Bioinspired Composite Nanomaterials for Photocatalytic Hydrogen Production

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Center for Bioinspired Nanomaterials
Pleotint LLC

DOE Project ID#: PDP36

Overview

Timeline

- Start - Oct. 2005
- End - Sept. 2009

- Barriers addressed
  - Enzyme stability/durability
  - Oxygen sensitivity
  - Light harvesting

Budget

- Total project funding

  $1,491,250

  - DOE $1,193,000
  - Contractor $298,250

Partners

- Montana State University
- Pleotint LLC

Overall Project Structure

- Montana State University
  - Peters
    - Hydrogenase purification
    - Immobilization / stabilization
    - Electron transfer
    - Polymer matrix
    - Devices
  - Douglas
    - Ferritin mineralization
    - Semiconductors
    - e^- transfer mediators
    - Oxygen scavenging
    - Devices
  - Young
    - Expression of ferritin
    - Purification of ferritin
    - Devices
- Pleotint LLC
  - Byker
    - Synthesis of poly-viologens
    - Incorporation of components in matrix
    - Devices

Objectives

1. Optimize the hydrogenase stability and electron transfer

2. Optimize the semiconductor nano-particle photocatalysis, oxygen scavenging, and electron transfer properties of protein nano-cages

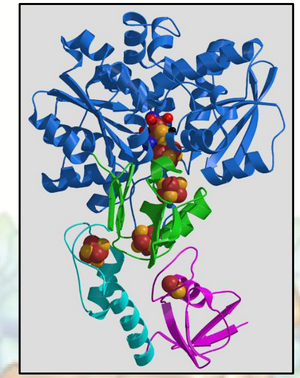
3. Gel/Matrix immobilization and composite formulation of nano-materials and hydrogenase

4. Device fabrication for H_2 production

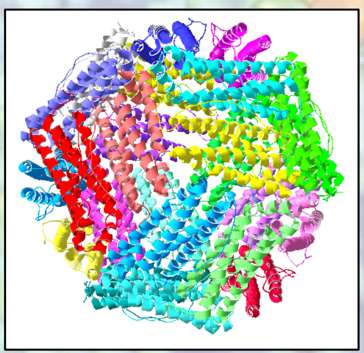
Approaches

Couple Different Catalyst Systems for Light Driven Hydrogen Generation

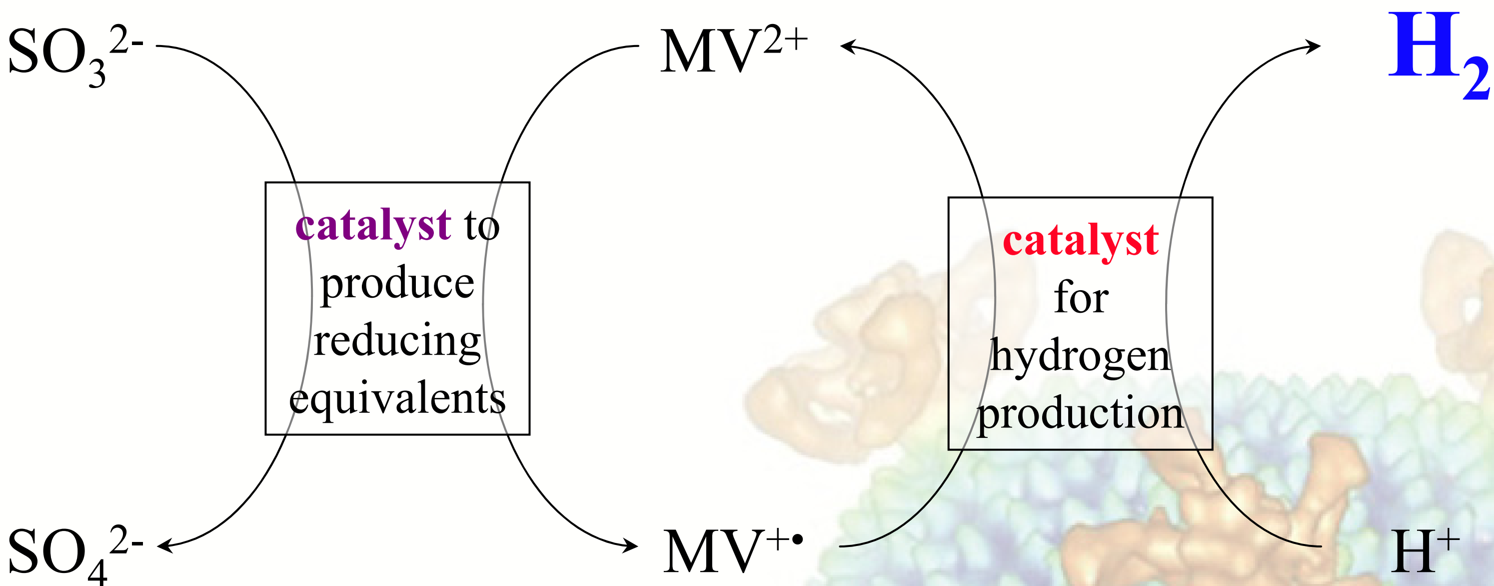
Biological catalysts (Hydrogenases)
- stabilization/immobilization
- electron transfer



