2008 DOE Hydrogen Program

Montana Palladium Research Initiative:

Use of Biological Materials and Biologically Inspired Materials for H_2 Catalysis

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and
Center for Bioinspired Nanomaterials

DOE Project ID#: PD34

MONTANA STATE UNIVERSITY

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

MONTANA STATE UNIVERSITY

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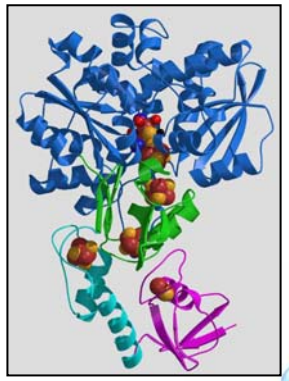
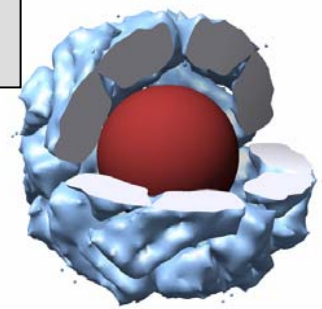
Approaches

Couple Different Catalyst Systems for Light Driven Hydrogen Generation



Biological catalysts (Hydrogenases)

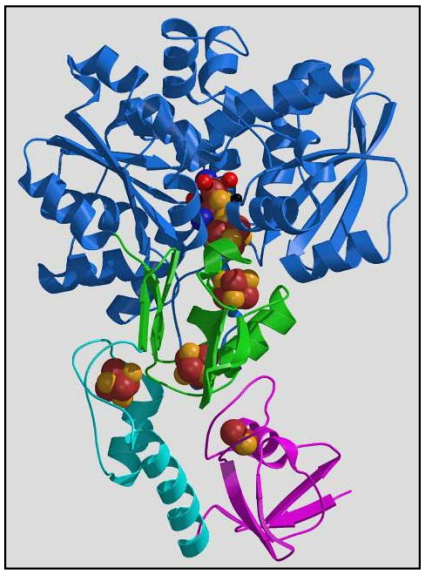
Nanoparticle biomimetic catalysts



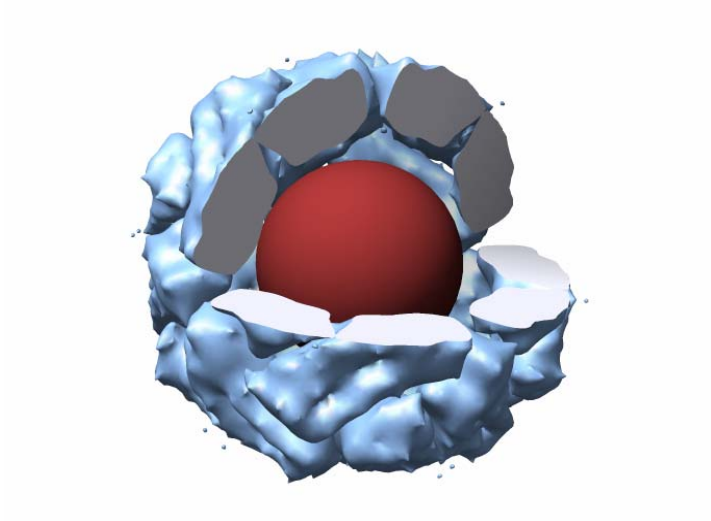
Objectives

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_2 production

Approach:
Biological and Biomimetic Catalysts for H_2 production

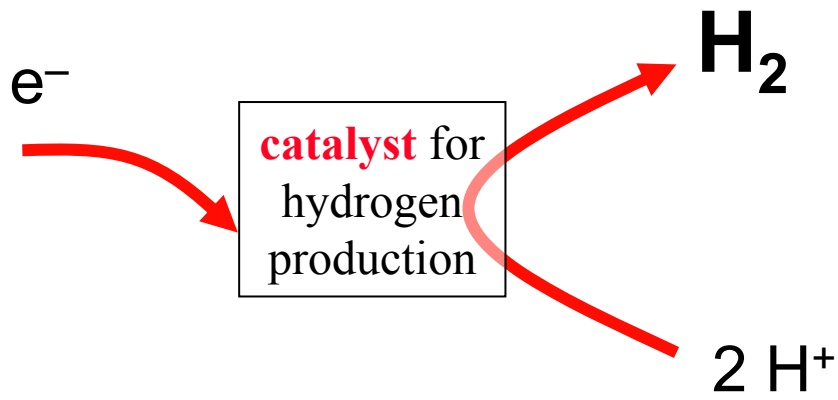


Hydrogenase Enzymes
(protein architecture protecting
Metal sulfide active site)



Protein encapsulated
nano-catalyst

Coupled Reactions to Generate Hydrogen



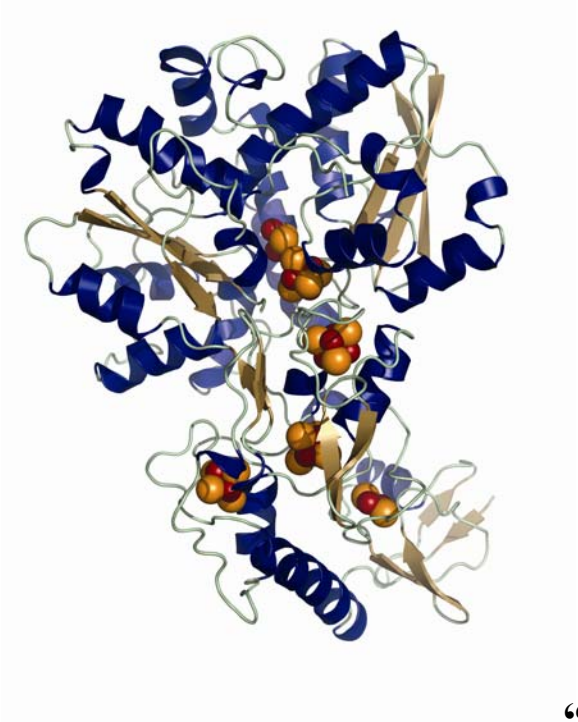
GOAL: use **biological catalysts** and develop **biomimetic catalysts** with a variety of sacrificial electron donors or electrochemical source of e^- to produce H_2

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

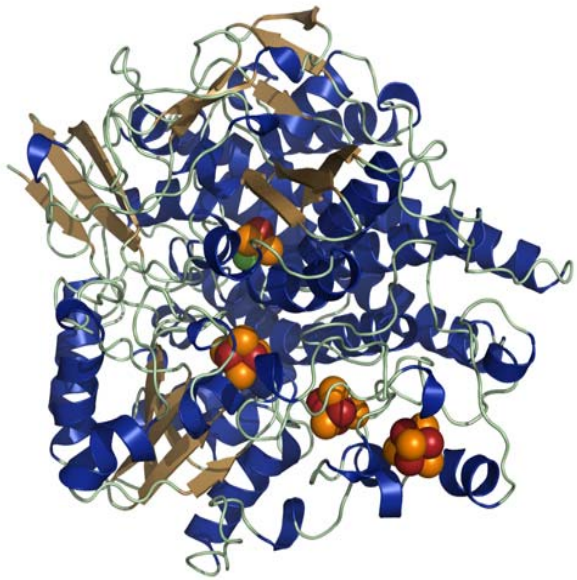
Hydrogenases: Highly evolved finely tuned catalysts for *hydrogen oxidation and proton reduction (hydrogen production)*

