

# 2008 DOE Hydrogen Program

## Montana Palladium Research Initiative: Use of Biological Materials and Biologically Inspired Materials for H<sub>2</sub> Catalysis

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and  
Center for Bioinspired Nanomaterials

DOE Project ID#: PD34



This presentation does not contain any proprietary or confidential information



# Overview

## Timeline

- Start - Aug. 2006
- End - Dec. 2008

## Budget

- Total project funding  
\$1,303,041
  - DOE \$1,031,433

## Barriers addressed

- Stability/Durability
- Oxygen Sensitivity
- Electron Donors
- Coupling

## Partners

- Montana State University

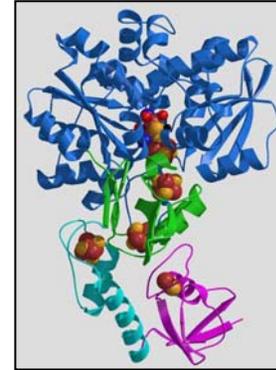


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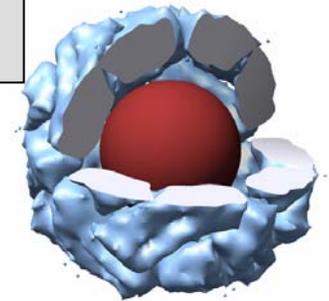
# Approaches

Couple Different Catalyst Systems for  
Light Driven Hydrogen Generation



Biological catalysts (Hydrogenases)

Nanoparticle biomimetic catalysts

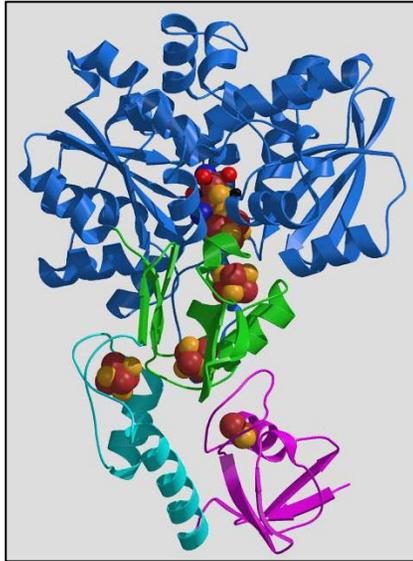


## Objectives

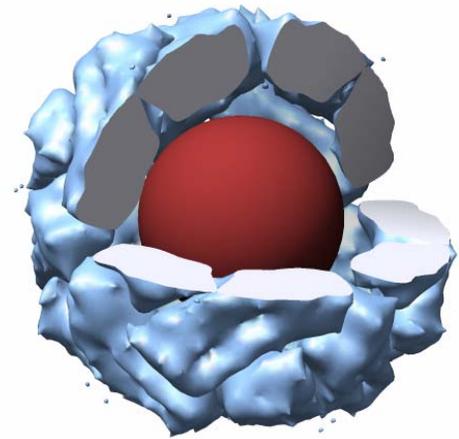
1. Optimize the hydrogenase stability and electron transfer
2. Optimize the semiconductor nano-particle photocatalysis, oxygen scavenging, and electron transfer properties of protein nano-cages
3. Gel/Matrix immobilization and composite formulation of nano-materials and hydrogenase
4. Device fabrication for H<sub>2</sub> production

# Approach:

## Biological and Biomimetic Catalysts for H<sub>2</sub> production

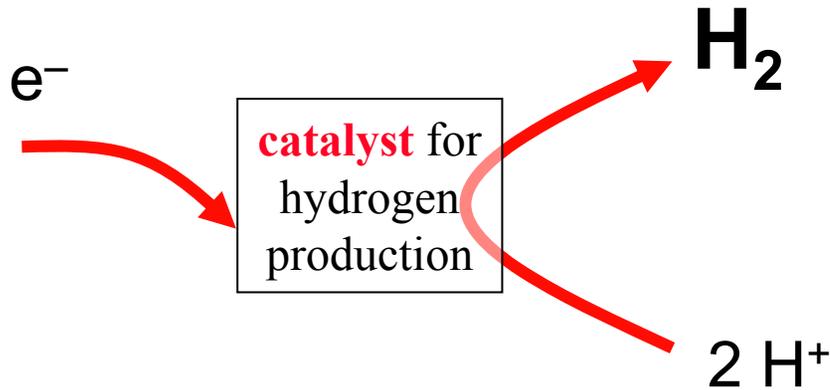


Hydrogenase Enzymes  
(protein architecture protecting  
Metal sulfide active site)



Protein encapsulated  
nano-catalyst

# Coupled Reactions to Generate Hydrogen



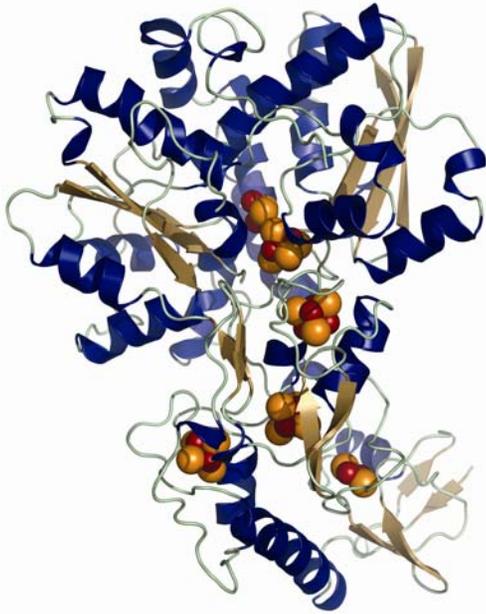
**GOAL:** use **biological catalysts** and develop **biomimetic catalysts** with a variety of sacrificial electron donors or electrochemical source of  $e^-$  to produce  $H_2$

# Issues and Barriers: Catalyst Stability

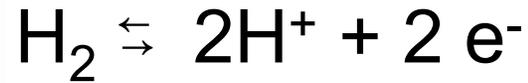
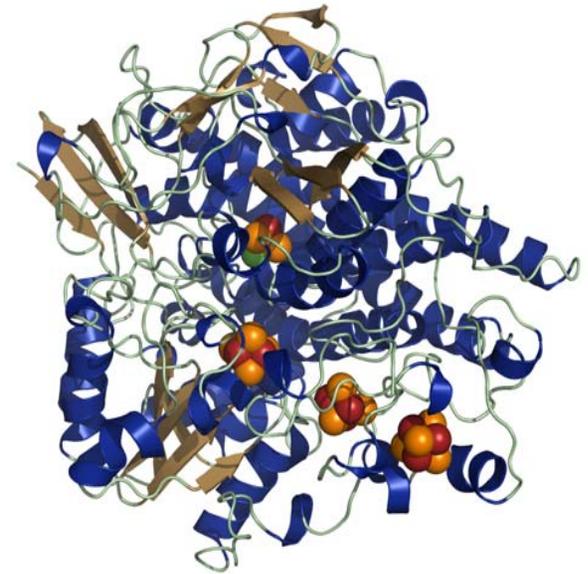
- Durability – shelf life
- Reusability
- Product Based Inhibition
- Oxygen tolerance / resistance
- Susceptibility to proteolytic inactivation
- Optimization – electron transfer, pH, ionic strength, mediators

