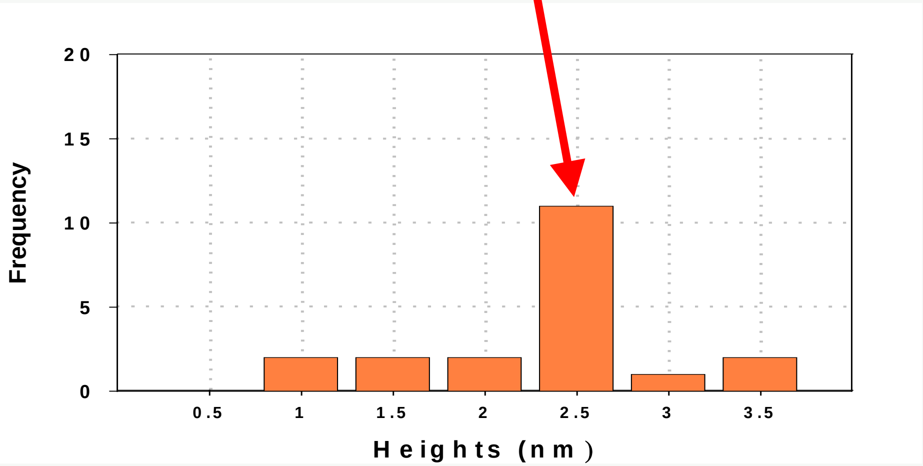
The high pressure cell coupled to UHV chamber where reduction of metal oxide to metal occurs and accompanying transfer apparatus.

Acoustic AC mode AFM Characterization of FeOOH nanoparticles



ISOLATED NANOPARTICLES

Average Height ONLY 2.5 nm!

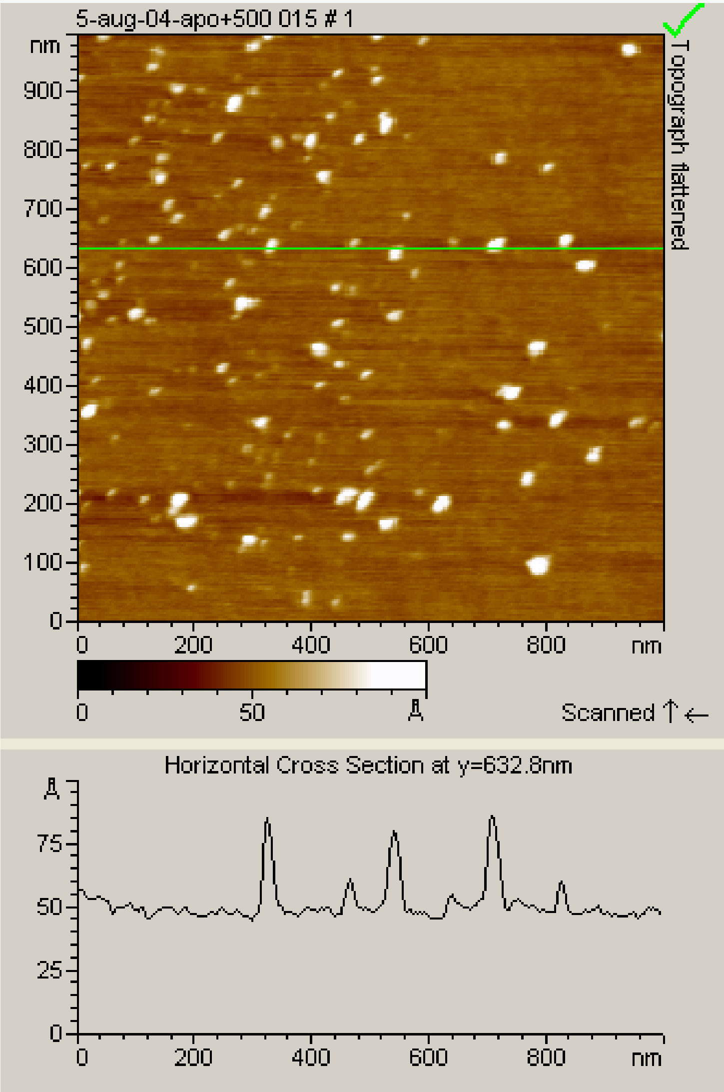


FeOOH nanoparticles prepared by UV-ozone treatment of 100 Fe loaded ferritin for 60 mins at 100°C under oxygen (<5psi)

