2008 DOE Hydrogen Program

Montana Palladium Research Initiative:
Use of Biological Materials and Biologically Inspired Materials for H₂ Catalysis

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Department of Chemistry and Biochemistry and Center for Bioinspired Nanomaterials

DOE Project ID#: PD34
Overview

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

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

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

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 $\text{H}_2$ production
Approach:
Biological and Biomimetic Catalysts for H₂ 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)

\[ \text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^- \]

**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 ~33 Å.

<table>
<thead>
<tr>
<th>Properties</th>
<th><em>Thiocapsa roseopersicina</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Large subunit</td>
<td>64kDa</td>
</tr>
<tr>
<td>Small subunit</td>
<td>34kDa</td>
</tr>
<tr>
<td>Temperature optimum, °C</td>
<td>80°C</td>
</tr>
<tr>
<td>Stability to Oxygen</td>
<td>stable</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Hydrogenase</th>
<th>Solution</th>
<th>Gel</th>
<th>Solution/Gel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>C. pasteurianum</em> (extract)</td>
<td>12550</td>
<td>7581</td>
<td>60.4±16</td>
</tr>
<tr>
<td><em>L. modestogalophilus</em></td>
<td>9150</td>
<td>6175</td>
<td>67.5±9</td>
</tr>
<tr>
<td><em>T. roseopersicina</em></td>
<td>12600</td>
<td>8834</td>
<td>70.1±3</td>
</tr>
</tbody>
</table>

*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. pasteurianum* (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

Reducing agent (DMAB/ BH\(_4^-\))

\[ \text{pH 6.5, 65^oC} \]

Small heat shock protein from *Methanococcus jannaschii*

Transmission electron microscopy

Size exclusion chromatography
Coupled Catalysis for H₂ Production

Initial rates (Pt):
- 4.47 x 10³ H₂/sec/Hsp
- 1.5 x 10⁴ H₂/sec/ferritin
(Hydrogenase => 6 x 10³ H₂/sec/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$^{2+}$ 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 H₂ Catalysts

Pd particles show significantly lower activity than Pt

Thermally stable 80-90°C
Oxygen insensitive
Polymer gels – control midpoint potential

poly(vinyl benzyl chloride)

γ-butyrolactone, 20 hours @ 80°C

Poly(vinylbenzyl chloride)

Crosslinked Viologen Unit

Non-Crosslinked Viologen Unit

Chemical incorporation of protein catalysts

Hepes, pH 6.5
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 MoSₓ - protein cage to GCE - H₂ 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

<table>
<thead>
<tr>
<th></th>
<th>Biomimetics</th>
<th>Hydrogenases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous</td>
<td>&gt; 60 min</td>
<td>&gt; 60 min</td>
</tr>
<tr>
<td>hydrogen production</td>
<td></td>
<td>Insensitive to O₂</td>
</tr>
<tr>
<td><strong>O₂</strong> tolerance</td>
<td>Insensitive to O₂</td>
<td>Reversibly oxidized in the presence of O₂ and retains activity</td>
</tr>
<tr>
<td>Efficiency of photon-to-H₂</td>
<td>Currently assessing*</td>
<td>Currently assessing*</td>
</tr>
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- 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 H₂ 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 \( \text{H}_2 \) production