# Hydrogenases: Highly evolved finely tuned catalysts for *hydrogen oxidation and proton reduction (hydrogen production)*

*C. pasteurianum*



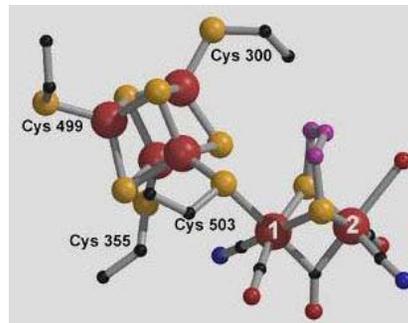
*Desulfovibrio gigas*



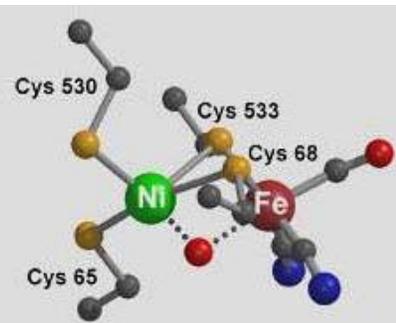
## Cellular location

Membrane Associated  
Soluble  
Periplasmic  
Cytoplasmic

## “H Cluster”



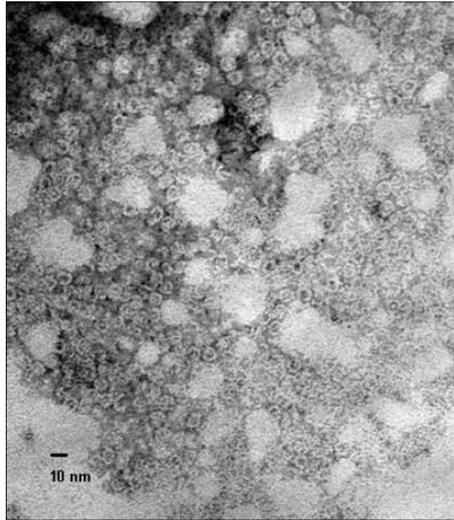
## NiFe Cluster



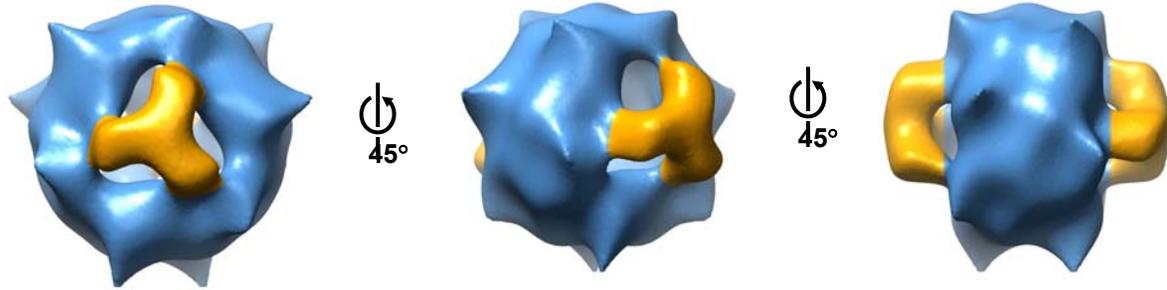
## Microorganisms:

hydrogen, acetate-grown, methanogenic, green, purple, cyanobacteria; algae; fungus.

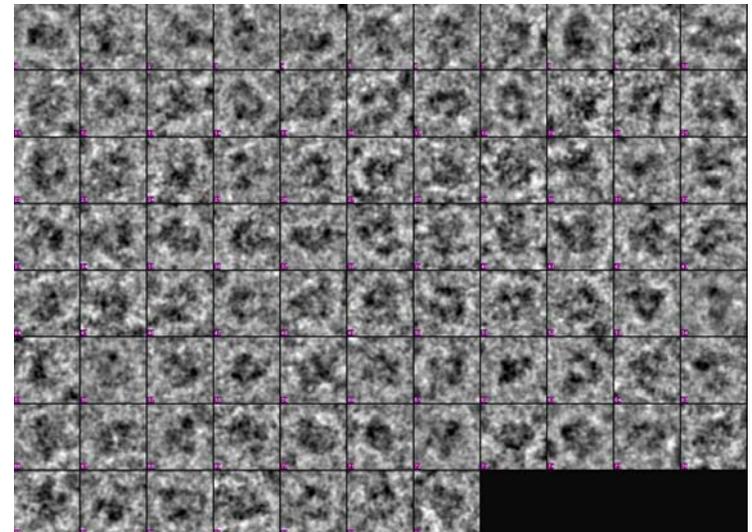
# Stable NiFe hydrogenase from purple sulfur bacteria form supermolecular structures



Electron microphotograph of hydrogenase complexes from *T. roseopersicina* negatively stained with 2% uranyl acetate

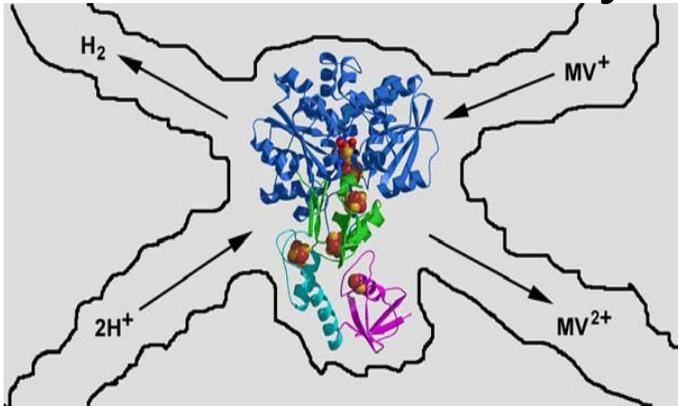


Cryo reconstruction of hydrogenase from *T. roseopersicina* at  $\sim 33$  Å.



Properties	<i>Thiocapsa roseopersicina</i>
Large subunit	64kDa
Small subunit	34kDa
Temperature optimum , °C	<b>80°C</b>
Stability to Oxygen	<b>stable</b>

# Encapsulation of purified active hydrogenases in tetramethyl ortho silicate gels



- Nanoscopic encapsulation;
- Immobilization of unaltered enzyme
- “Heterogeneous material”