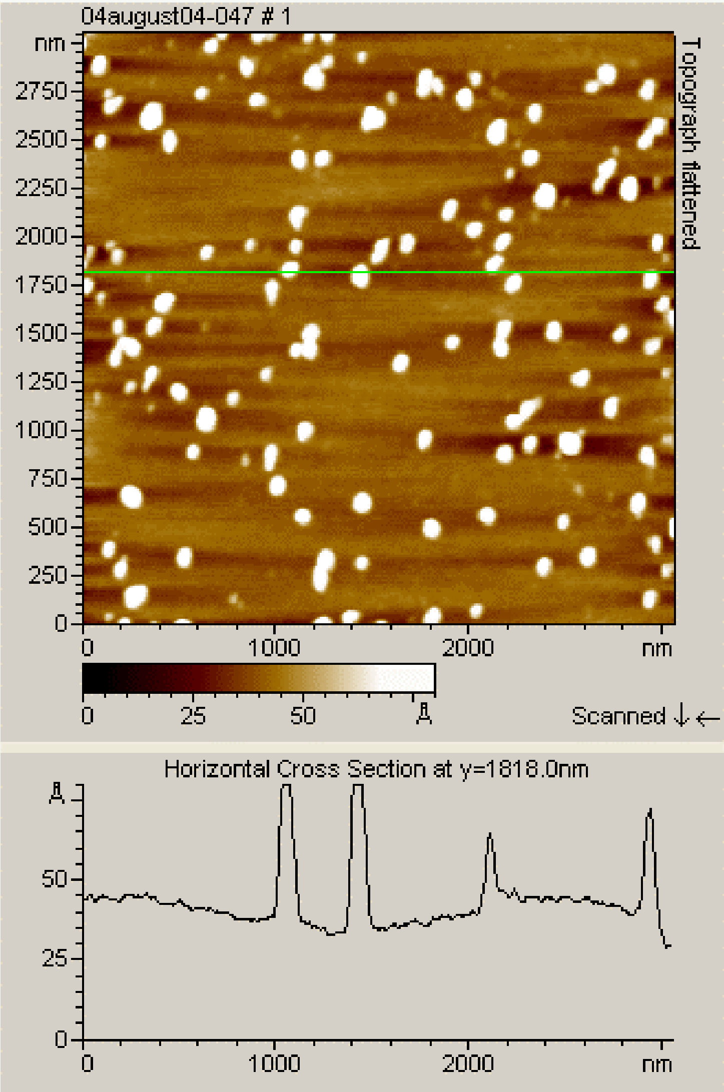
Relative height distribution of particles

