

## II.F.4 Discovery of Photocatalysts for Hydrogen Production

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### Objectives

- Design and construct tools for high-throughput screening.
- Employ modeling to prioritize materials candidates for analysis.
- Support commercialization of photoelectrochemical (PEC) water splitting through a materials discovery process.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AP) Materials Efficiency
- (AQ) Materials Durability
- (AR) Bulk Materials Synthesis

### Technical Targets

This project will help to identify materials that will allow achievement of the technical targets for PEC hydrogen production. These targets are shown in Table 1.

**TABLE 1.** Technical Targets: Photoelectrochemical Hydrogen Production<sup>a</sup>

Characteristics	Units	2003 Status	2010 Target	2015 Target <sup>b</sup>
Usable semiconductor bandgap <sup>c</sup>	eV	2.8	2.3	2.0
Chemical conversion process efficiency (EC) <sup>d</sup>	%	4	10	12
Plant solar-to-hydrogen efficiency (STH) <sup>e</sup>	%	Not avail.	8	10
Plant durability <sup>f</sup>	hr	Not avail.	1,000	5,000

See <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/> for superscript explanations.

### Introduction

The ability to generate hydrogen from the surface of a semiconductor utilizing water as the feedstock and sunlight as the energy source has been described as a “Holy Grail” of chemistry [1]. This hydrogen generation process is termed photoelectrochemical (PEC) hydrogen generation and involves the direct utilization of photogenerated charge carriers (electrons and holes) in the splitting of water into hydrogen and oxygen. Efficient PEC hydrogen production requires a suitable photocatalyst that simultaneously satisfies four stringent requirements: 1) the material must have a bandgap width value of 1.5–1.9 eV to efficiently utilize the solar spectrum, 2) the conduction and valence band energies, or the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), of the materials must overlap the H<sub>2</sub>/H<sub>2</sub>O and O<sub>2</sub>/H<sub>2</sub>O redox potentials, 3) charge transfer across the material-liquid interface must be fast, and 4) the material surface must be chemically stable in the aqueous media under solar illumination. There are materials that satisfy some of these requirements; for example, InGaP<sub>2</sub> has shown promising efficiencies but suffers from poor stability [2], while TiO<sub>2</sub> is very stable but is very inefficient, i.e., low solar energy to hydrogen conversion.

The goal of this project is to develop tools that will allow for high-throughput screening of materials for use in PEC hydrogen production. The use of high-throughput screening will allow for the investigation of a greater number of materials and will increase the probability that appropriate materials for PEC hydrogen production can be discovered.

## Approach

The approach of the project is to take advantage of the high surface area of nanoparticles to increase the efficiency of  $\text{TiO}_2$  and  $\text{TiO}_2$ -based materials. The  $\text{TiO}_2$  nanoparticles are produced using a proprietary laser pyrolysis process (see Figure 1). The materials are tested for PEC hydrogen production using a 25-cell analysis module, shown in Figure 2. We have incorporated a modeling aspect that has provided evidence that nano-rod core-shell materials may provide for increased efficiencies.