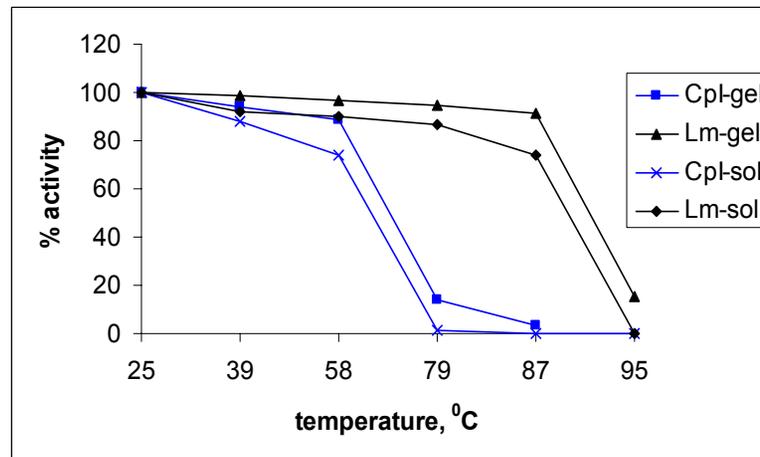
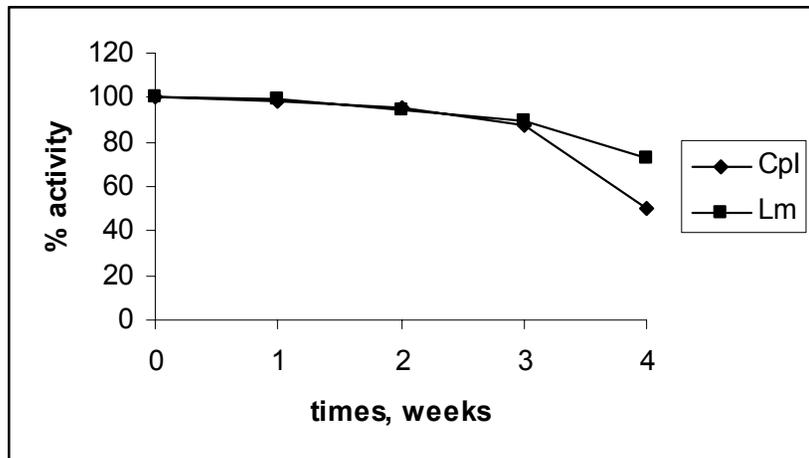
## Recovery of hydrogenase activity\* encapsulated in Sol-Gel

Hydrogenase	Solution	Gel	Solution/Gel (%)
<i>C. pasterianum</i> (extract)	12550	7581	60.4±16
<i>L. modestogalophilus</i>	9150	6175	67.5±9
<i>T. roseopersicina</i>	12600	8834	70.1±3

\*Activity measure at 25° C indicated in nmol/min/mg protein. Values represent average rate over a four-hour period.

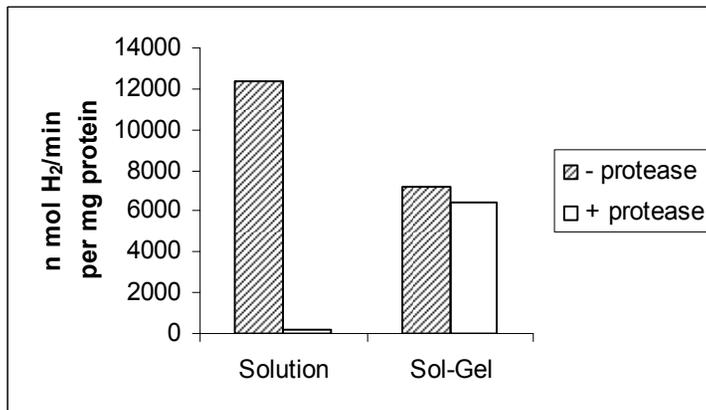
# Hydrogenase stability can be enhanced by gel encapsulation

Increased half-life and increased temperature stability



Sol-gel encapsulated hydrogenases from *C. pasterianum* (Cpl) and *L. modestogalophilus* (Lm) retain activity for a month.

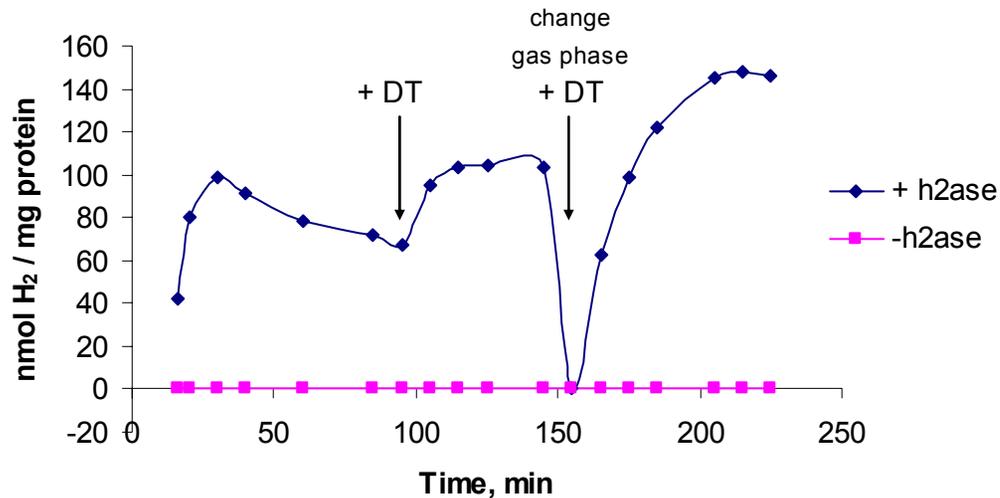
Stability of hydrogen production activity of Cpl and Lm hydrogenases enhanced when encapsulated



Encapsulated hydrogenases are insensitive to proteases.

# Hydrogenase can be reused and recycled in gels

Activity of hydrogenase encapsulated in silica-gel in presence MV as a mediator in solution :

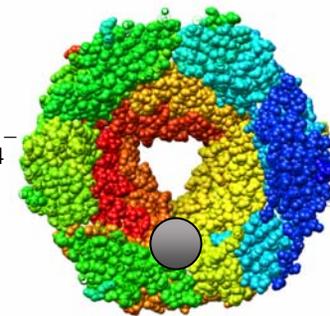
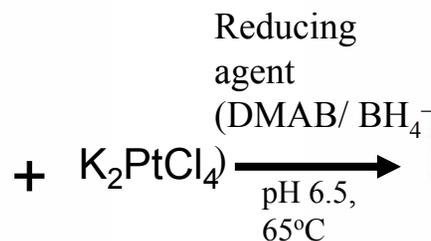
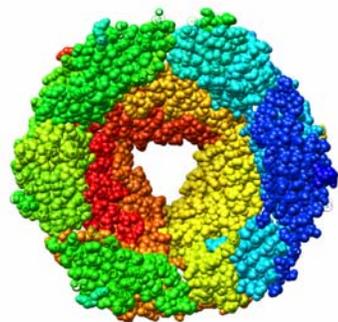


Multiple additions of reduction  
Maximum yields obtained when hydrogen is removed from the system presumably relieving product based inhibition



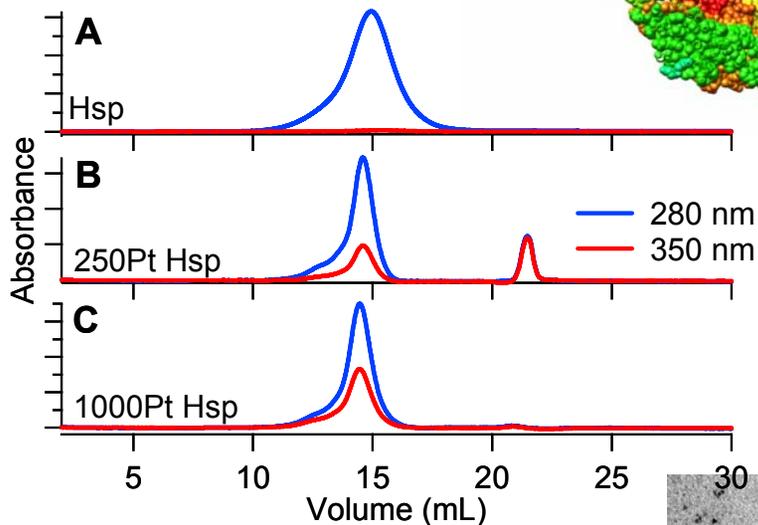
Reduced methyl viologen is captured by the gel presumably due to electrostatic interactions between the positively charged methyl viologen and the negatively charged Sol-Gel. We are examining using high ionic strength solutions and doped Sol Gel preparations to maximize electron flux.