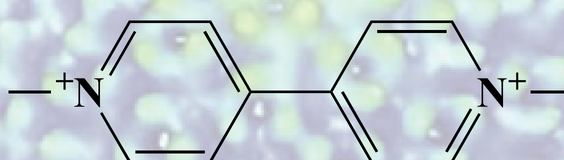
Nanoparticle Photocatalysts
- light harvesting
- O_2 scavenging



Hydrogen from Water: Coupled Reactions



GOAL: use a **catalyst** to reduce an electron mediator (methyl viologen, MV^{2+}) with SO_3^{2-} as electron donor. Another **catalyst** then uses $MV^{+\bullet}$ to produce H_2.

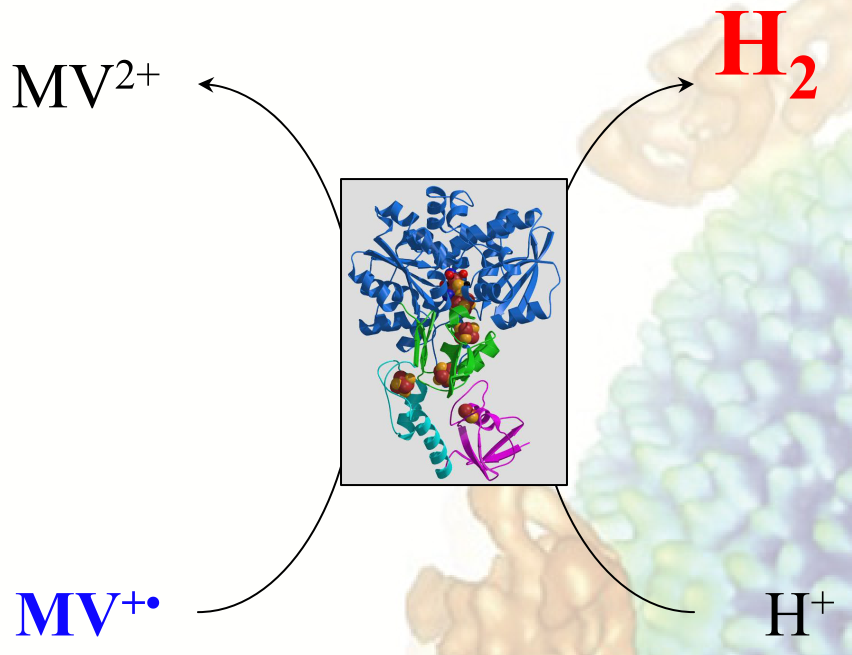


methyl viologen, MV^{2+}

Enzymatic H_2 Formation

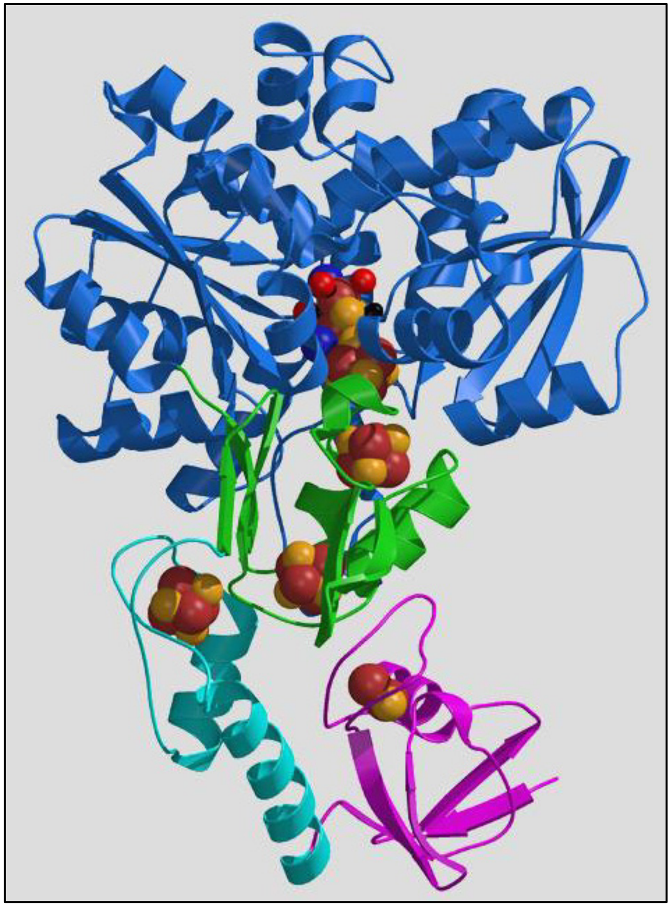
Hydrogenase enzymes

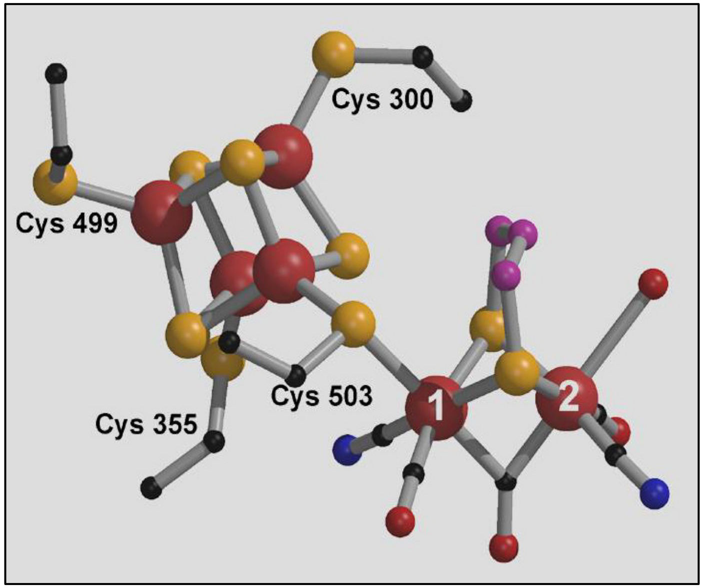
- Highly active catalysts (9,000 H_2/enz/sec)
- Utilize MV^+ as reducing equivalents



Biological Hydrogen Production

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$





Hydrogenase

Peters et al, *Science* (1998)

