IV.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 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.

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Table 1. Technical Targets: Photoelectrochemical Hydrogen Production

Characteristics	Units	2003 Status	2010 Target	2015 Target
Usable semiconductor bandgap	eV	2.8	2.3	2.0
Chemical Conversion process efficiency (EC)	%	4	10	12
Plant solar-to-hydrogen efficiency (STH)	%	Not avail.	8	10
Plant durability	hr	Not avail.	1000	5000

For further explanation see http://www.eere.energy.gov/hydrogenandfuelcells/mypp/

Approach

- Develop tools for high-throughput analysis
- Use modeling to identify candidate materials for further study via high-throughput screening

Accomplishments

- TiOxNy and TiOS materials show improved efficiency relative to TiO_2
- Efficiency still a factor of 5-10 lower than 2010 target
- Stability: TiOS <5% loss after 20 hours
- $(AgIn)_xZn_{(1-x)}S$ investigated
- Solar simulator constructed for long-term experiments
- Modeling indicates core-shell nano-rods as potential structures for improved PEC hydrogen production

Future Directions

- Complete analysis of nanoparticle semiconductors
- Generate proof of concept of core-shell nano-rod modeling
- Conduct long-term testing, >20 hours, of best materials

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_2/H_2O and O_2/H_2O 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, $InGaP_2$ has shown promising efficiencies but suffers from poor stability [2], while TiO_2 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 TiO_2 and TiO_2-based materials. The 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.

Results

Modeling

We find that core-shell InP-CdS and InP-ZnTe nano-rods, where both energies and wave-function distributions of electrons and holes can be tailored to a considerable extent, can meet all criteria and therefore serve as promising photocatalysts for PEC hydrogen production.

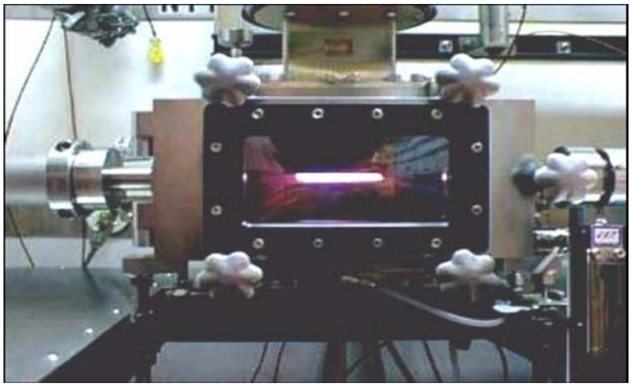

Figure 1. Close-Up of the Reaction Zone in the NanoGram Laser Pyrolysis Process

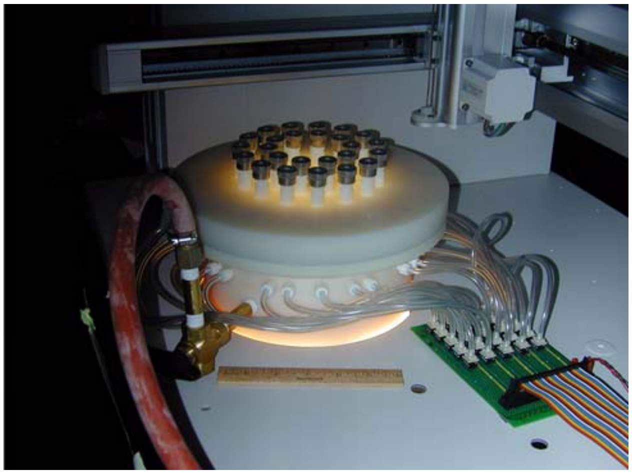

Figure 2. 25-Cell Photolysis Analysis Module

The calculations are carried out on a cubic grid with periodic boundary conditions. First, the strain is calculated using linear continuum elastic theory [3]. The strain energy for the system is computed using a finite differencing approximation, and then minimized using the conjugate gradient algorithm. The electronic structure is solved in the envelope approximation using a four-band strain-dependent *k.p* Hamiltonian, which has been proven to be reliable to predict electronic structures in various nanostructures.