# Biomimetic Catalysts - Synthesis of Pt<sup>0</sup> Encapsulated Within a Protein Cage Architecture

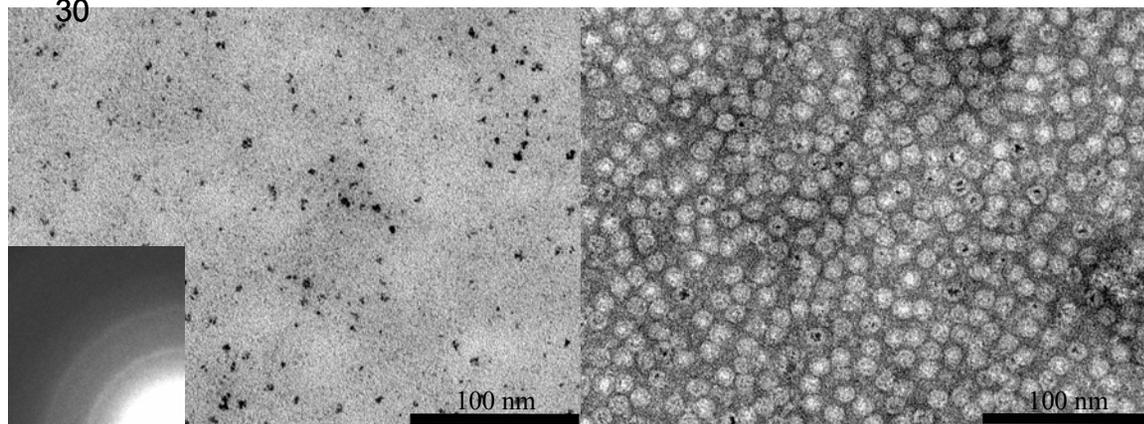


Small heat shock protein  
from *Methanococcus jannaschii*

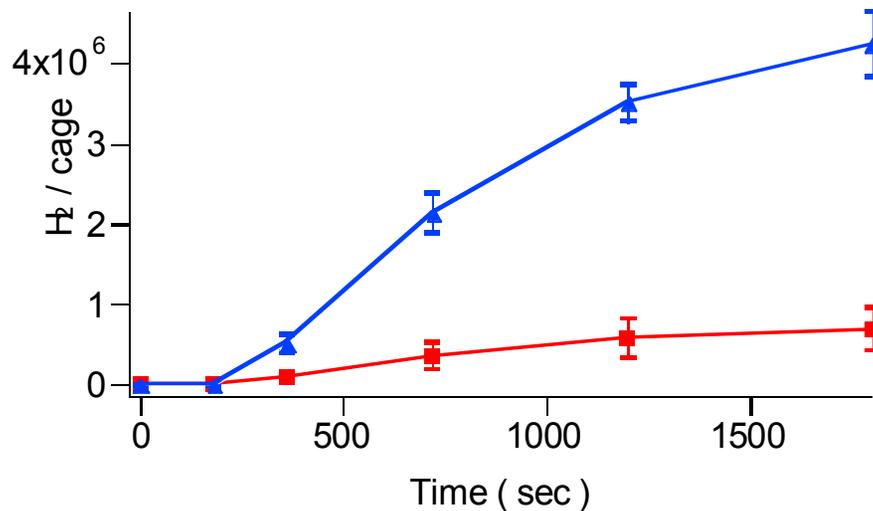
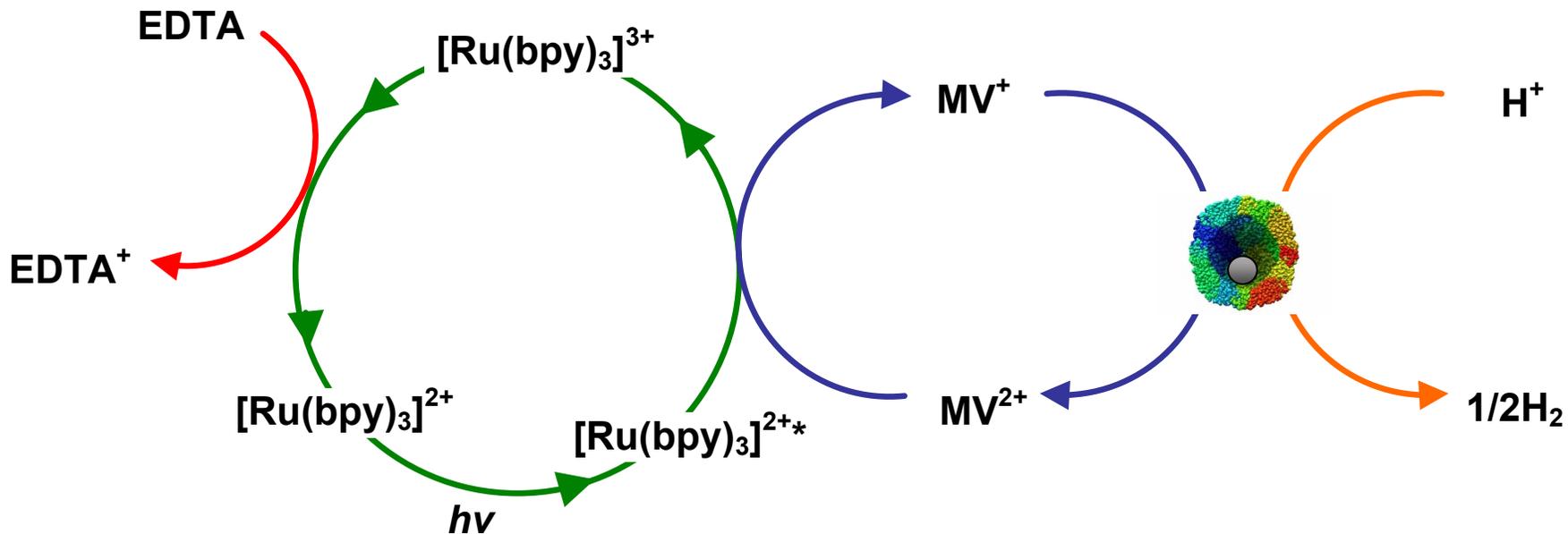
Transmission electron microscopy