C. pasteurianum



$$H_2 \leftrightarrows 2H^+ + 2\,e^-$$

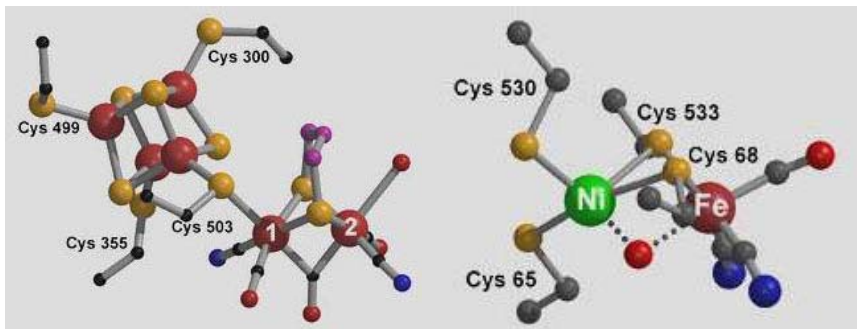
Desulfovibrio gigas



Cellular location

Membrane Associated
Soluble
Periplasmic
Cytoplasmic

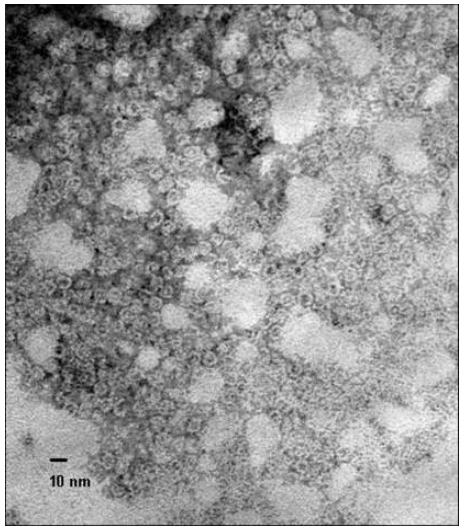
“H Cluster” **NiFe Cluster**



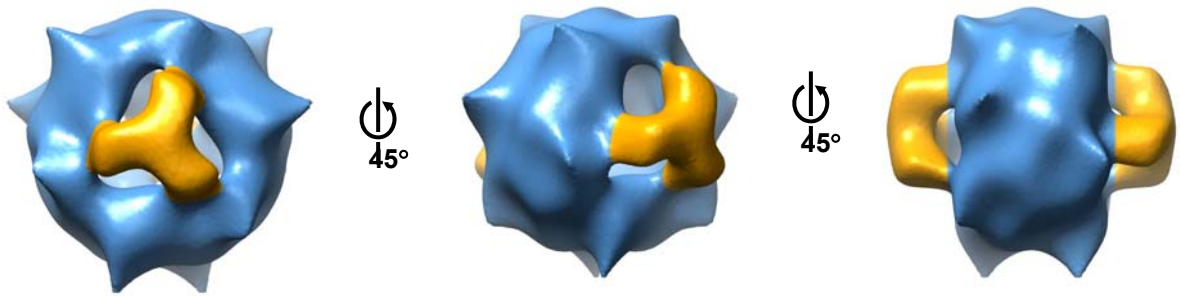
Microorganisms:

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

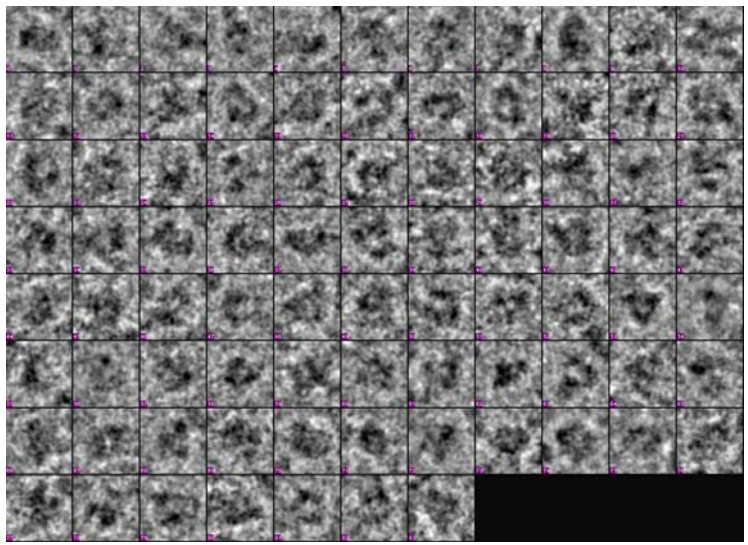
Stable NiFe hydrogenase from purple sulfur bacteria form supermolecular structures



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

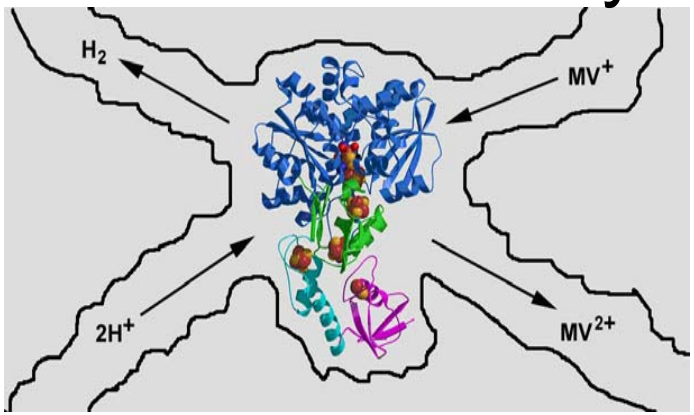


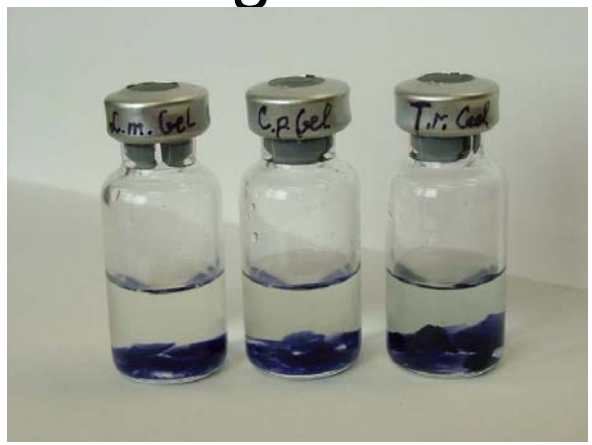
Cryo reconstruction of hydrogenase from *T. roseopersicina* at ~33 Å.



Properties	*Thiocapsa roseopersicina*
Large subunit	64kDa
Small subunit	34kDa
Temperature optimum , °C	**80ºC**
Stability to Oxygen	**stable**

Encapsulation of purified active hydrogenases in tetramethyl ortho silicate gels





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

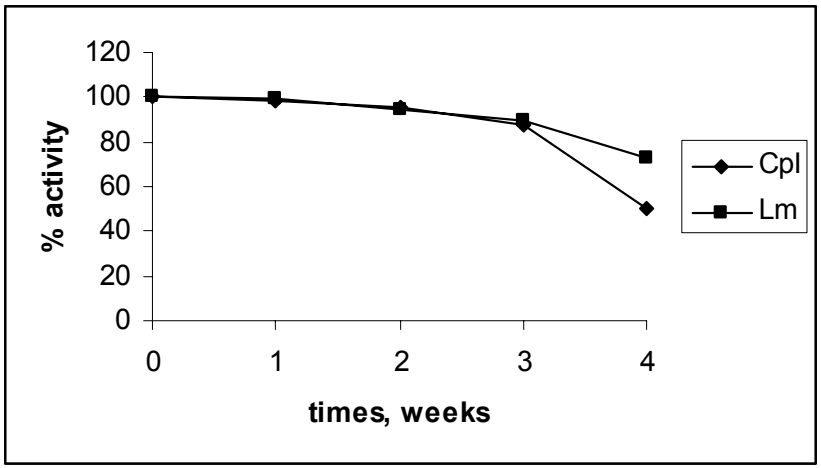
Recovery of hydrogenase activity* encapsulated in Sol-Gel