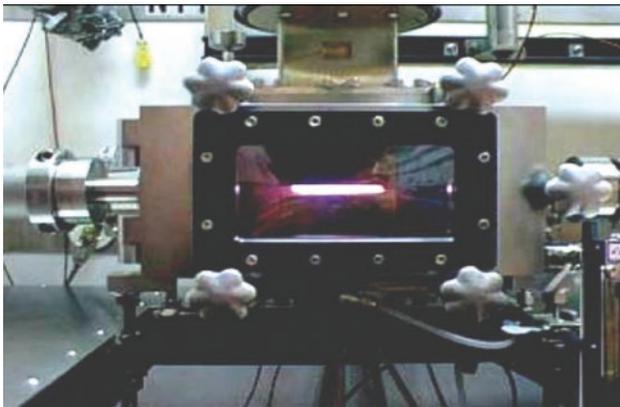


FIGURE 1. Close-Up of the Reaction Zone in the NanoGram Laser Pyrolysis Process

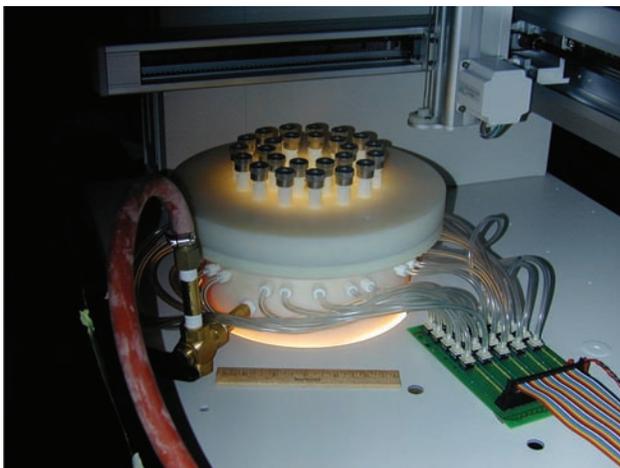


FIGURE 2. 25-Cell Photolysis Analysis Module

## FY 2006 Progress

This project concluded on January 31, 2006. The progress made in FY 2006 included modeling refinement and generation of nanostructures in an attempt to validate the models. In the modeling analysis [3] we employed a strain-dependent  $k.p$  Hamiltonian, which can describe various nanostructures made from III-V and II-VI semiconductors, and calculated electronic structures and wave functions of some core-shell nano rods (Figure 3). We find that InP-CdS and InP-ZnTe core-shell nano-rods can be tailored to satisfy all the criteria established for efficient PEC hydrogen production, and therefore are promising nano photocatalysts. For example, the results of modeling 2 nm InP core with a 3 nm shell are shown in Figure 4. As indicated upon photoexcitation of the InP (left side of diagram) the hole will be energetically favored to remain in the core while electron will be energetically favored to migrate to the ZnTe shell. The opposite is predicted for the ZnTe shell with the photogenerated hole migrating to the InP core and the electron remaining in the shell. This efficient charge separation should increase the quantum efficiency of PEC hydrogen generation as well as to increase stability of the system.

The synthetic aspect of this project has not been successful in generating structures similar to those that the modeling predicts to exhibit improved performance. The primary difficulty was getting an array of nano-gold catalyst on a conducting substrate with suitable dimensions, both diameter and pitch. As a result, the minimal diameter of the rods that were grown were on the order 100 nm. Since the completion of this project strategies to overcome this obstacle have been generated and further funding is being pursued to continue this work.

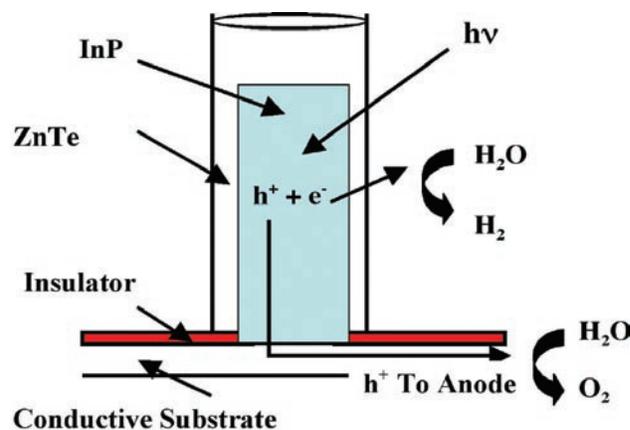
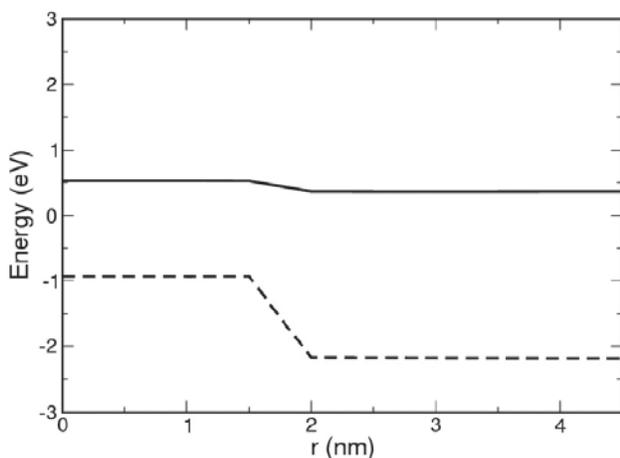


FIGURE 3. Core-Shell Structure Generated from Modeling Indicating Charge Carrier Flow



**FIGURE 4.** Calculated Energy Level Diagram of InP-ZnTe Core-Shell Nanorods

### FY 2006 Publications/Presentations

1. Yu Z. G., Pryor C. E., Lau W. H., Berding M. A. and MacQueen DB. Core-Shell Nanorods for Efficient Photoelectrochemical Hydrogen Production. *J. Phys. Chem. B* 2005, **109**, 22913-22919.

### References

1. A. J. Bard and M. A. Fox, *Acc. Chem. Res.*, **28**, 141 (1995).
2. O. Khaselev and J. Turner, *J. Electrochem. Soc.*, **145**, 3335-3339 (1998).
3. Z. G. Yu, C. E. Pryor, W. H. Lau, M. A. Berding and D. B. MacQueen Core-Shell Nanorods for Efficient Photoelectrochemical Hydrogen Production. *J. Phys. Chem. B* 2005, **109**, 22913-22919.

### Conclusions and Future Directions

- Nanoparticles show improved activity relative to monoliths primarily as a result of increased surface area on a per weight basis for the nanoparticles.
- Engineering complications of using nanoparticles will probably offset their surface area advantage.
- Modeling of nanostructures indicates potential for improved performance of PEC systems through proper design and synthesis.
- B. MacQueen is a consultant on an EPSCOR funded three year effort lead by Jawwad Darr, Queen Mary University-London, to assist development of PEC catalysts using his continuous hydrothermal synthesis technology.
- DOE-BES funding is being pursued to continue the nanorod core-shell modeling and synthetic efforts.