Size exclusion  
chromatography



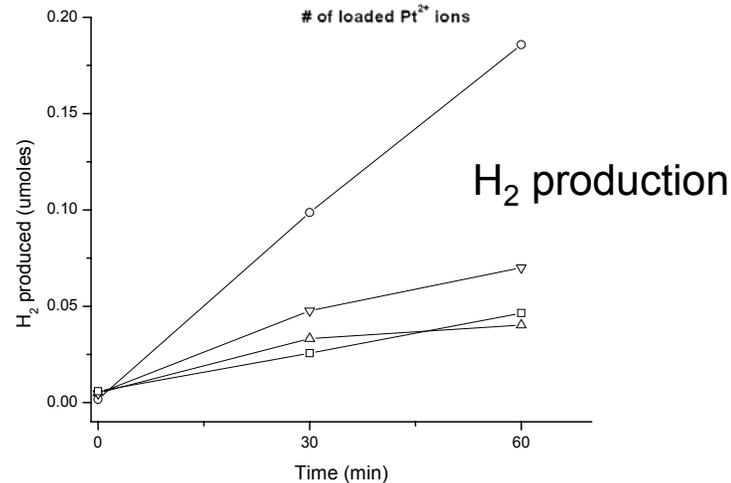
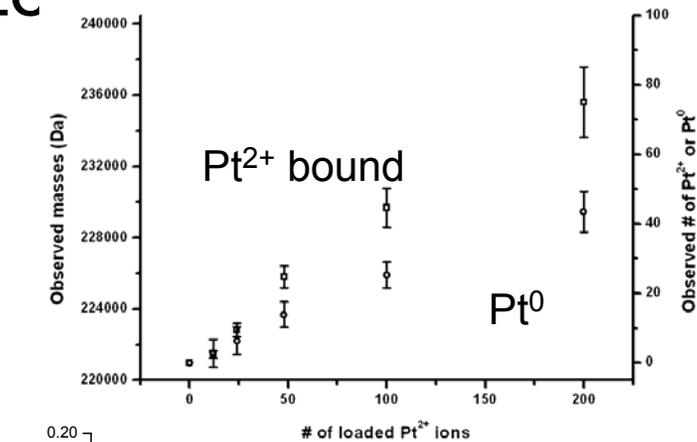
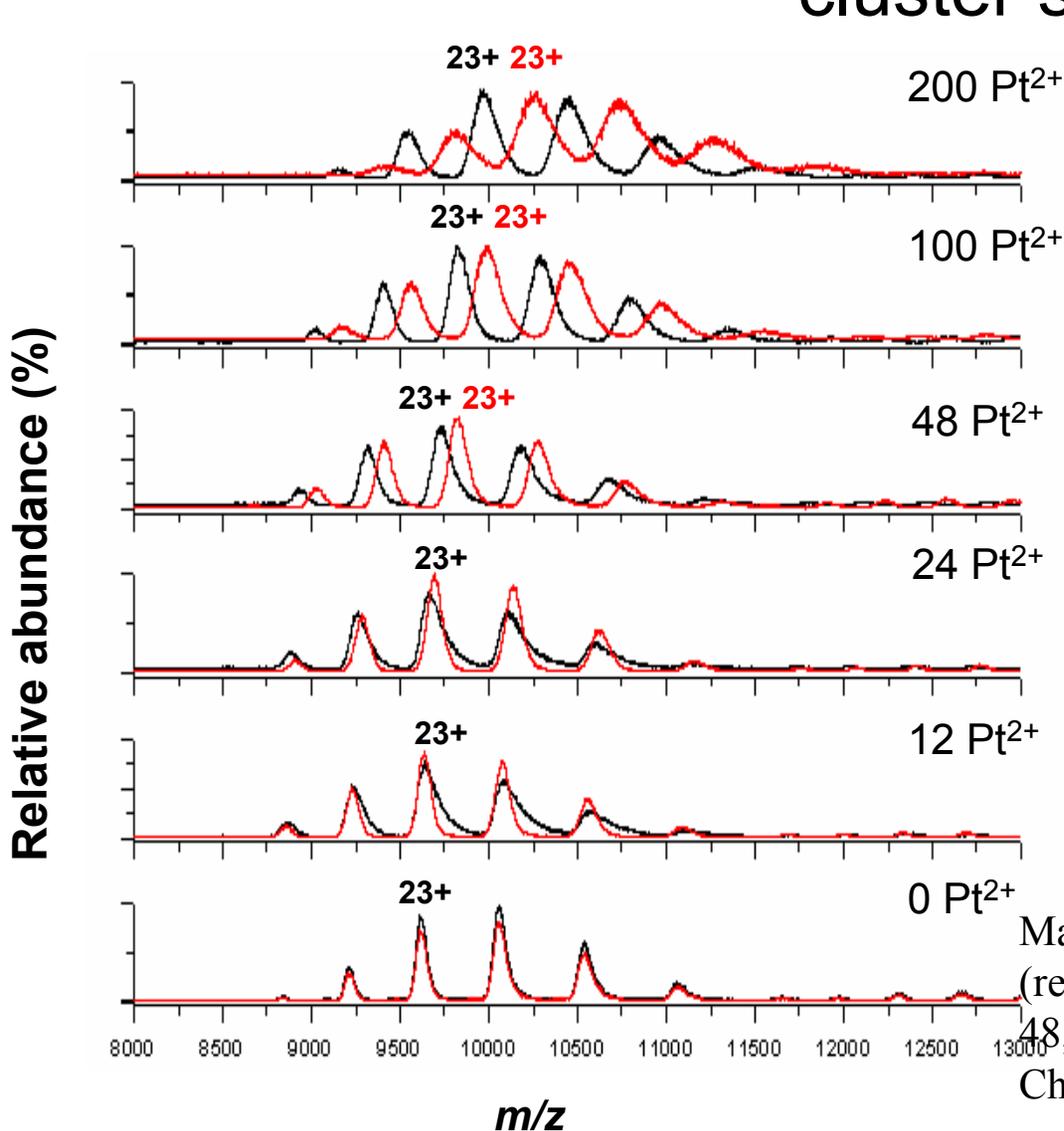
# Coupled Catalysis for H<sub>2</sub> Production



Initial rates (Pt):  $4.47 \times 10^3 \text{ H}_2/\text{sec}/\text{Hsp}$   
 $1.5 \times 10^4 \text{ H}_2/\text{sec}/\text{ferritin}$   
(Hydrogenase  $\Rightarrow 6 \times 10^3 \text{ H}_2/\text{sec}/\text{hydrogenase}$ )

Thermally stable 80-90°C  
Oxygen insensitive

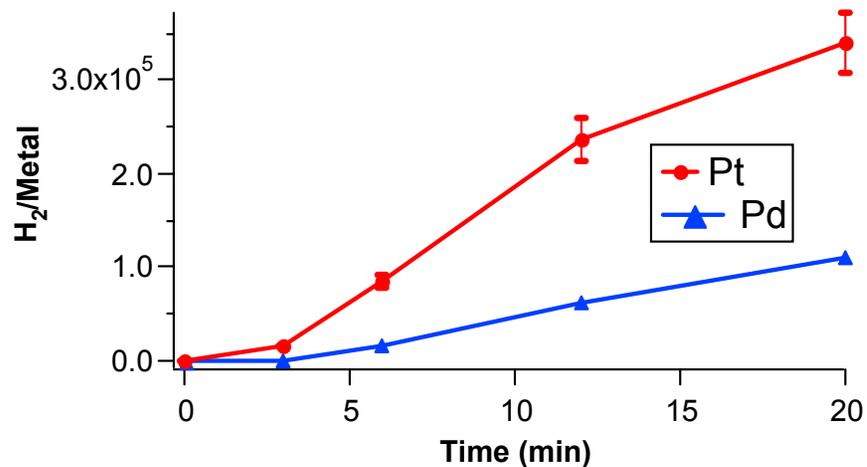
# Control of Pt cluster size (monitored by NCMs) correlation between activity and cluster size