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

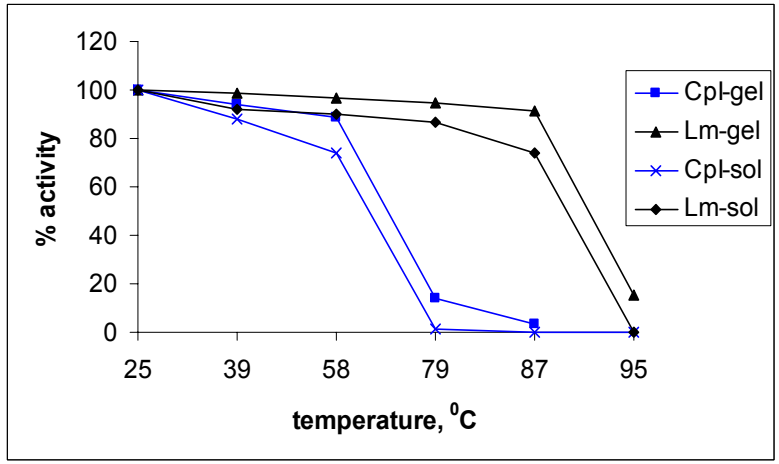
•Activity measure at 25º C indicated in nmol/min/mg protein. Values represent average rate over a four-hour period.

Hydrogenase stability can be enhanced by gel encapsulation

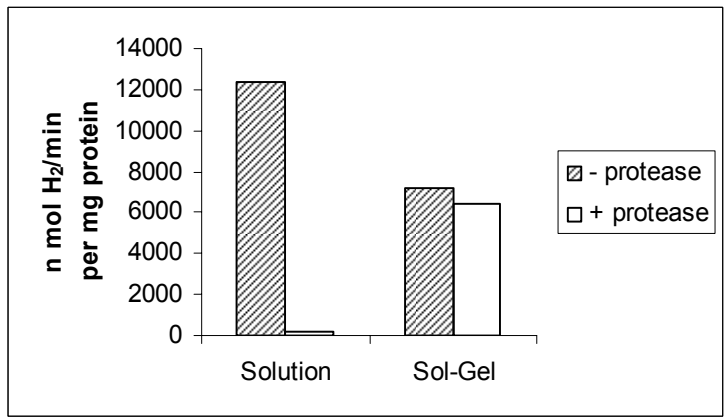
Increased half-life and increased temperature stability



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

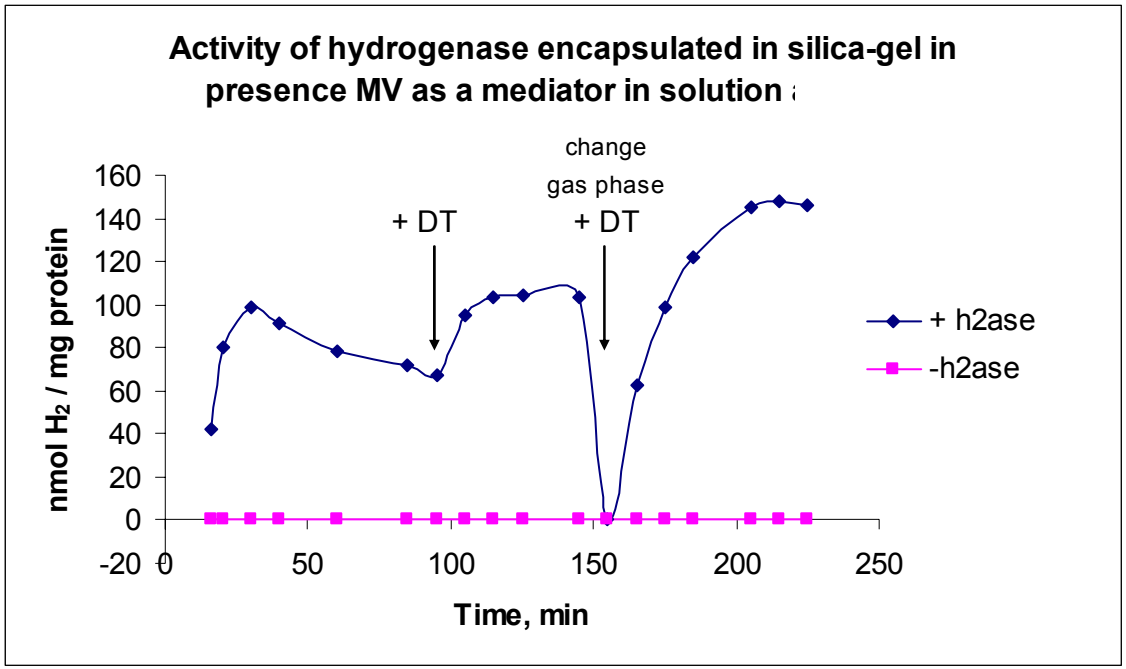


Stability of hydrogen production activity of CpI and Lm hydrogenases enhanced when encapsulated



Encapsulated hydrogenases are insensitive to proteases.

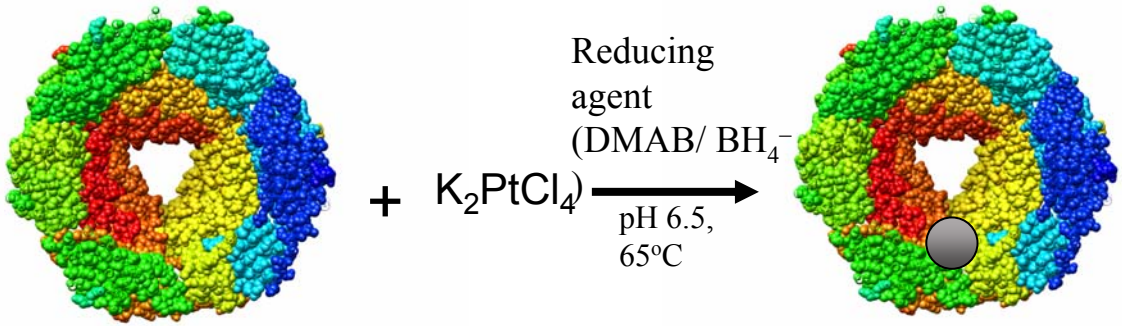
Hydrogenase can be reused and recycled in gels



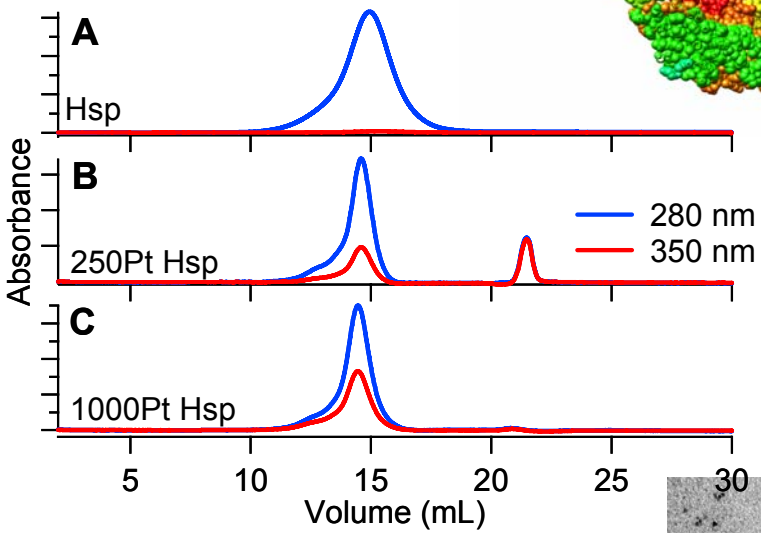
Multiple additions of reduction
Maximum yields obtained when hydrogen is removed from the system presumably relieving product based inhibition