AC Mode AFM Images: Apoferritin + FeFn mixtures

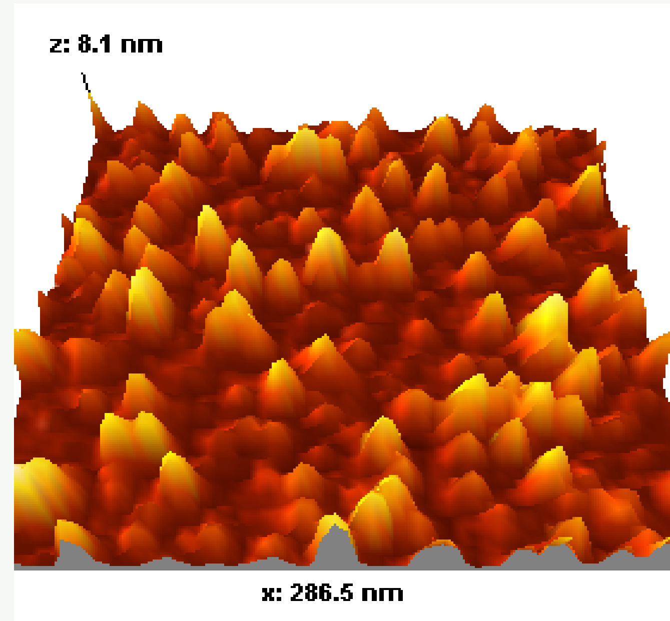
Apoferritin + 500 FeFn mixture



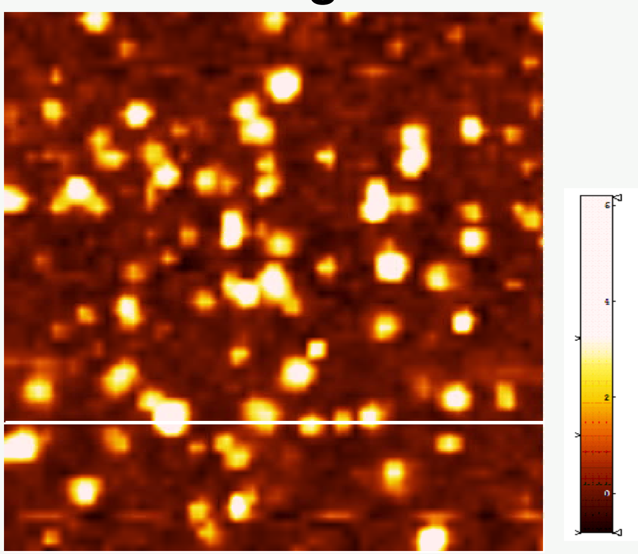
Apoferritin + 2000 FeFn mixture



TM-AFM Characterization of Iron nanoparticles

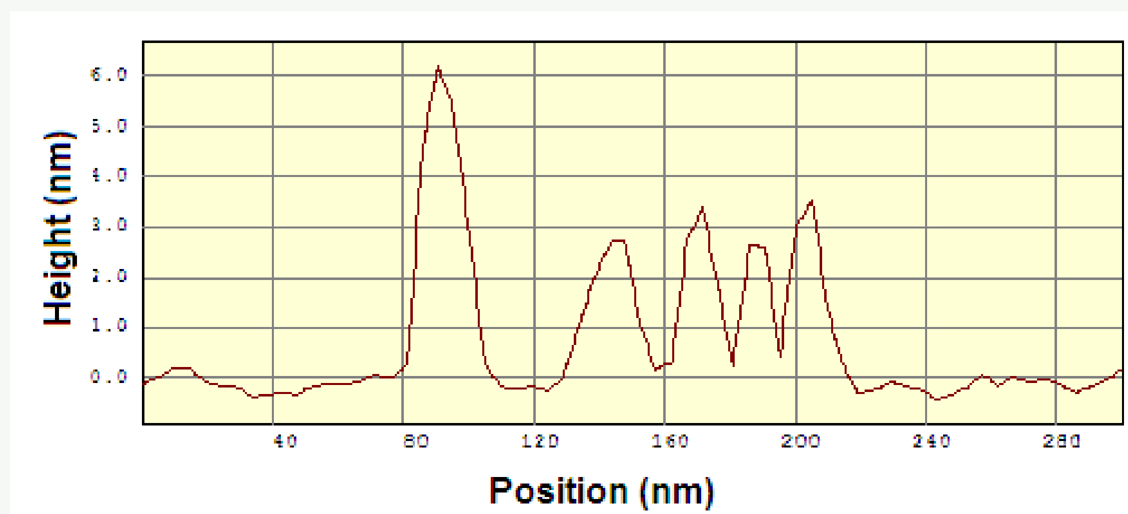


- ISOLATED NANOPARTICLES
- **Peak-to-valley height differences for the large features in the cross-section are in the 4-6 nm range.**
- **Full range of height values = 8.0 nm**
- **RMS roughness = 1.47 nm**



Height mode; 286 x 286 nm

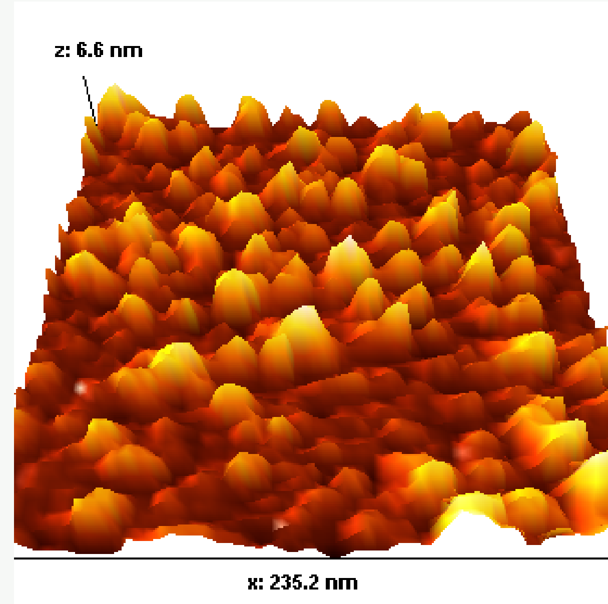
Fe nanoparticles prepared by heating FeOOH nanoparticles in H_2.



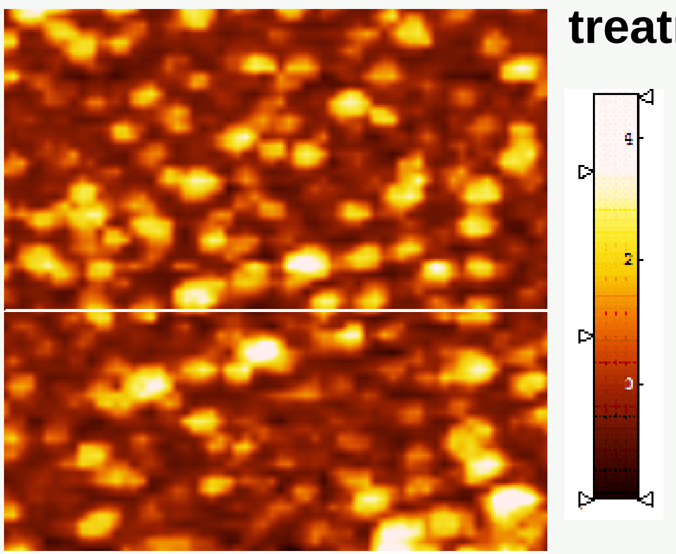
TM-AFM Characterization of Co_3O_4 nanoparticles