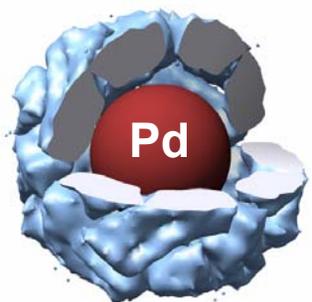
Mass spectra Pt<sup>2+</sup> bound (black) and Pt<sup>0</sup> (red) cages - loading of Pt<sup>2+</sup> (0, 12, 24, 48, 100, and 200 Pt/cage). Charge state 23+ are shown

# Moving beyond Pt...

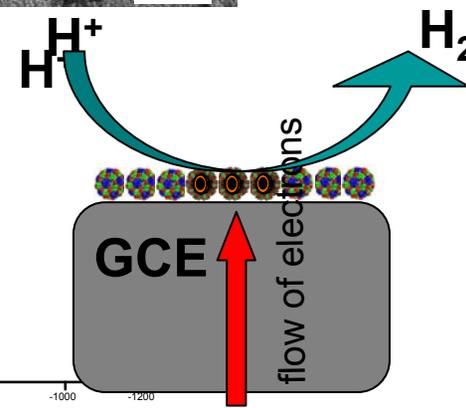
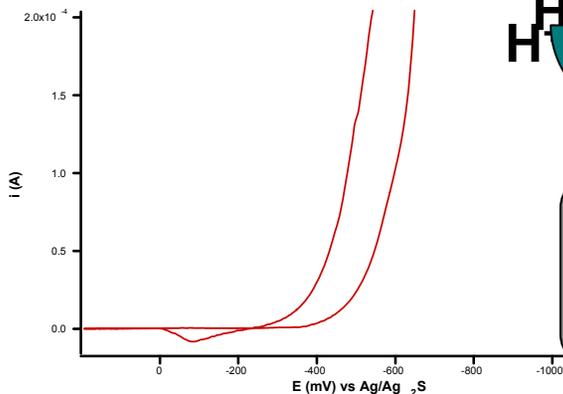
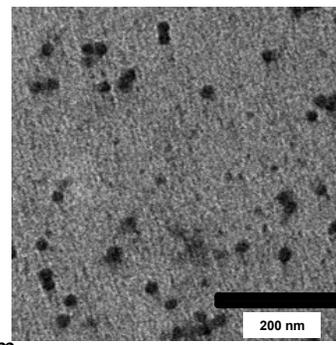
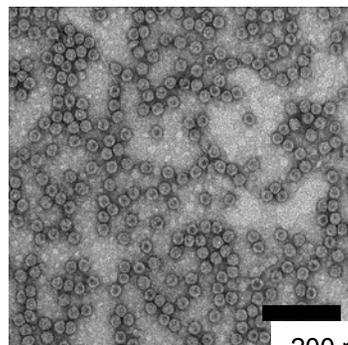
## Pd and Metal Sulfide Nanoparticles as H<sub>2</sub> Catalysts



Pd particles show significantly lower activity than Pt

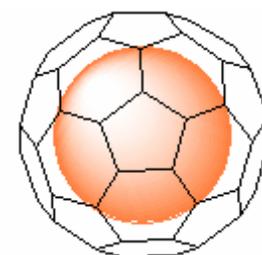


Thermally stable 80-90°C  
Oxygen insensitive



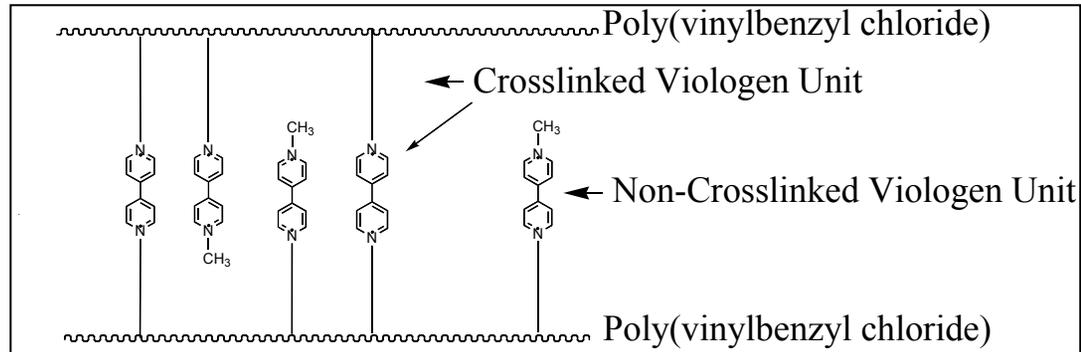
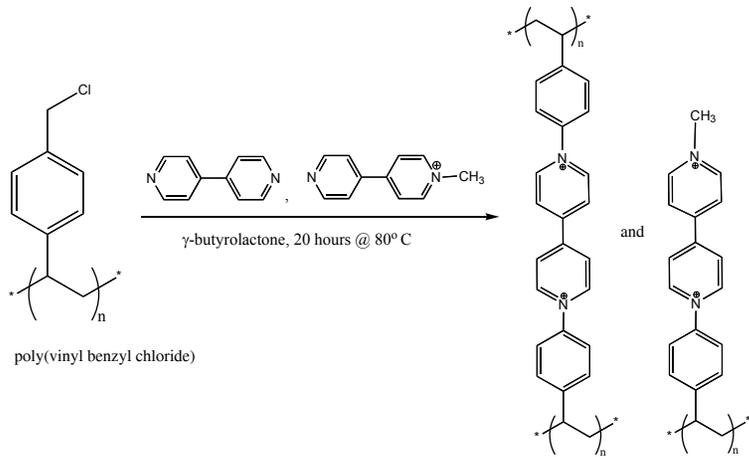
Mo<sub>x</sub>O<sub>y</sub>

H<sub>2</sub>S<sub>(g)</sub> pH 4.5  
4 hours

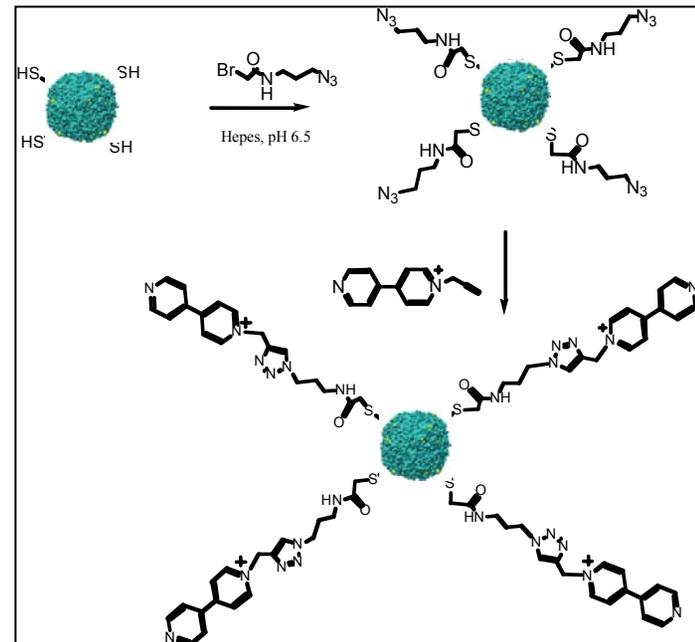
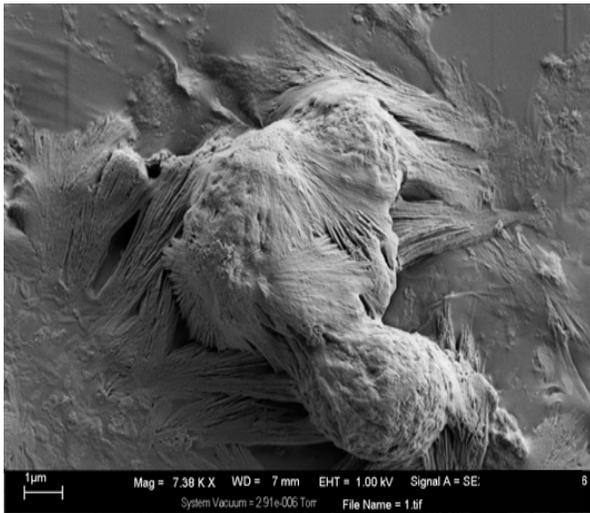