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^0 Encapsulated Within a Protein Cage Architecture

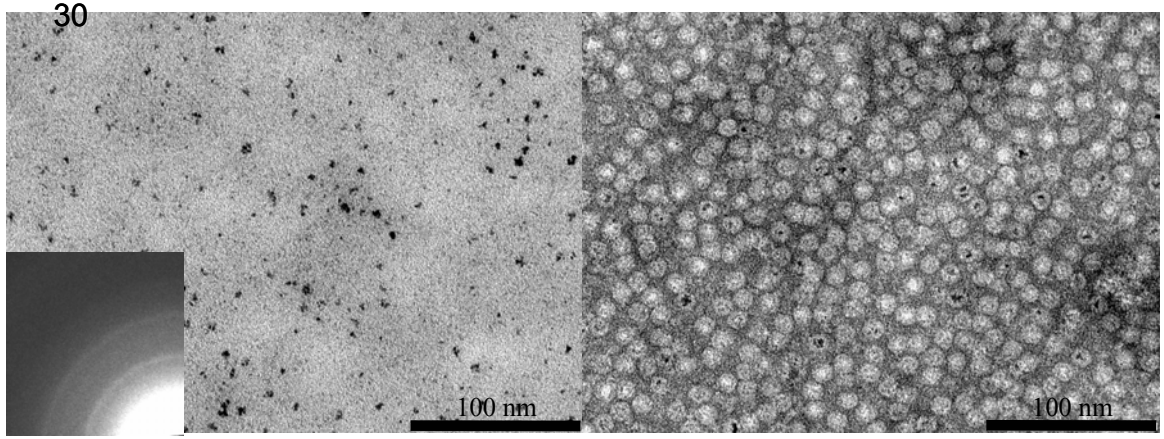


Small heat shock protein from *Methanococcus jannaschii*

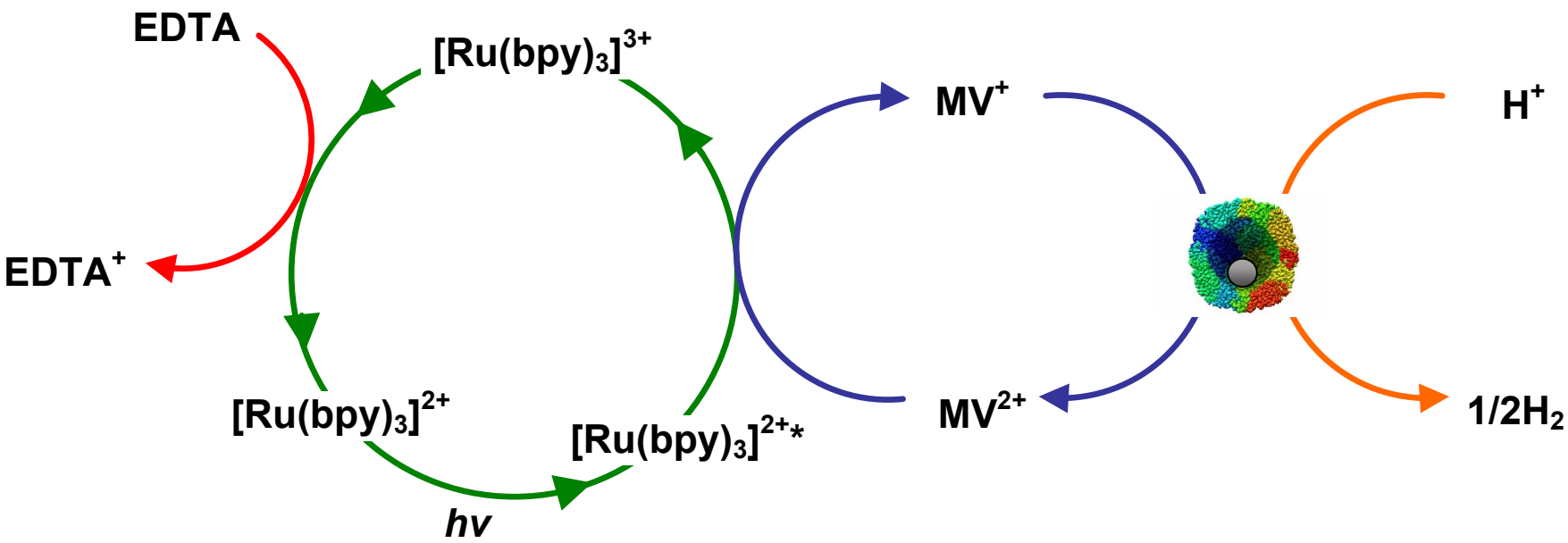


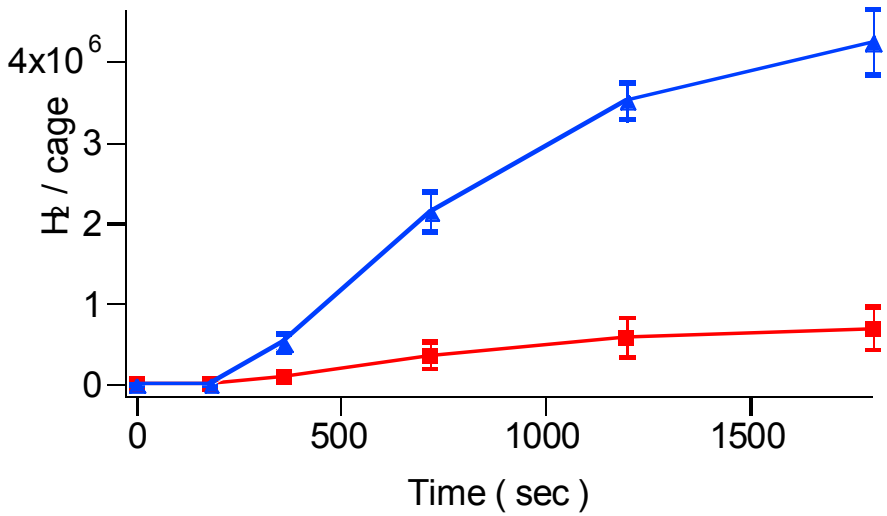
Size exclusion chromatography

Transmission electron microscopy



Coupled Catalysis for H_2 Production





Initial rates (Pt): 4.47×10^3 H_2/sec/Hsp

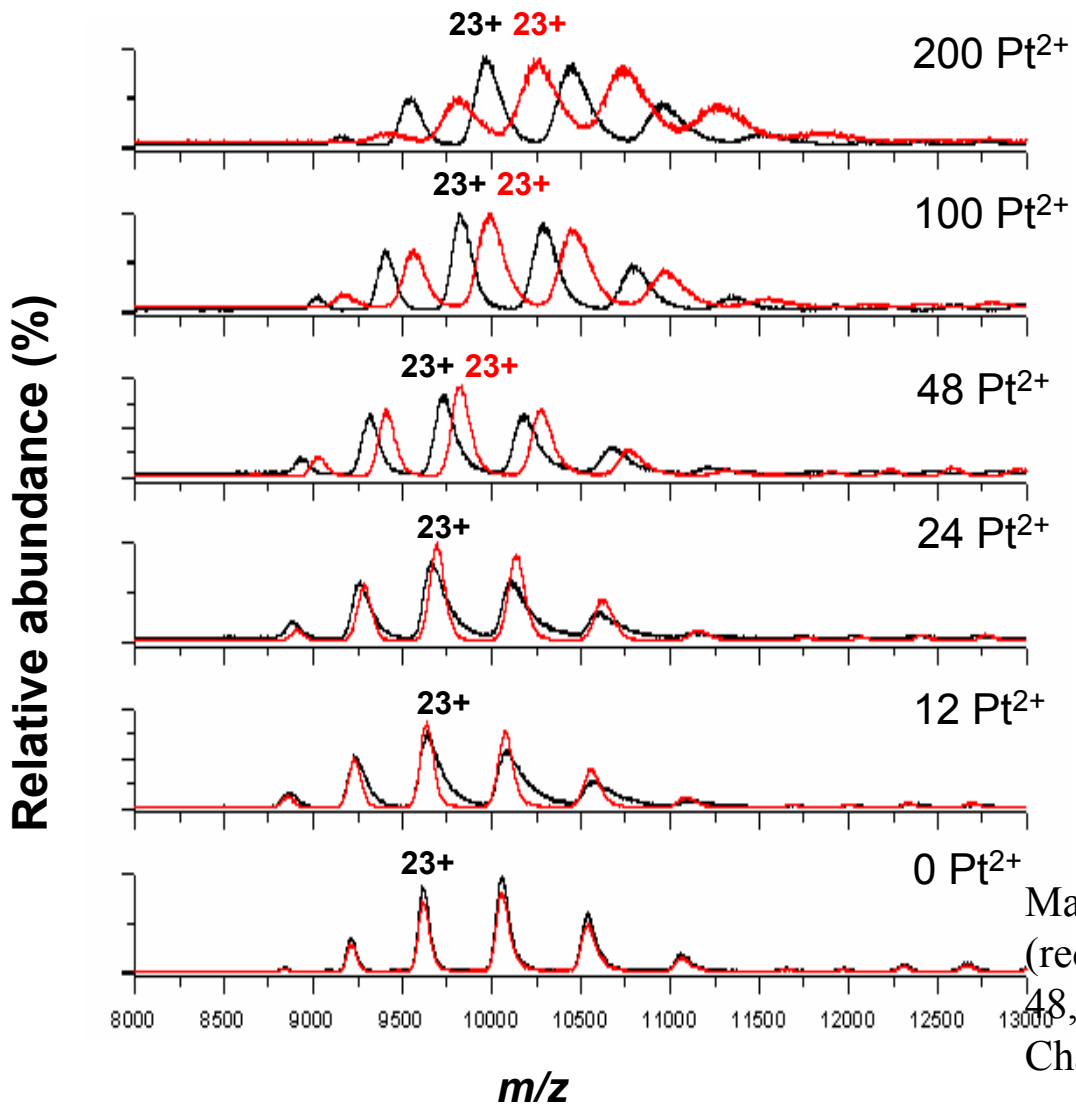
1.5×10^4 H_2/sec/ferritin