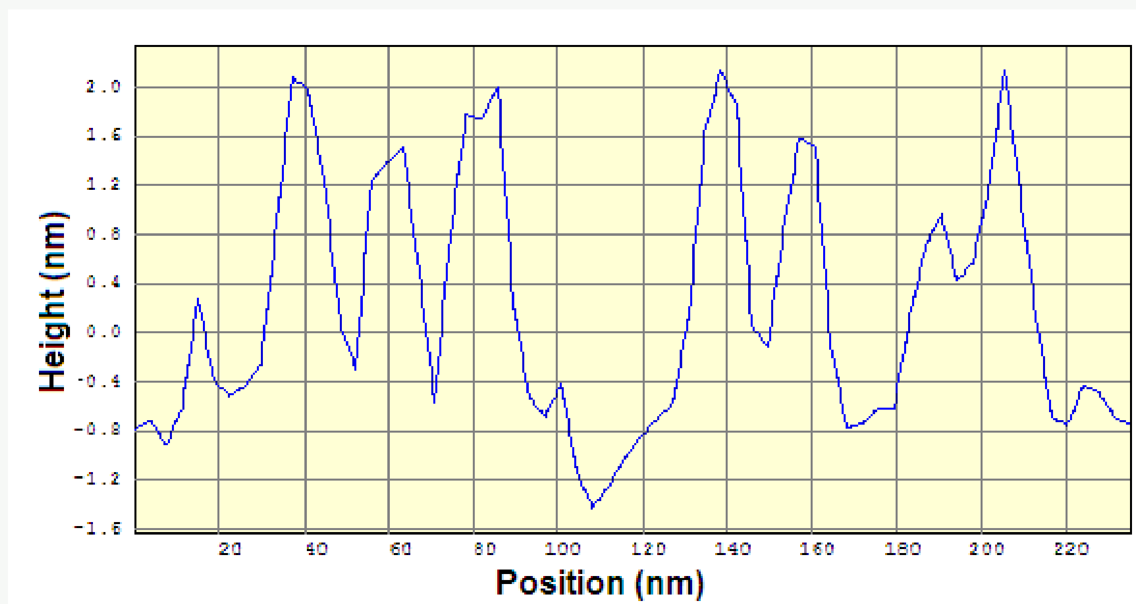
Narrow Distribution of particle sizes: 2.5-3.0 nm