MoS<sub>x</sub>

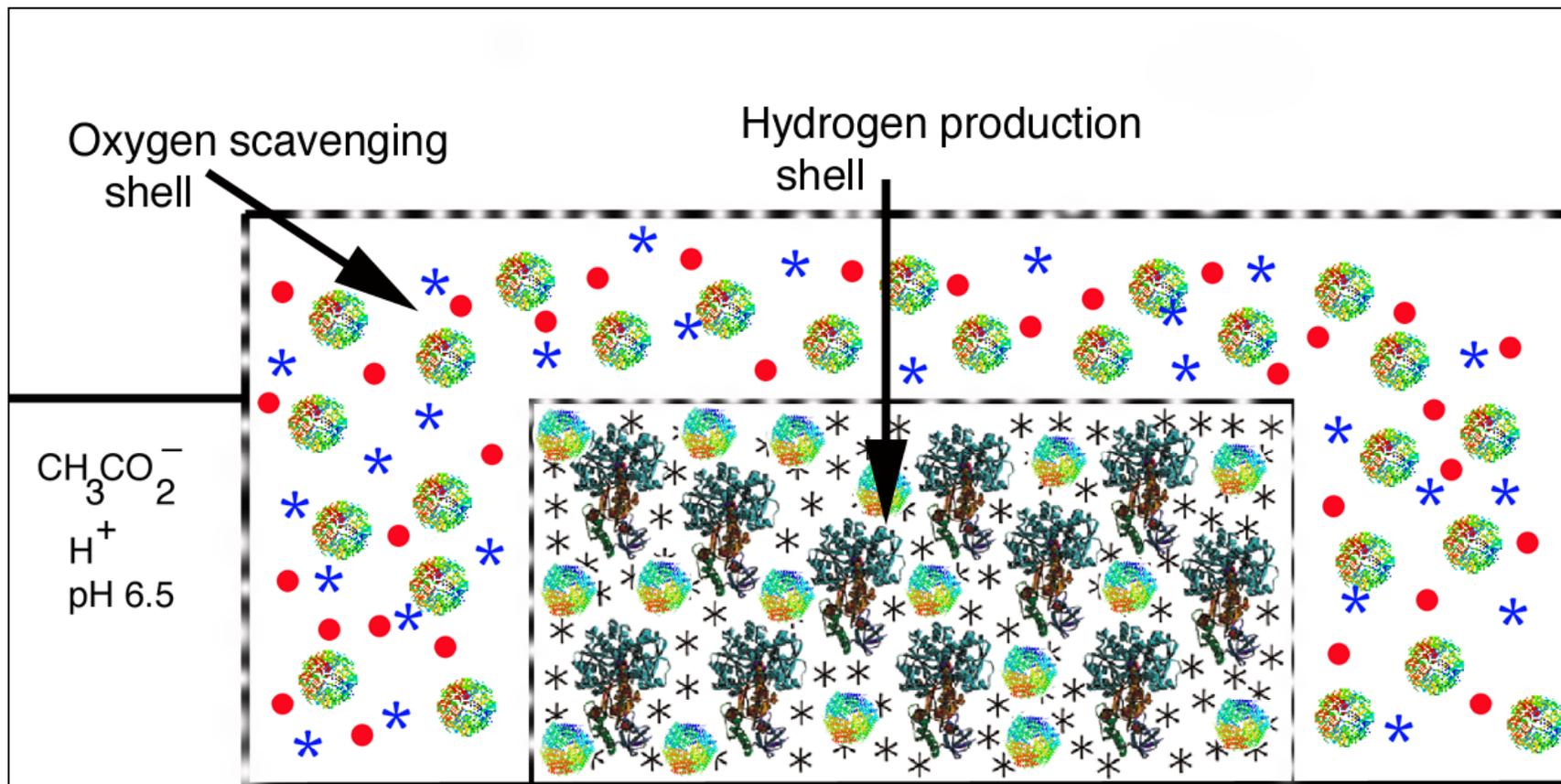
# Polymer gels – control midpoint potential



## Chemical incorporation of protein catalysts

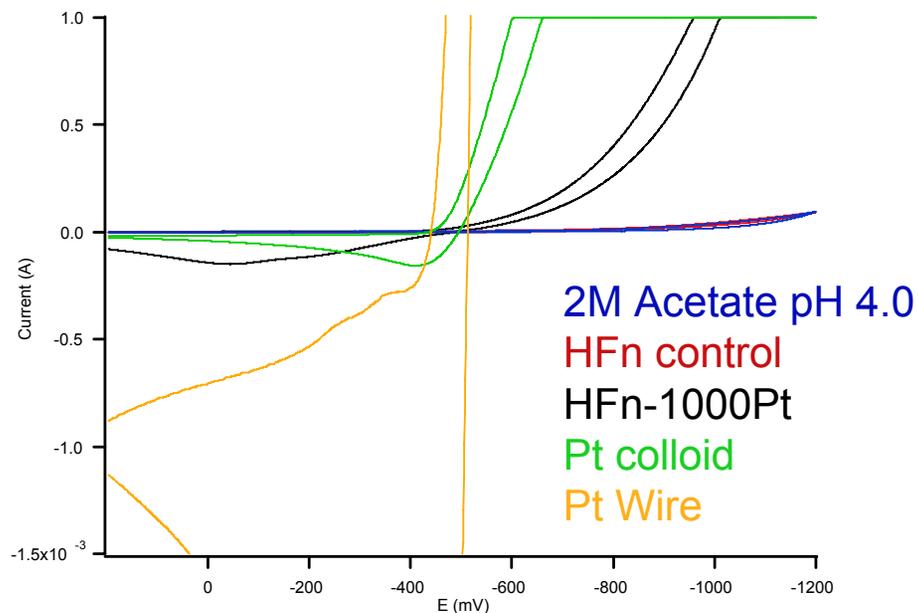
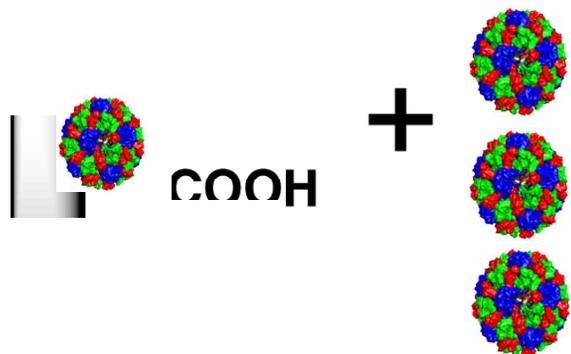