Hydrogenase Immobilization

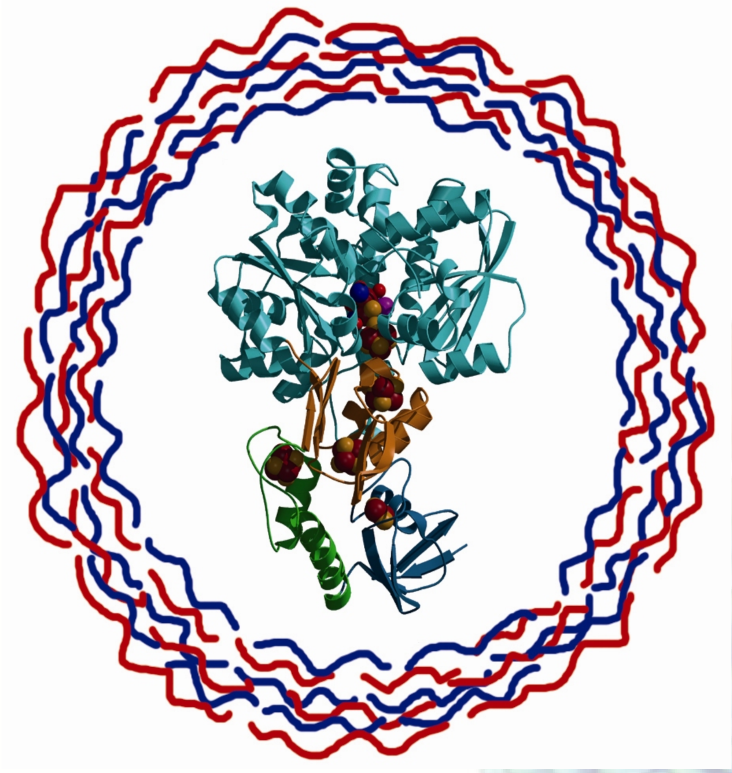
Advantages

- Solid Phase – free flow of substrates and products
- Durability – Proteolysis resistance, temperature stability, pH stability, increased shelf life

Approaches

- Silica oxide Sol-Gel (Tim Elgren)
- Poly(viologen) electro-active polymers (Pleotint LLC)

Encapsulation/Immobilization



Incorporation of hydrogenase enzymes into materials to facilitate electron transfer reactions, provide oxygen protection, and enhance stability

Procedure for making Sol-Gel hydrogenase materials

Prepared Sol-Gel mixture

↓

1.57 ml Tetramethyl-ortho-silicate (TMOS)
350 μL H_2O
11 μL 0.04 M HCl

Sonicated solution for 30 min in cold bath (with degassing)