We exploit quantum confinement as well as its interaction with strains in coaxial cylindrical core-shell nano-rods (see Figure 3) for dimension definitions, to effectively tailor the electronic structures. We plot P_{core} (Figure 4), the integrated charge distribution in the core, and the energies (Figure 5) of the HOMO and LUMO as a function of core radius R_1 in InP-CdS nanorods with fixed height H=2 nm and overall radius R=5 nm. P_{core} measures whether an eigenstate is mainly in the core (P_{core}>0.5) or in the shell (P_{core}<0.5). We see that at small core radii, the HOMO and the LUMO are well spatially separated, with the HOMO predominantly in the core and the LUMO in the shell. With increase of the core radius, the LUMO gradually moves from the shell to the core, and eventually both the HOMO and the LUMO become localized in the core. As the core radius increases from R_1=1 nm to 4 nm, the HOMO energy changes

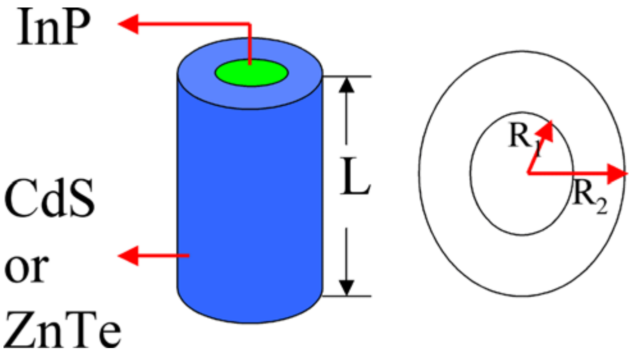

Figure 3. Core-Shell Nano-Rod Structure Indicating Dimension Definitions

from -1.33 eV to -1.08 eV, and the LUMO changes from 0.56 eV to 0.72 eV. Both energy changes are large enough to satisfy the overlap requirement.

The envisioned device structure based on the core-shell InP-CdS nano-rods for hydrogen production is illustrated in Figure 6. In this structure, InP is protected from corrosion in water by the large-gap CdS. The electron (LUMO) and the hole (HOMO) of a photoexcited electron-hole pair are spatially separated, with the former in the shell while the latter is in the core, leading to faster and more efficient charge transfer. The energies of the HOMO and LUMO can be shifted upward or downward to overlap the water redox potentials. Thus, all the aforementioned criteria are satisfied.

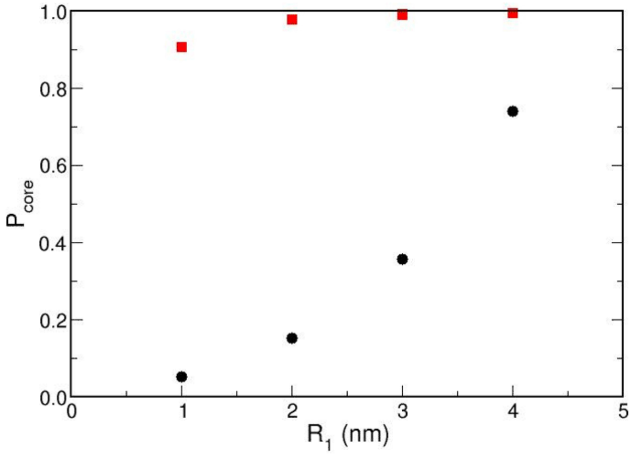

Figure 4. Integrated Charge Distribution in the Core for the HOMO (squares) and the LUMO (circles) as a Function of R_1 in Core-Shell InP-CdS Nano-Rods with Fixed R=5 nm and H=2 nm