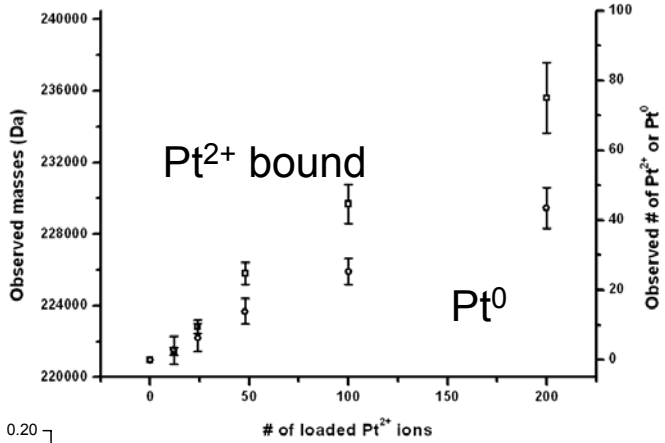
(Hydrogenase => $6 \times 10^3 H_2$/sec/hydrogenase)

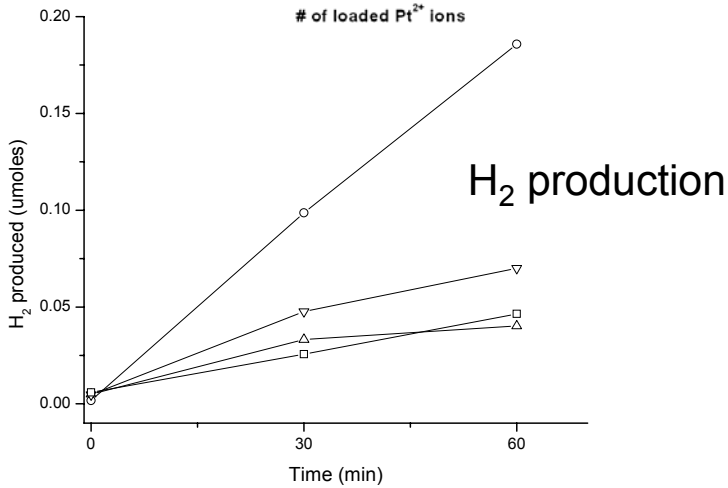
Thermally stable 80-90ºC

Oxygen insensitive

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

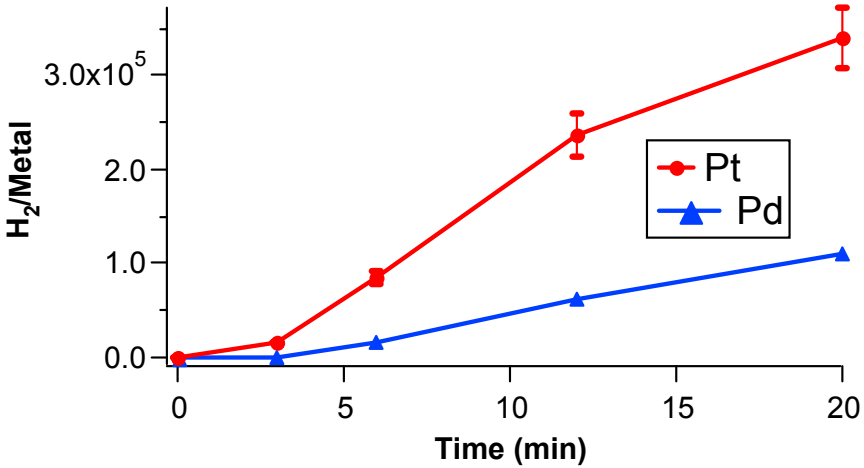




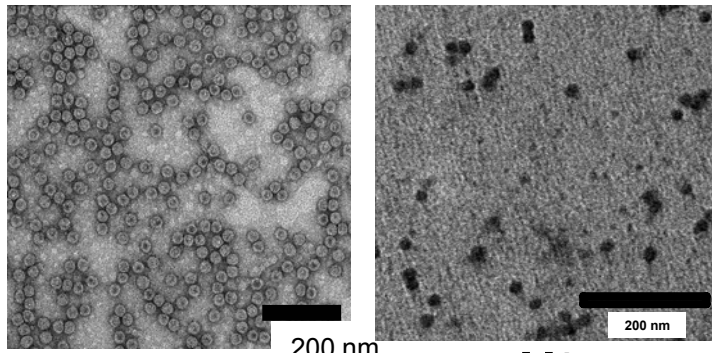


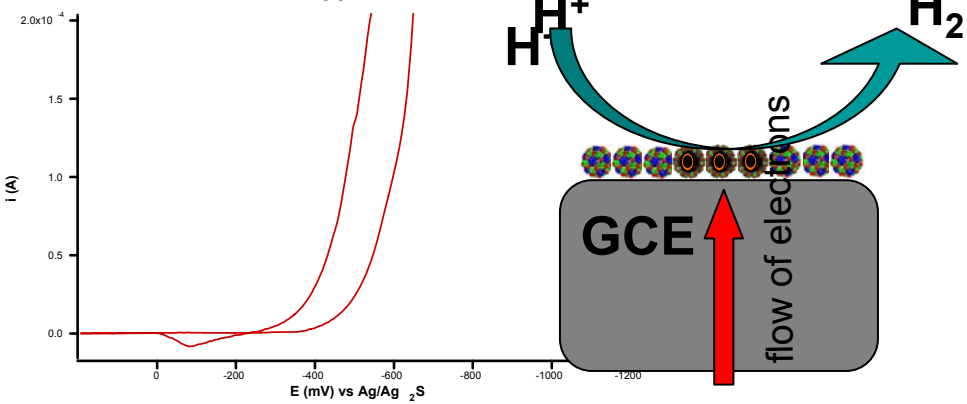
Mass spectra Pt^{2+} bound (black) and Pt^{0} (red) cages - loading of Pt^{2+} (0, 12, 24, 48, 100, and 200 Pt/cage).
Charge state 23+ are shown