↓

Making Sol-Gel hydrogenase materials

↓

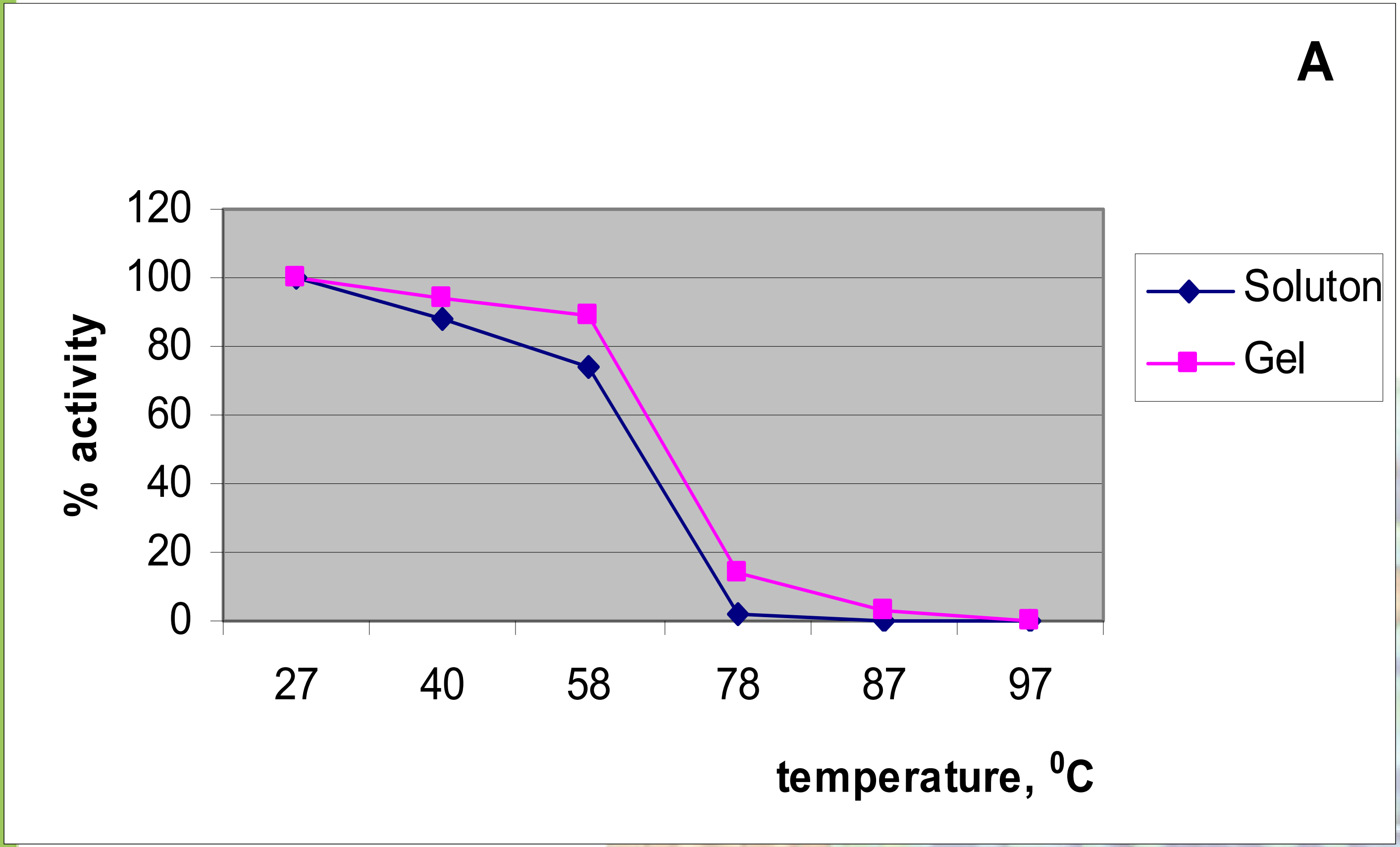
100 μL hydrogenase (100 μg of protein in 50 mM Tris- HCl pH 8,0) :
100 μL Sol-Gel mixture

Polymerization of Sol- Gel material for 3-5 min

Recovery of hydrogenase activity encapsulated in Sol-Gel

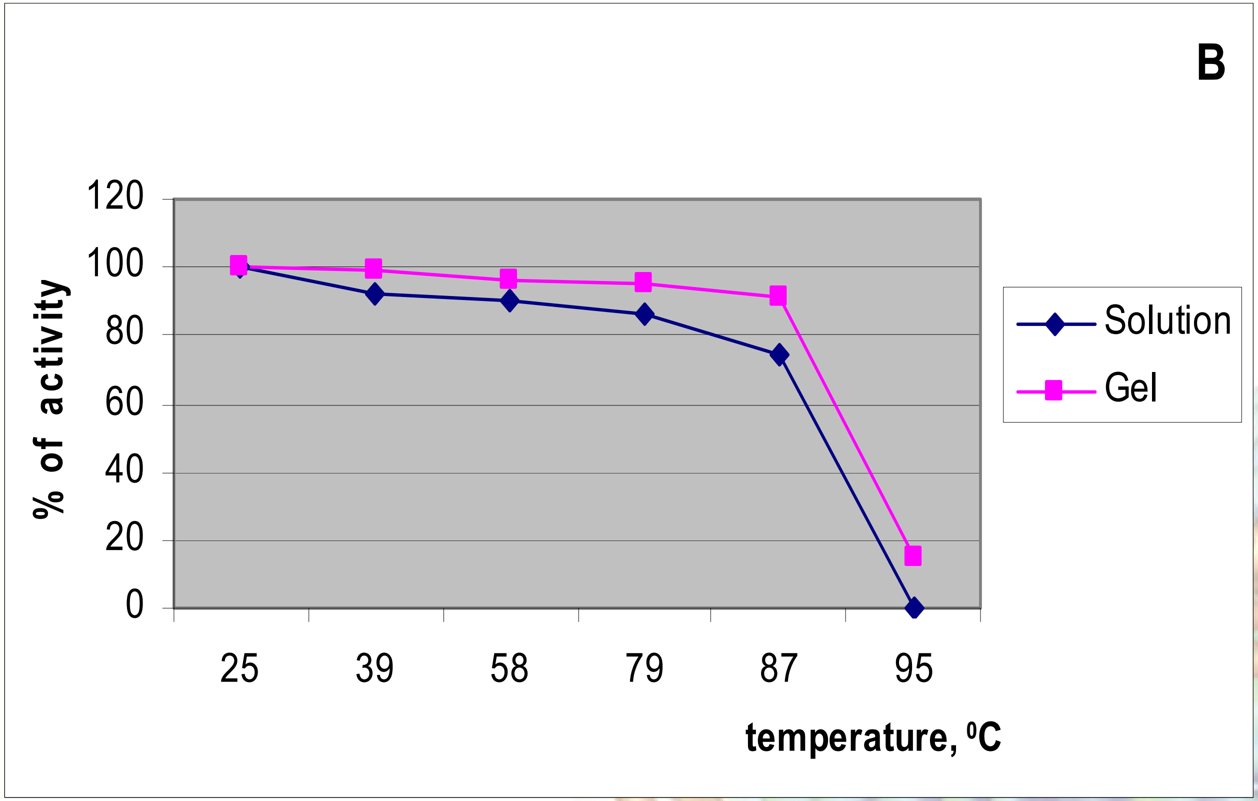
Hydrogenase		% activity	
		Solution	Sol-Gel
1.	*Clostridium pasterianum*	100	63.8±15.8
2.	*Lamprobacter modestogalophilus*	100	67.5±8.8
3.	*Thiocapsa roseopersicina*	100	70.1±2.5