RMS roughness = 1.07 nm

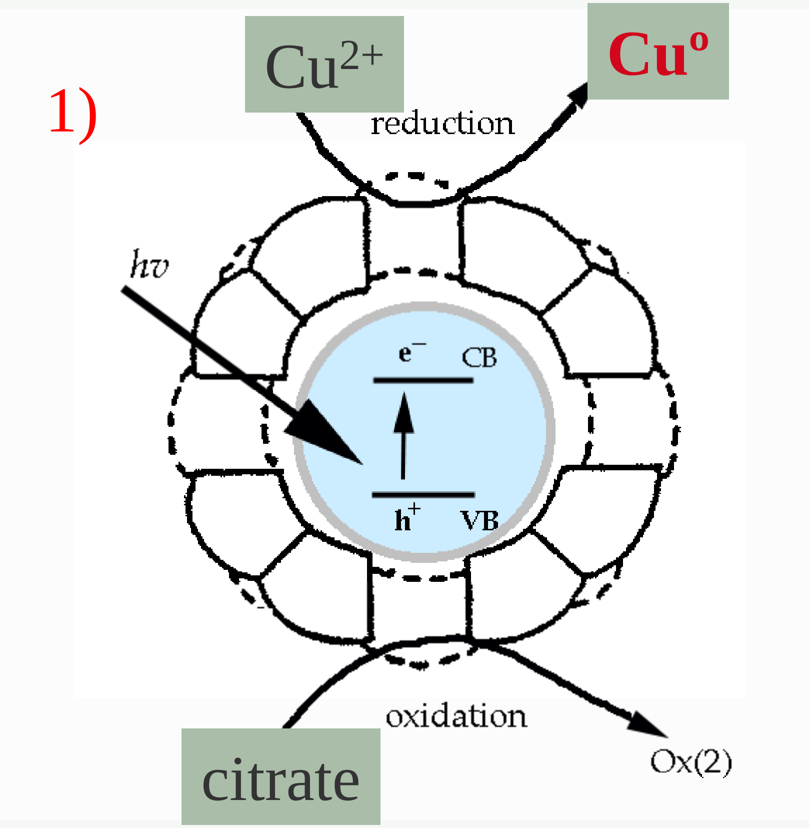


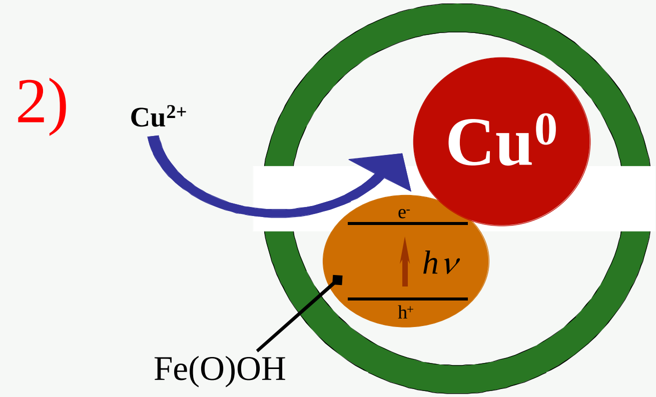
Co_3O_4 nanoparticles on SiO_2 prepared by UV-ozone treatment of LFLP for 1 hr at 100^{o}C under oxygen (<5psi)