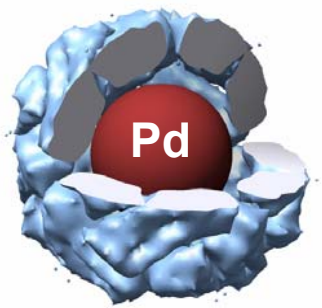
Moving beyond Pt…
Pd and Metal Sulfide Nanoparticles as H_2 Catalysts



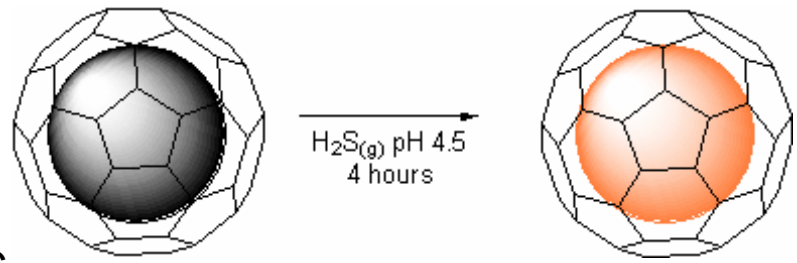
Pd particles show significantly lower activity than Pt







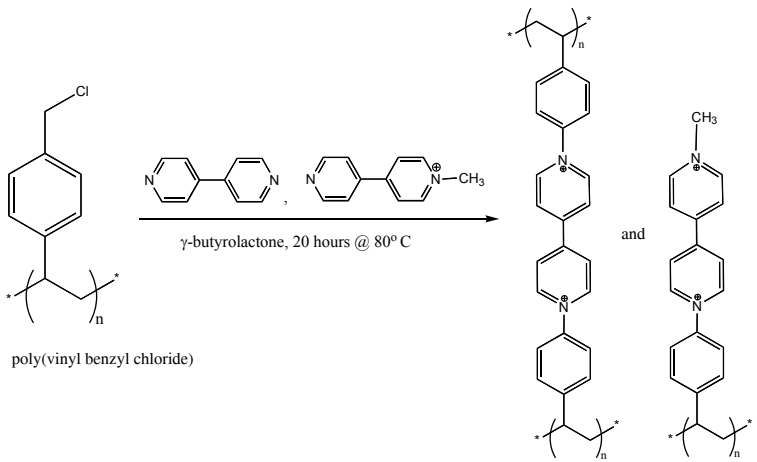
Thermally stable 80-90ºC
Oxygen insensitive

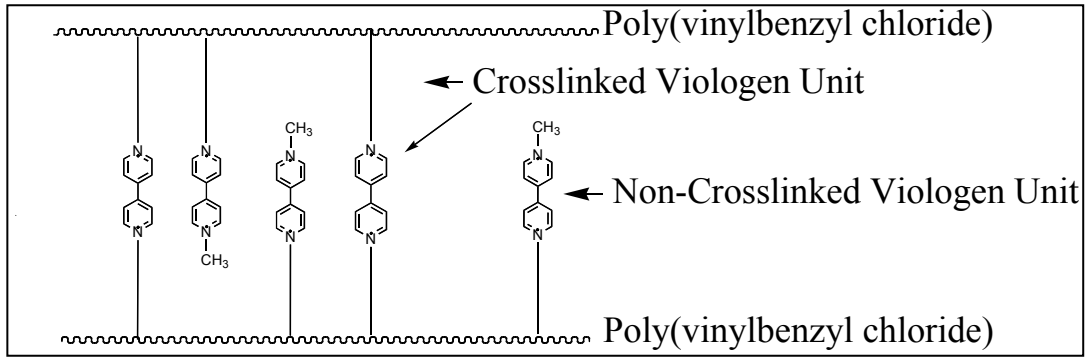


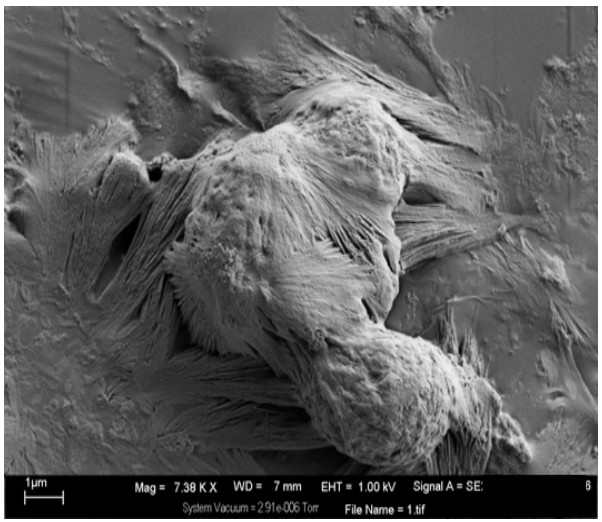
Mo_xO_y

MoS_x

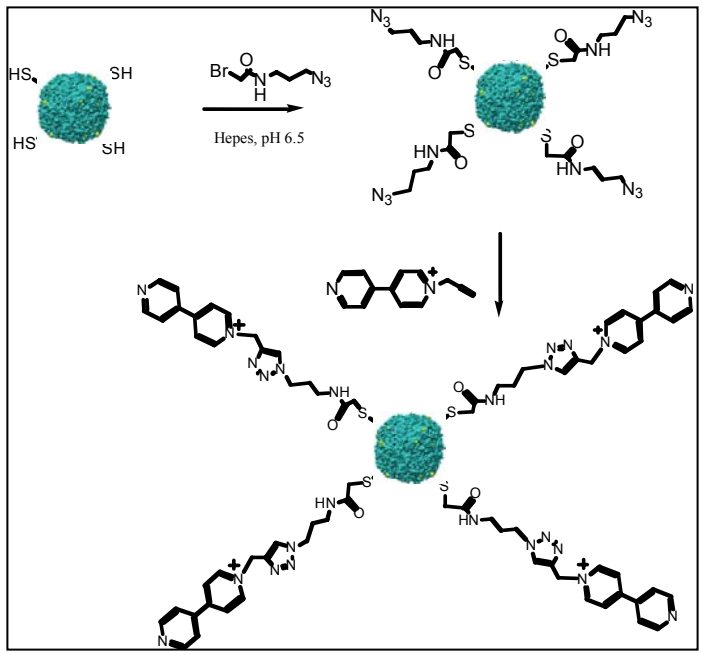
Polymer gels – control midpoint potential