Thermal stability of hydrogenases encapsulated in Sol-Gel materials



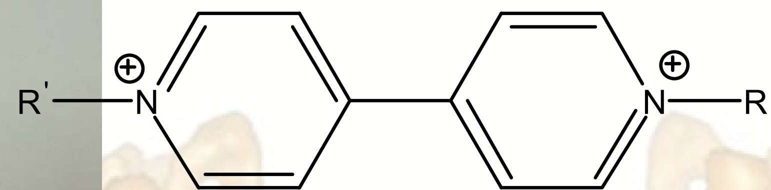
A - *Clostridium pasterianum hydrogenase*

Thermal stability of hydrogenases encapsulated in Sol-Gel materials



B - *Lamprobacter modestogalophilus hydrogenase*

Association of Redox Mediator with Gel Matrix



R, R' = CH_3

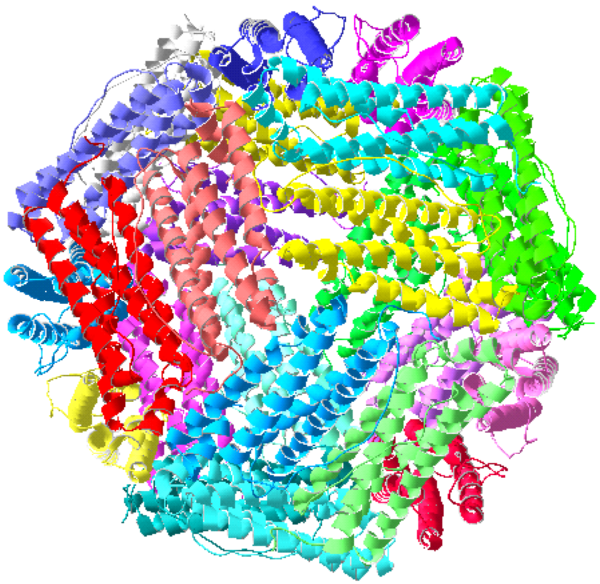
$CH_2CH_2CH_2\text{-}SO_3^-$

$CH_2CH_2CO_2^-$

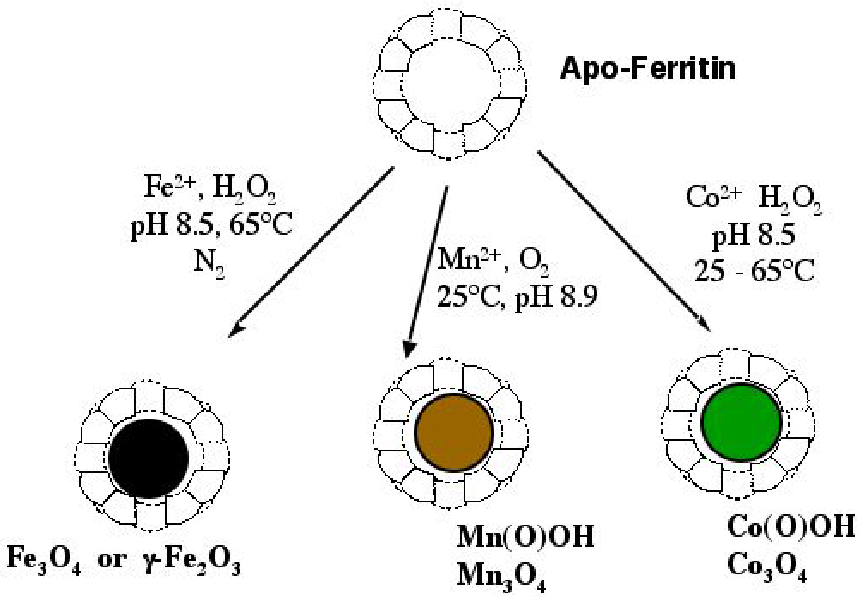
$CH_2CH_2NH_3^+$

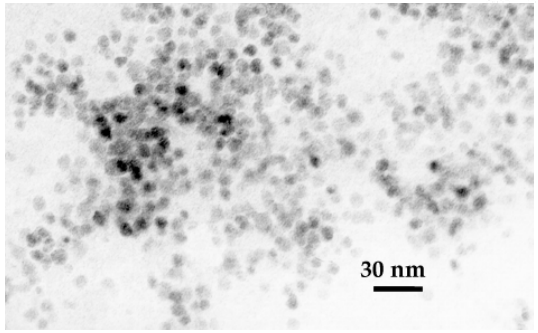
$(CH_2)_n\text{-}PO_3H_2$

Nanoparticle synthesis within the Ferritin Protein Cage