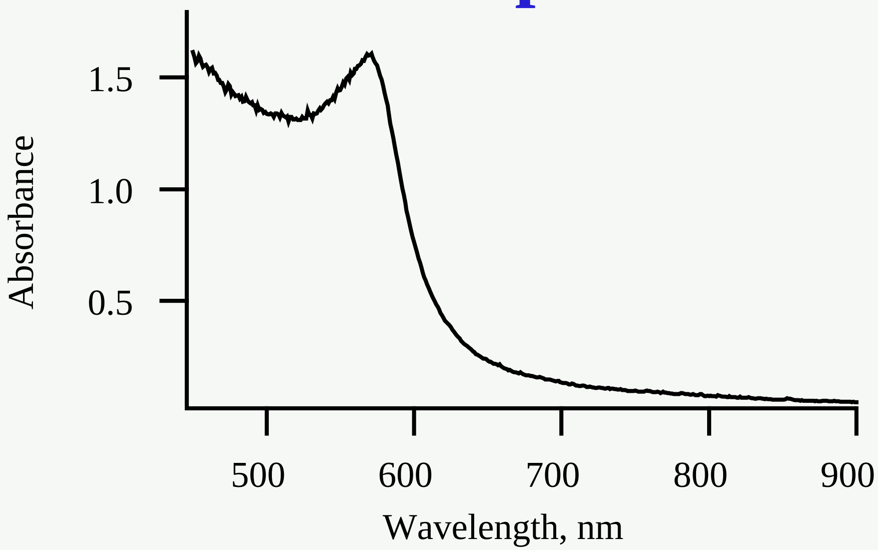


Height mode; 235 x 235 nm

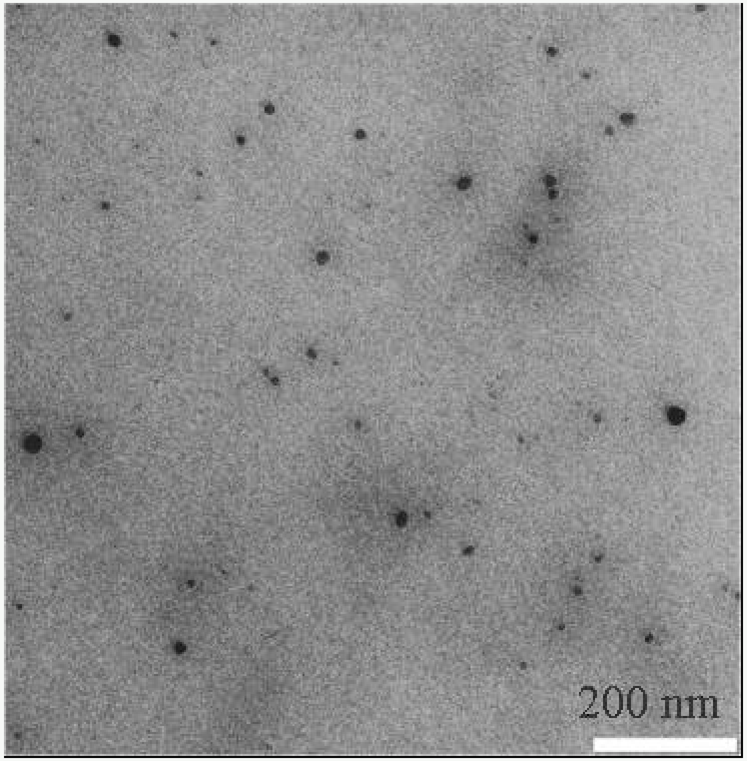




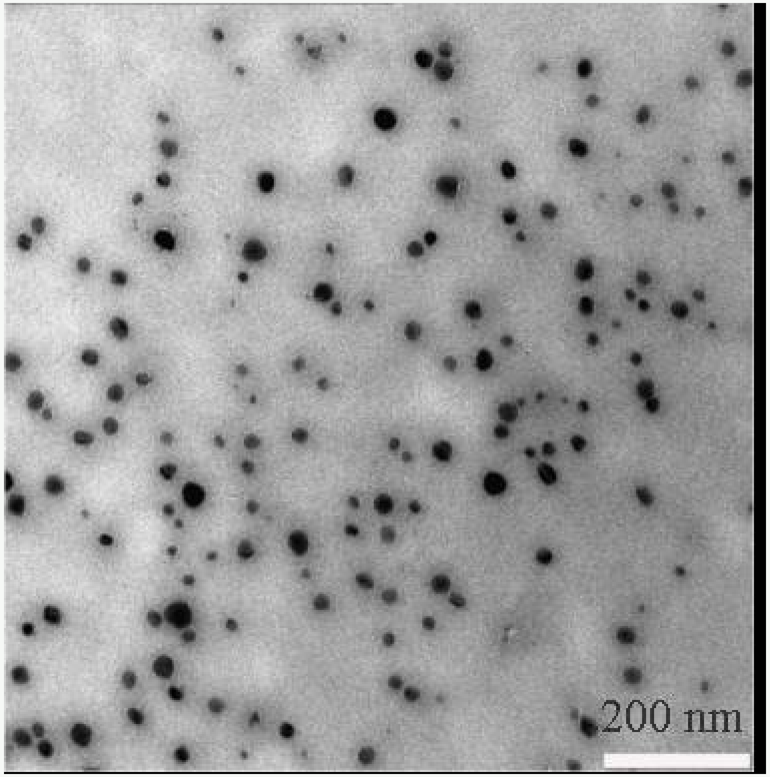
Photocatalytic Synthesis of Cu nanoparticles



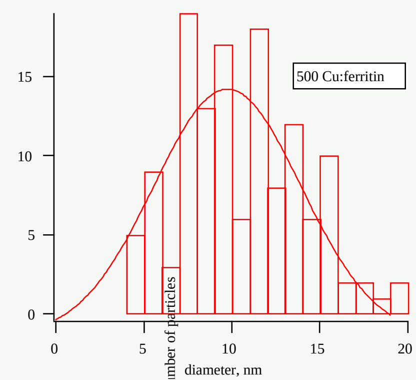
D. Ensign, M. Young, T. Douglas *Inorg. Chem* (2004)



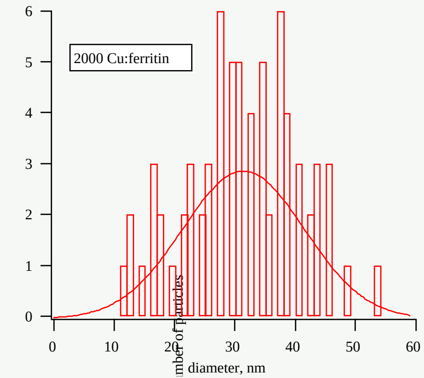
500 Cu/Fn



2000 Cu/Fn



9.7 ± 3 nm



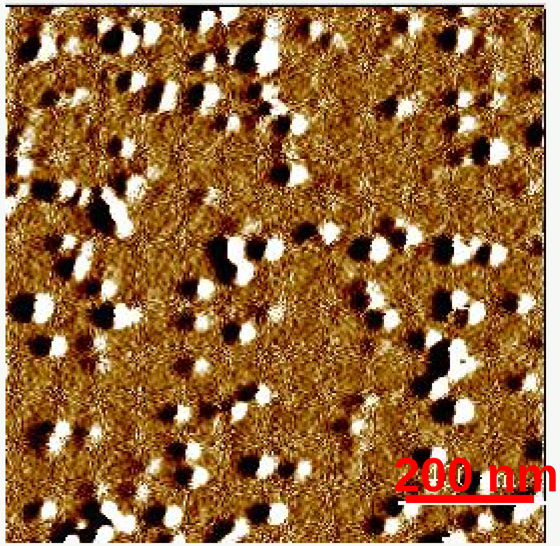
31 ± 8 nm

QuickTime™ and a
GIF decompressor
are needed to see this picture.