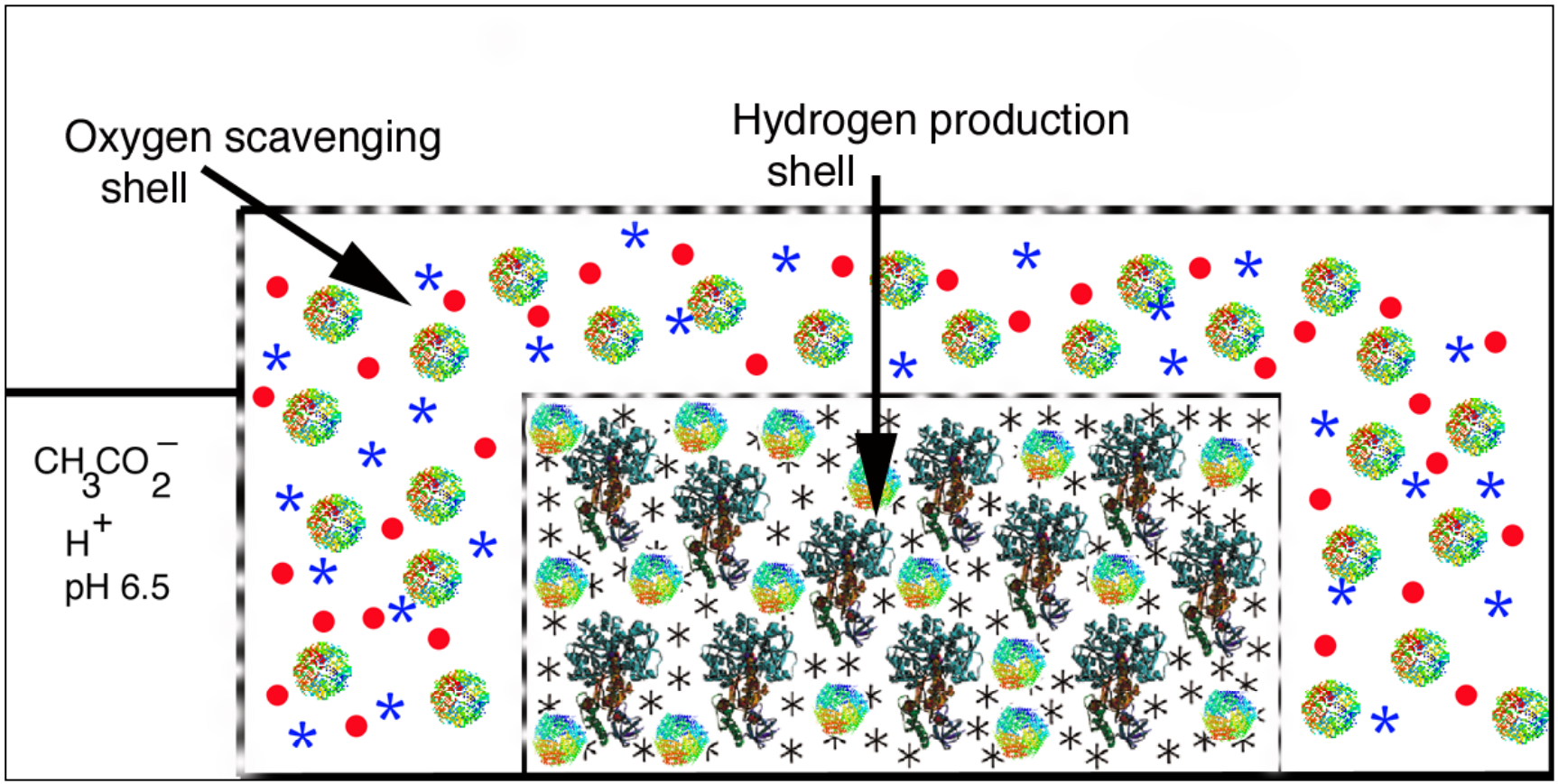




Chemical incorporation of protein catalysts

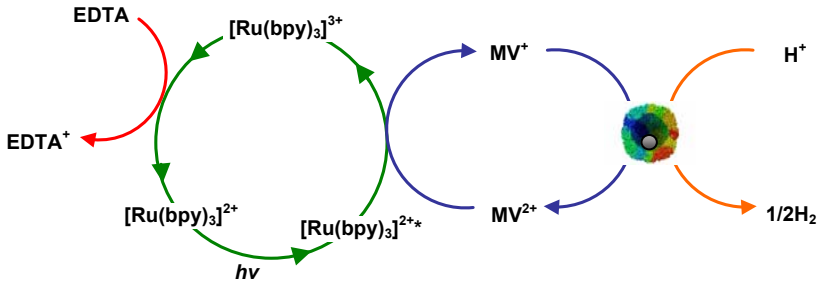


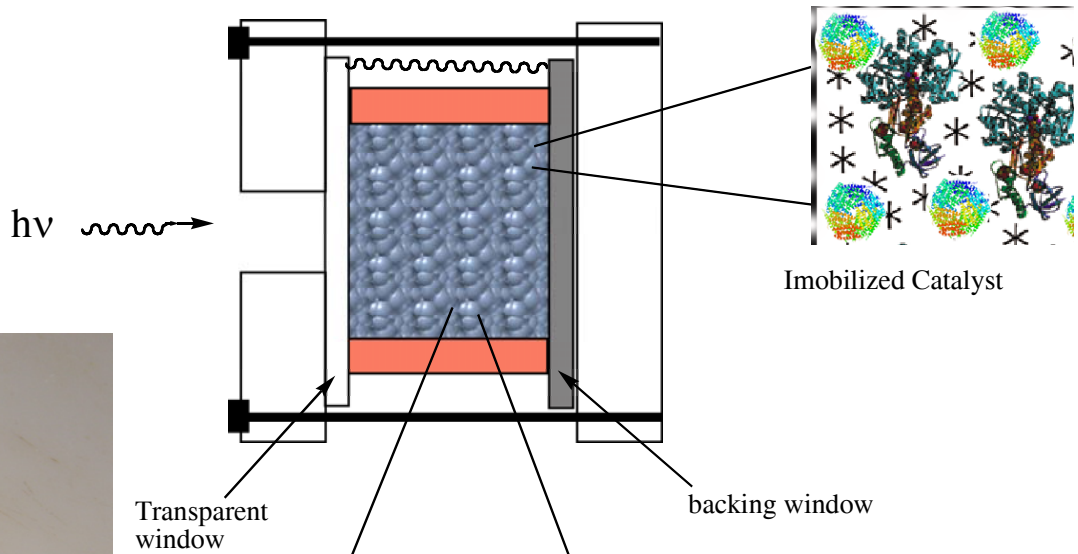
Long-Term Goal – Device for hydrogen production – composite materials (nanoparticles and hydrogenase enzymes)