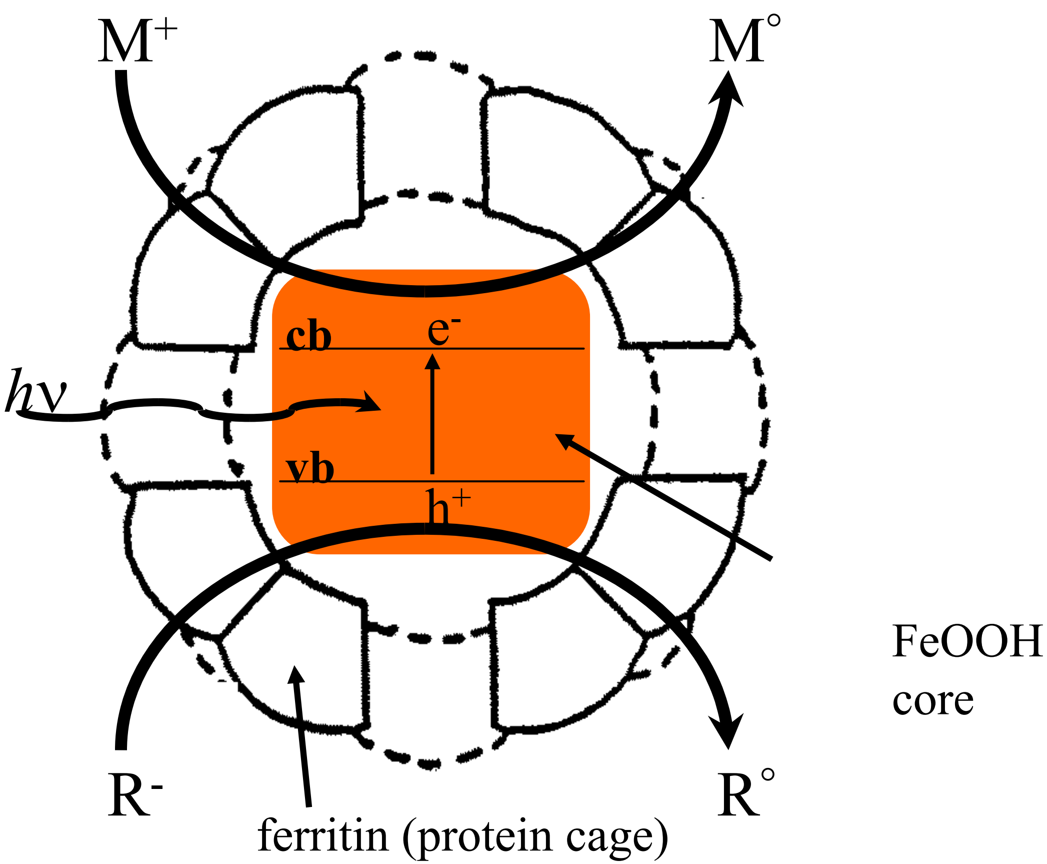
Ferritin protein cage
24 subunits - 12 nm diam





TEM of metal oxide nanoparticles

Protein Cage Photocatalysts



Light absorption by ferritin core (FeOOH) causes charge separation oxidizes R^- and reduces M^+ catalytically.

Examples:

- Reduction of CrO_4^{2-} to Cr(III) using tartrate as electron donor (Kim et al., *Chem. Mater.*, 2002).
- Reduction of Cu(II) to Cu(0) particles using citrate as electron donor (Ensign et al., *Inor. Chem.*, 2004).

Current: use this photocatalytic system (or an analogue) to reduce MV^{2+} to $MV^{+\bullet}$ using sulfite as electron donor.