Atomic Force Microscopy

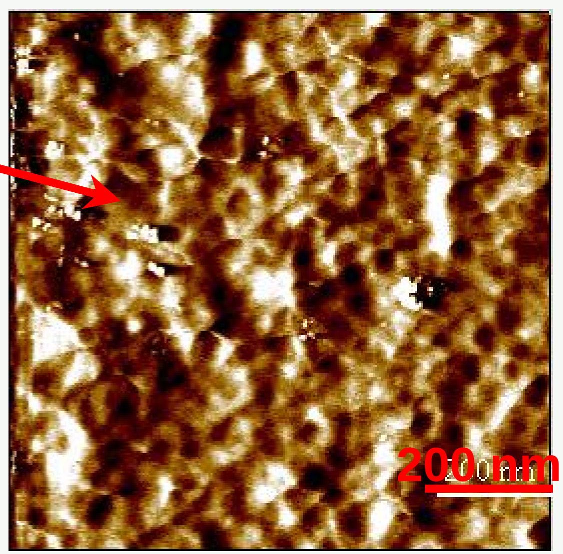
Sequestration of Aqueous As(III) by FeOOH nanoparticles

FeOOH Nanoparticles Supported on Si wafer

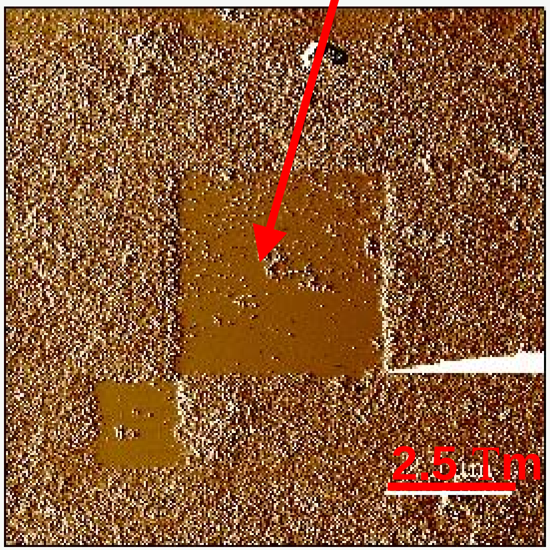


As(III) addition

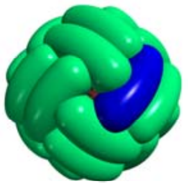
Insoluble precipitate



No nanoparticles
No precipitate



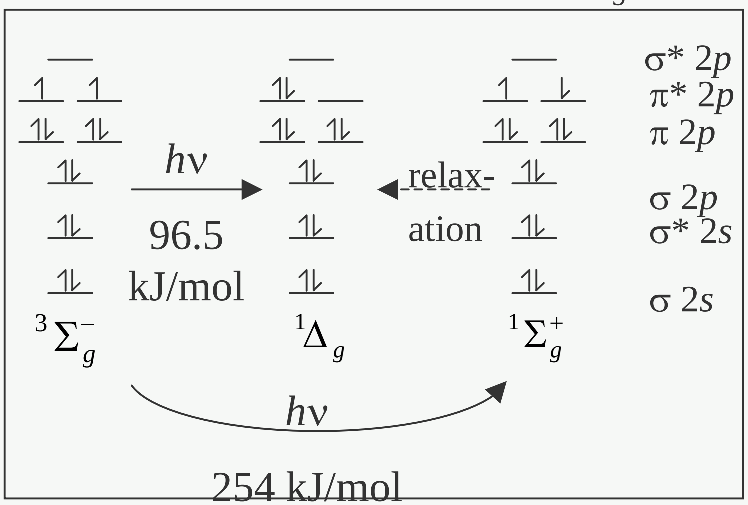
Wide scan

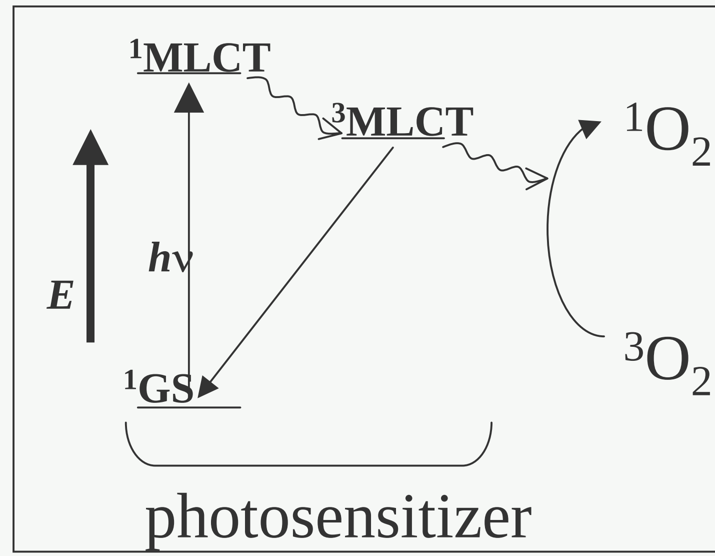


Functionalization of the ferritin

Visible Light-Induced Production of Singlet Oxygen

Ground triplet state $^3\Sigma_g$
First excited singlet state $^1\Delta_g$
Second excited singlet state $^1\Sigma_g$

