IV.F.7 Bioinspired Composite Nanomaterials for Photocatalytic Hydrogen Production

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Objectives

- Research the feasibility of various biological and bio-inspired materials for hydrogen production
- Couple highly efficient hydrogen producing enzymes (hydrogenases) to specifically engineered photocatalysts for generating hydrogen from low-cost renewable feedstocks

Technical Barriers

This project addresses the following technical barriers described in the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- X. Light Utilization Efficiency
- Y. Rate of Hydrogen Production
- Z. Continuity of Photoproduction
- AA. Systems Engineering

Technical Targets

Photolytic Biological Hydrogen Production:

This project is conducting fundamental studies on hydrogenase long term stability and durability and semiconductor photocatalyst design and implementation. Insights gained from these studies will be applied toward the design of matrix immobilized composite hydrogen producing materials with the main components consisting of hydrogenases, photocatalysts, and electron carriers.

Approach

The project, which has not yet started, will develop the formulation of composite materials that will couple biological enzymatic catalysis and semiconductor photocatalysis for the efficient production of H₂ from simple renewable feedstocks:

The proposed work will be conducted under the following four technical tasks:

- Optimize hydrogenase stability and electron transfer capabilities
- Optimize the semiconductor nanoparticle photocatalysis, oxygen scavenging, and electron transfer properties of protein nano-cages (Figure 1)
- Gel/Matrix immobilization and composite formulation of nanomaterials and hydrogenases
- Device fabrication for H₂ production (Figure 2)

Accomplishments

To date, the research has focused on progress on the first three tasks. Toward this end, hydrogenase enzymes have been purified from the bacterium *Clostridium pasteurianum* and evaluated for their capacity to utilize various exogenous sources of electrons for the reduction of H^+ to form H_2 . Semiconductor protein-encapsulated nanoparticles have been synthesized and shown to be catalysts for the photochemical reduction of diffusible molecular electron carriers such as methyl viologen. These reduced electron carriers have also been shown to scavenge oxygen and to transfer their reducing equivalents to the hydrogenase enzymes. The hydrogenase enzymes and the protein-encapsulated nanoparticles have been encapsulated within a gel matrix and shown to retain activity. These results provide strong proof of concept in support of the overall approach of the project.



Figure 1. (a) Topology of the overall fold of the Fe-only hydrogenase from *Clostridium pasteurianum*, divided into four structural domains on the basis of the location of protein-associated [Fe-S] clusters and sequence similarity of the individual domains to individual domain or free proteins. The [Fe-S] clusters are represented as space-filling models (Fe, rust; S, yellow).
(b) The semiconductor nanoparticle encapsulated within the ferritin protein cage, which acts as a wide band gap semiconductor capable of catalysizing redox transformations such as the reduction of methyl viologen.



Figure 2. Prototype for H₂ Generating Device. This incorporates a Cu° containing outer layer for O₂ removal. Electron transfer mediators, nanoparticle photocatalysts, and hydrogenase are incorporated into the polymerized gel matrix. (• = Cu nanoparticles, * = viologen mediators)