# Long-Term Goal – Device for hydrogen production – composite materials (nanoparticles and hydrogenase enzymes)

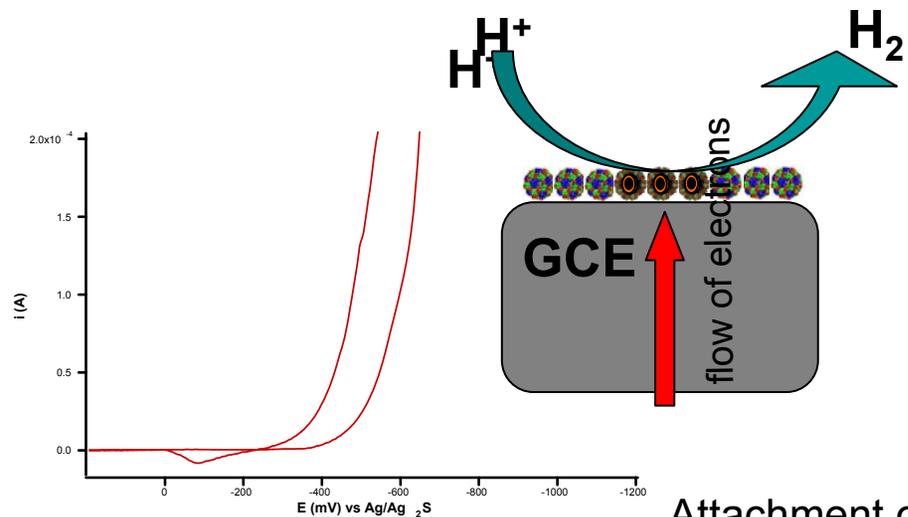




# Cyclic Voltammetry to probe e<sup>-</sup> transfer to catalysts

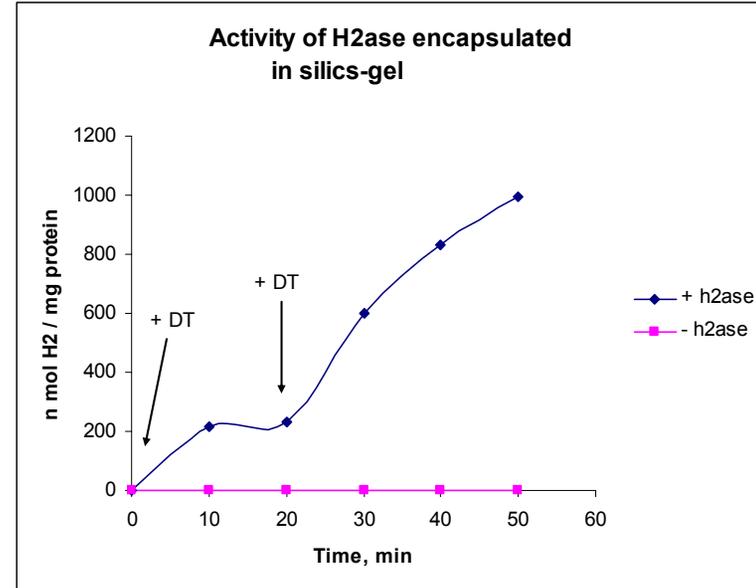
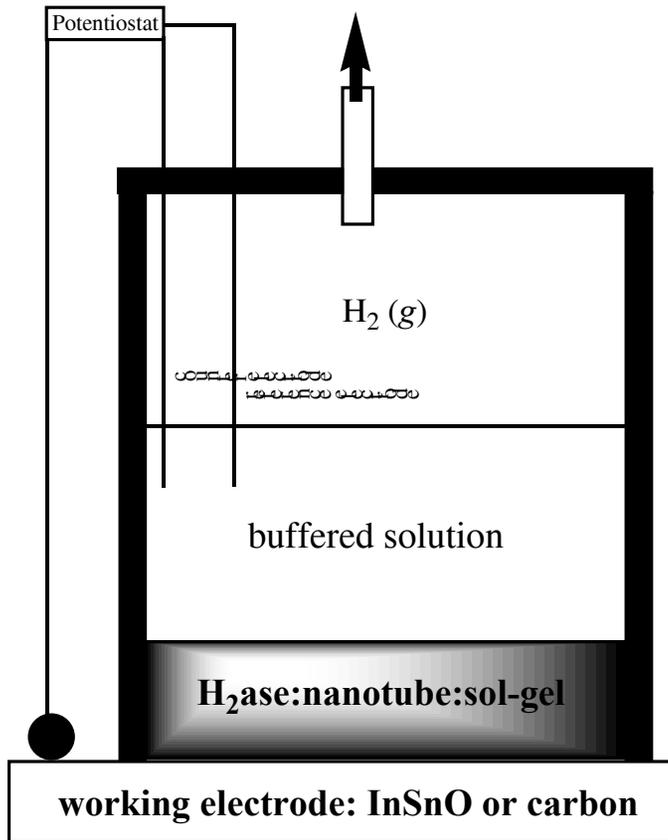


Protein shell requires an overpotential of ~200mV compared to naked Pt colloid



Attachment of MoS<sub>x</sub> - protein cage to GCE - H<sub>2</sub> production

# Carbon nanotubes incorporated into Sol Gels



- Enhance electron transfer
- Facilitate electron transfer between immobilized mediators and hydrogenase
- Facilitate electron transfer between electrodes and hydrogenase in devices

# Current properties in the context of technical targets

	Biomimetics	Hydrogenases
Continuous hydrogen production	> 60 min	> 60 min
O <sub>2</sub> tolerance	Insensitive to O <sub>2</sub>	Insensitive Reversibly oxidized in the presence of O <sub>2</sub> and retains activity
Efficiency of photon-to-H <sub>2</sub>	Currently assessing*	Currently assessing*

•Reported quantum efficiency of Ru(bpy)<sub>3</sub><sup>2+</sup> photoreduction of MV<sup>2+</sup> to MV<sup>+</sup> using EDTA as sacrificial reductant is 25%. (Johansen, O. *et al Chem. Phys. Letters*, **1983**, *94*, 113-117)

•We are currently assessing the efficiency of the MV<sup>+</sup> to H<sub>2</sub> with both the hydrogenases and synthetic systems using devices described.

# Summary

Use of biological and biomimetic catalysts for H<sub>2</sub> production

Incorporation of hydrogenase and mimetics into stabilizing matrices

Incorporation of hydrogenase and mimetics into electroactive poly(viologen matrices)

Initial incorporation of catalyst systems into devices

# Future Work

Establish Benchmarks for Hydrogen production efficiency

Incorporate catalyst(s) into poly(viologen)matrices (electrostatic/covalent)

Evaluate Hydrogen production efficiency (electrochemical, photochemical, chemical reducing equivalents)

Incorporate solution chemistry into device

Evaluate device for durability and sustained H<sub>2</sub> production