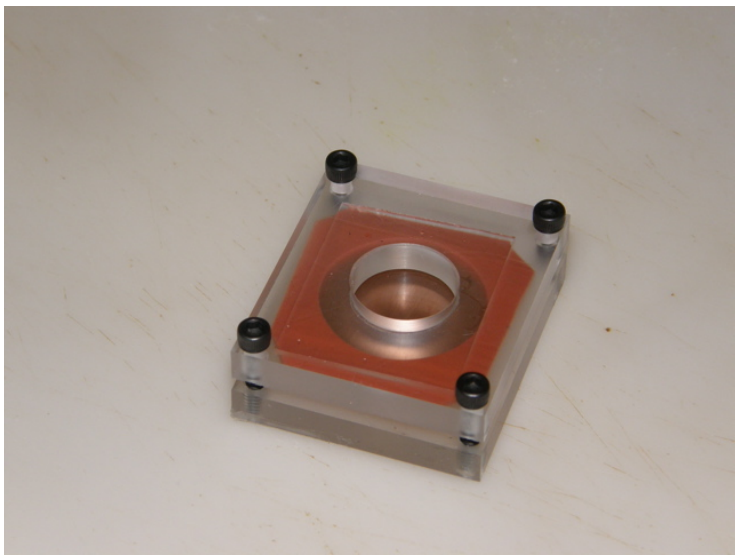


Design and Fabrication of prototype devices

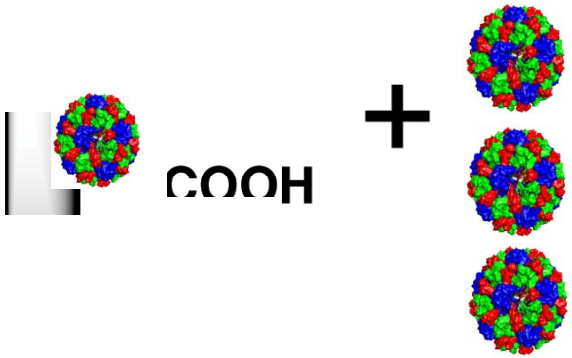
Based initially on the solution assay

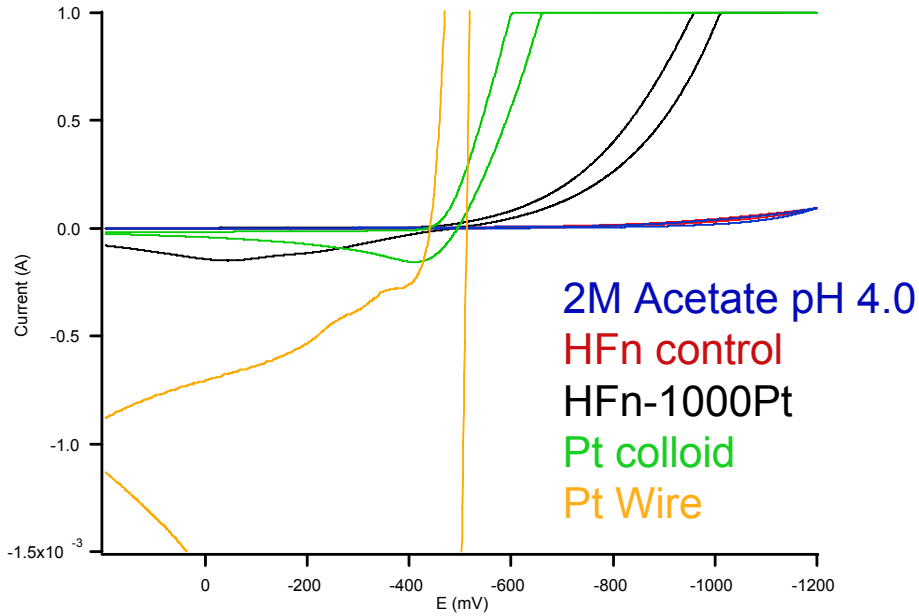


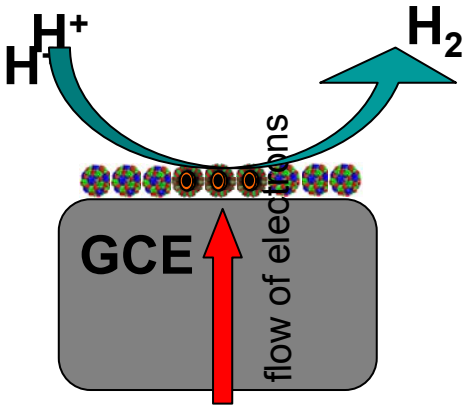


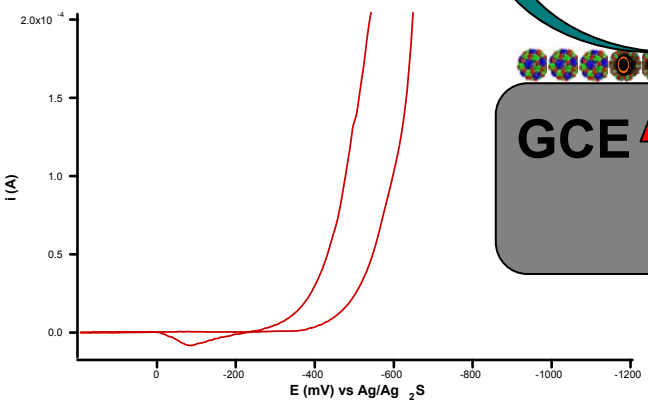


Cyclic Voltammetry to probe e⁻ transfer to catalysts





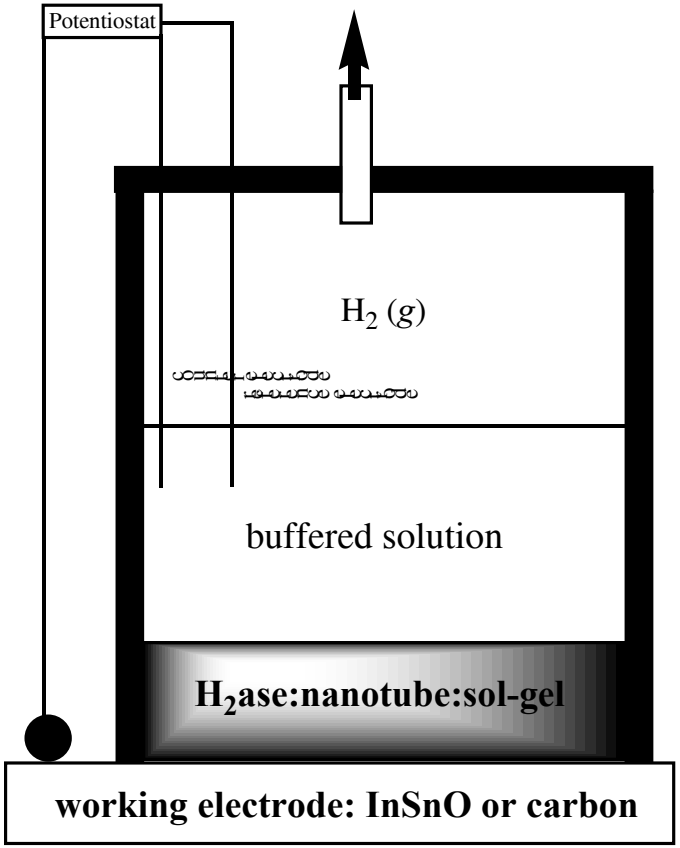


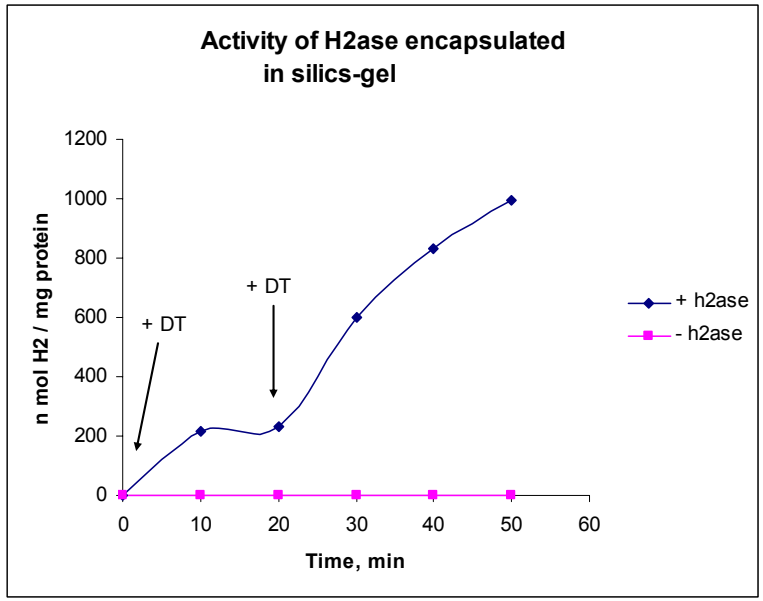


Protein shell requires an overpotential of ~200mV compared to naked Pt colloid

Attachment of MoS_x - protein cage to GCE - H_2 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_2 tolerance	Insensitive to O_2	Insensitive Reversibly oxidized in the presence of O_2 and retains activity
Efficiency of photon-to-H_2	Currently assessing*	Currently assessing*

- Reported quantum efficiency of $Ru(bpy)_3^{2+}$ photoreduction of MV^{2+} to MV^{+} 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^{+} to H_2 with both the hydrogenases and synthetic systems using devices described.

Summary

Use of biological and biomimetic catalysts for H_2 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 catayst(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_2 production