Thermodynamics and Kinetics

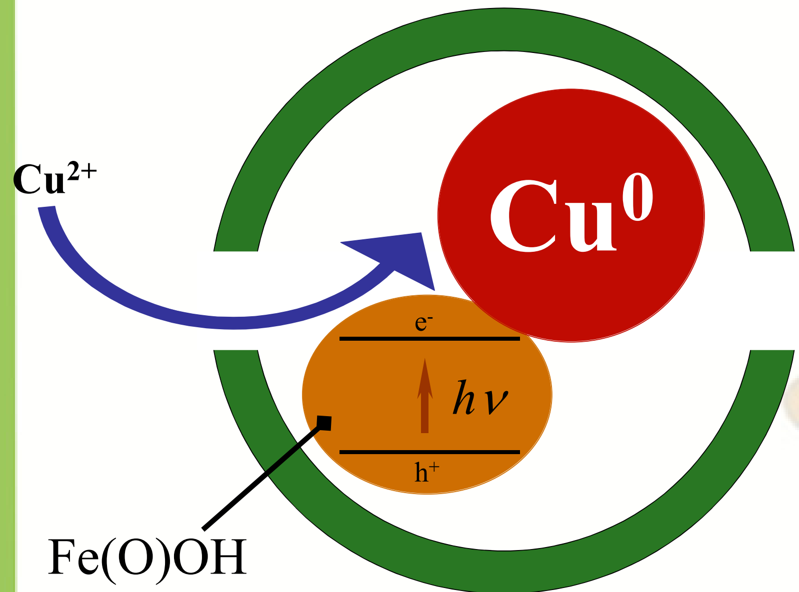
- electron transfer from sulfite to methyl viologen is thermodynamically favorable, ΔG = -48 kJ/mol
- reduction of methyl viologen by sulfite does not normally occur (kinetic barrier)

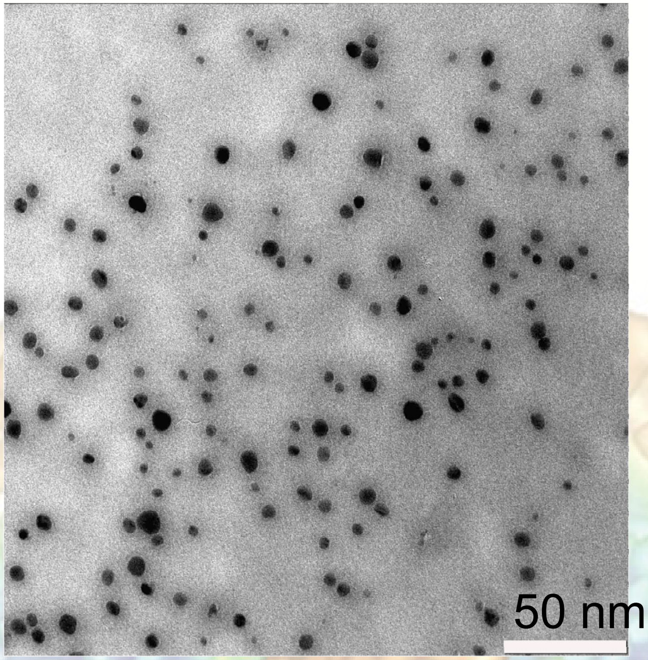
<u>viologen reduction</u>

$$\frac{1}{2}SO_3^{2-} + MV^{2+} \not\rightarrow \frac{1}{2}SO_4^{2-} + MV^{+\bullet}$$

A catalyst is required for viologen reduction by sulfite

Photoreduction of Cu(II)