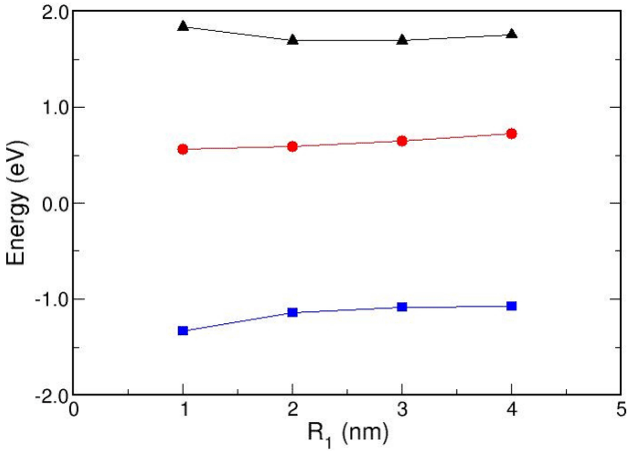

Figure 5. Energies of the HOMO (squares) and the LUMO (circles) as well as the Energy Gap (triangles) as a Function of R_1

Synthesis

A series of TiON materials was prepared by the hydrolysis reaction of Ti(isopropoxide) and diethylamine, similar to that reported by [4]. Another series of TiON samples was prepared by the reaction of NanoGram's TiO_2 nanoparticles with ammonia at temperatures from 400°C to 600°C, similar to the procedure reported by [5]. All particle sets were platinized at 2% using the previously described photo-decomposition method. The results with the materials made by the hydrolysis reaction were similar to those reported of the NanoGram-made materials but with a somewhat improved performance relative to what has been reported.

Work has also been initiated on the growth of InP nano-rods on surfaces using protocols established in the literature, see for example [6-7].

Part of the synthetic work performed this reporting period focused on $(AgIn)_xZn_{(1-x)}S$. The materials were prepared in a similar fashion as that reported by [8], with some modification to the stochiometries and process conditions. The yields of hydrogen have yet to be determined in detail; however, initial data indicate that this material is approximately 20 times more efficient than the P25 reference material.

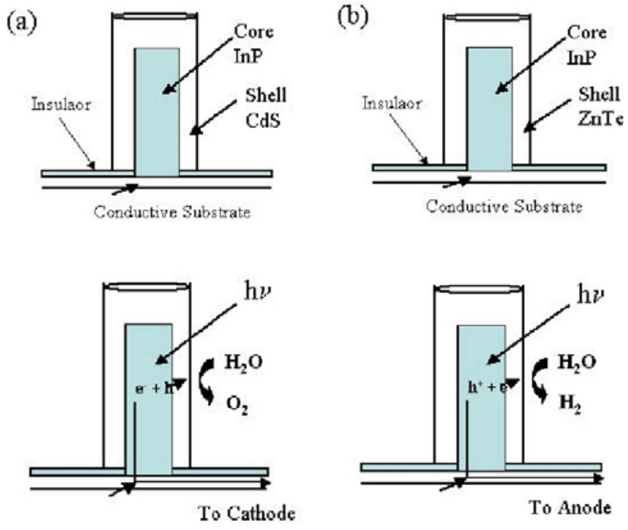

Figure 6. Suggested Nano-Rod Core-Shell Structures and Mechanism of Charge Separation

Instrumentation

This year, a solar simulator, air mass (AM) 1.5 and 3 inch illumination area, was constructed from existing parts at SRI as well as those purchased from a surplus retailer. This unit will be used to determine photolysis products over longer (>20 hours) periods.

Conclusions

- Efficiencies have been improved, although still significantly below 2010 targets.
- Modeling indicates core-shell nano-rod approach should improve efficiencies.

FY 2005 Publications

1. Progress Report 7, covering 1st quarter FY 2005
2. Progress Report 8, covering 2nd quarter FY 2005
3. Progress Report 9, covering 3rd quarter FY 2005 (in progress)

FY 2005 Presentations

1. *Discovery of Photocatalyst for Hydrogen Production, NanoSig Clean Energy & Nano Catalyst Conference, August 20th, 2004, SRI International, Menlo Park, CA.*

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