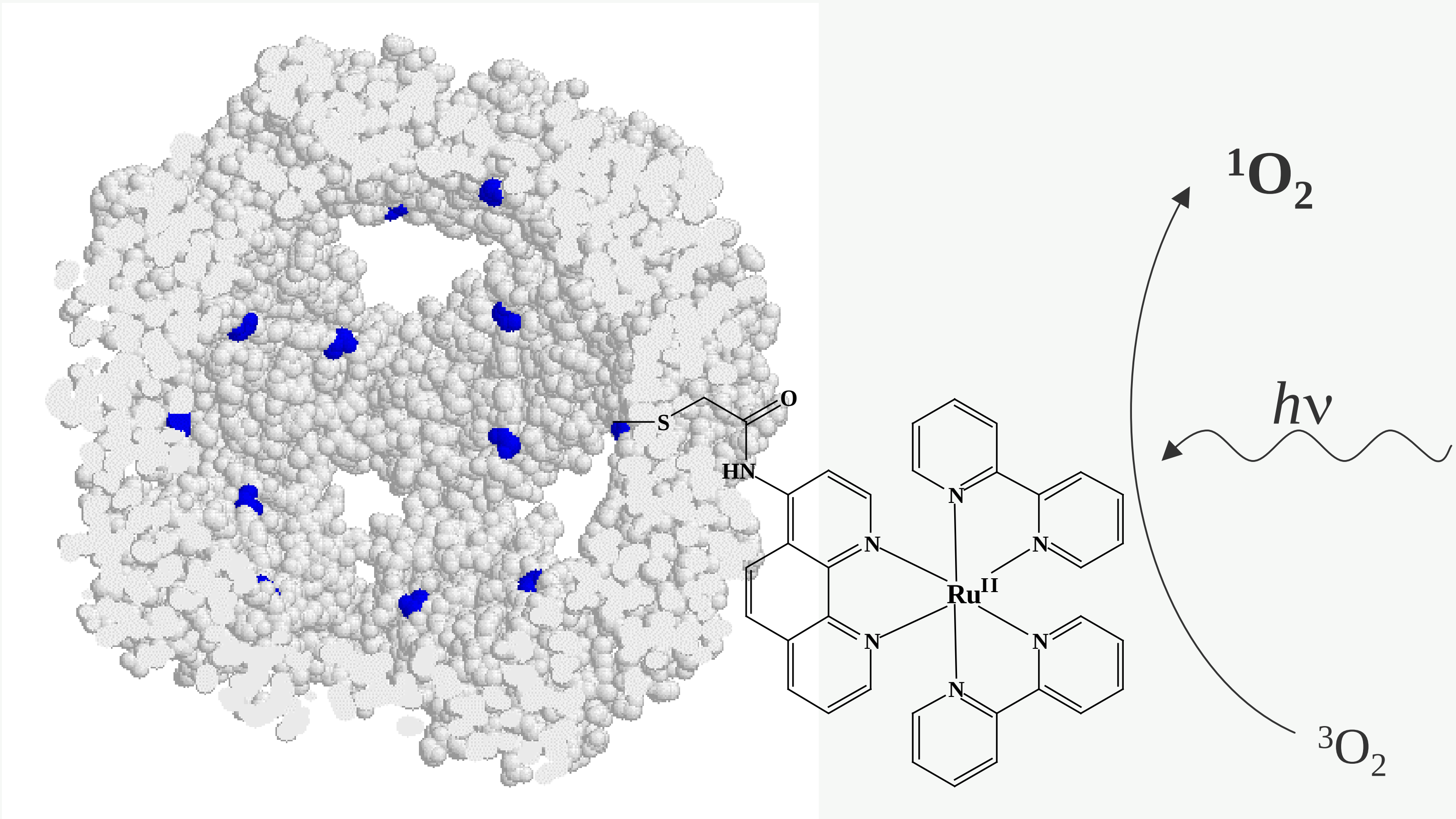




Why?

- Delivery of photosensitizers to cells
- Illumination produces $^1O_2$
- $^1O_2$ is about 1 V more oxidizing than $^3O_2$

Visible Light-Induced Production of Singlet Oxygen



$Ru(phen)(bpy)_2^{2+}$ covalently linked to HSP G41C = photosensitizer

Excitation of the Ru(II)-HSP complex increases the rate
Of singlet oxygen production by a factor of 50 compared
To the Ru(II) complex alone!

SUMMARY

- Ferritin facilitates
  Reduction of Cr(VI) to Cr(III)

- Ferritin as a Template for the growth of oxide and metallic nanoparticles
  Fe and Co oxides / Fe, Co, and Cu metals

- *Functionalization of the ferritin-like protein shell to form photosensitizer*

Acknowledgments

Hazel-Ann Hosein - Temple Univ.
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