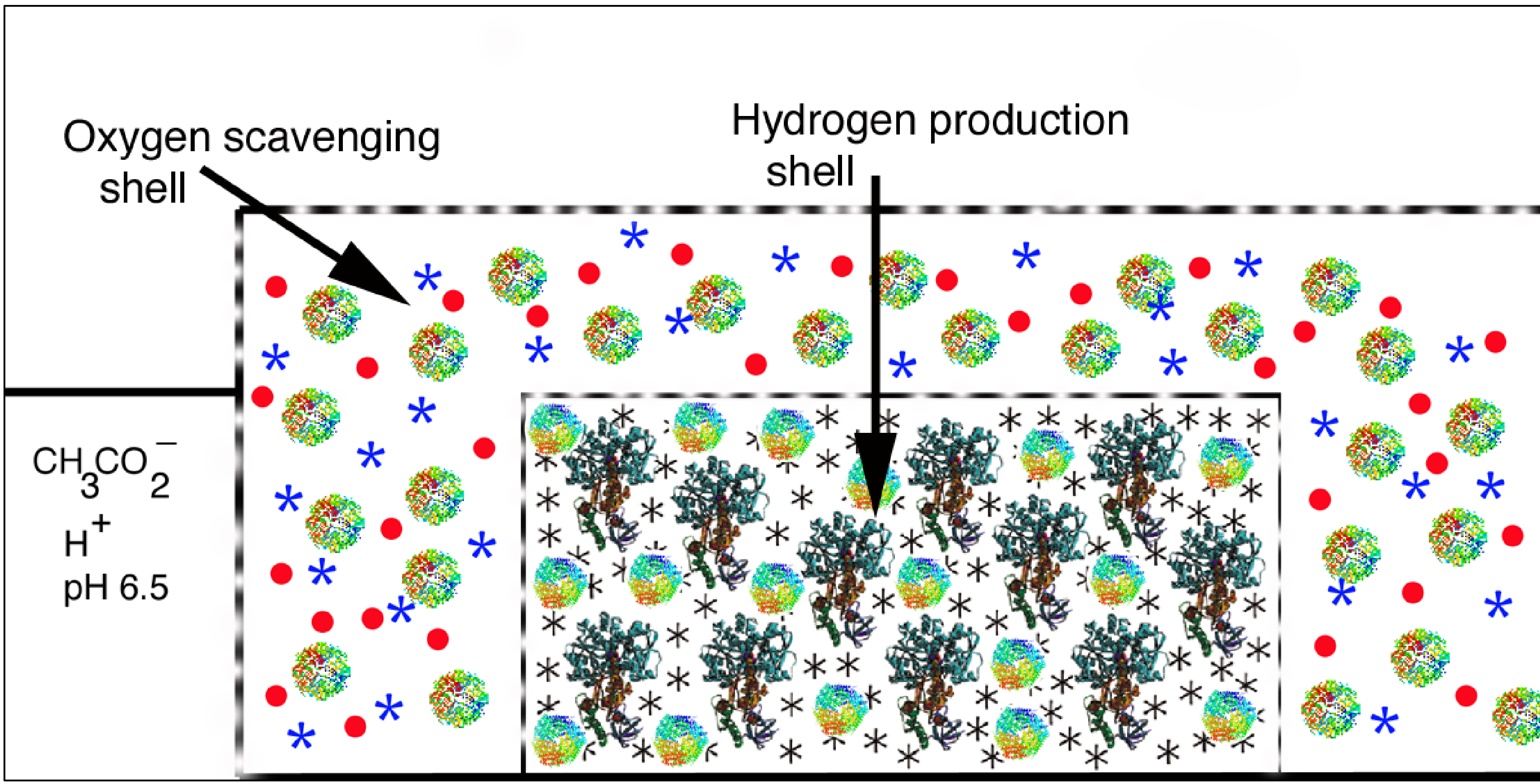
TEM of Ferritin encapsulated Cu nanoparticles

Photoreduction of Cu(II) to form protein encapsulated Cu^o nanoparticles

Very efficient scavenging of O_2 from the media

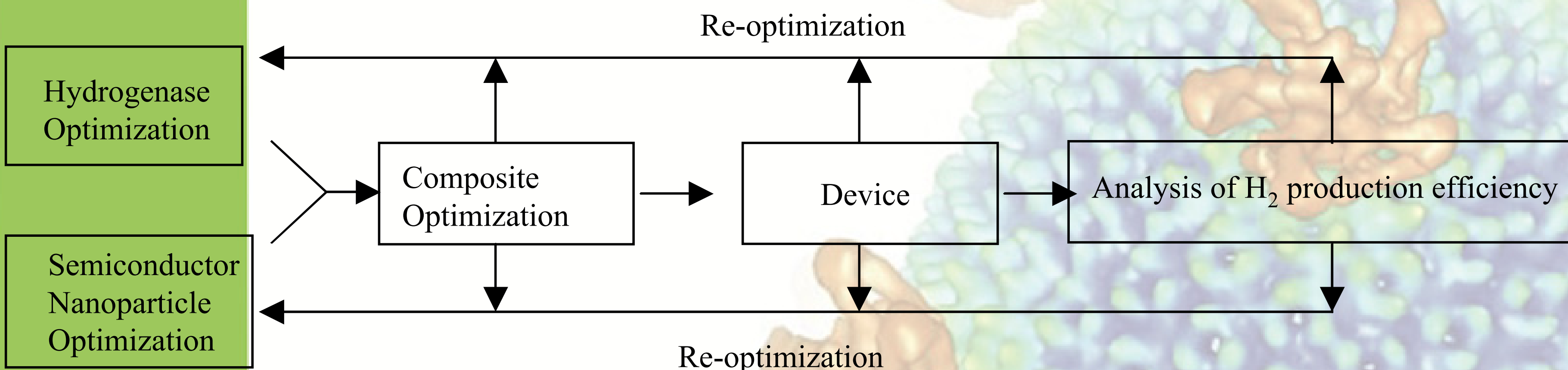
$2\ Cu^o + O_2 + 4H^+ \longrightarrow 2\ Cu(II) + 2H_2O$

Long-Term Goal – Device for photocatalytic hydrogen production – composite materials (nanoparticles and hydrogenase enzymes)



Future Goals

Development of device prototype
demonstration of light harvesting



Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Accidental ignition of hydrogen gas; leading to injury of personnel and damage to equipment from both fire and explosive debris such as: glassware and/or chemicals

Hydrogen Safety

Our approach to deal with this hazard is:

- Follow lab protocol of wearing safety glasses, gloves
- Keep glove box H_2 level below 3%
- Vent gases in fume hood
- Keep away from open flame and flammable chemicals
- Keep quantity of H_2 production to a minimum
- In event of accidental explosion contact
- Jeff Shada, Safety and Risk Management, Advanced Tech Park, 406-994-2711