

Photoelectrochemical Systems for H₂ Production

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Objectives

- Identify and characterize new semiconductor materials that are capable of splitting water using sunlight as the only energy input.
- Improve the durability (stability) of semiconductor materials in aqueous solutions.
- Develop multijunction high-efficiency water-splitting systems to meet the 2015 target of 14% solar-to-hydrogen efficiency.
- Apply basic science understanding for control of the energetics of the semiconductor in solution (band edge engineering).
- Develop techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.

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 R,D&D Plan:

- M. Material Durability
- O. Photoelectrochemical Efficiency

Approach

- Discover, research and develop semiconductor materials for improved photoelectrochemical (PEC) systems.
- Optimize and control energetics, developing a fundamental understanding of semiconductor surface interactions with aqueous solutions.
- Identify materials for protective coatings and materials for catalysis.

Accomplishments

- First PEC study of In_xGa_{1-x}N (0<x<0.14) material.
- First PEC study of GaAsPN material.

- First synthesis of CuInGaSSe material with band gaps in the range 1.6-2.0 eV.
- First study of the surface modification of GaInP₂ with water soluble metallo-porphyrins.

Future Directions

- Evaluate nitride materials as longer lifetime water splitting systems.
- Develop multijunction systems for high efficiency.
- Explore thin film materials as low-cost water splitting systems.
- Develop protective coatings that reduce corrosion and provide catalysis.
- Explore approaches for control of surface energetics.

Introduction

The direct PEC splitting of water is a one-step process for producing H₂ using solar irradiation; water is split directly upon illumination. This type of direct conversion system combines a photovoltaic material and an electrolyzer into a single monolithic device. For this one-step process to be viable, two basic criteria must be met: the light harvesting system must have the correct energetics to effect the decomposition of water, and the system also must be stable in an aqueous environment. Direct conversion photoelectrochemical systems not only eliminate most of the costs of an electrolyzer, but they also have the possibility of increasing the overall efficiency of the process (as compared to photovoltaic (PV)/electrolysis), leading to a further reduction in the cost of delivered hydrogen.

Approach

PEC hydrogen production is in an early stage of development, and it depends on a breakthrough in materials development. The primary effort in this project is to synthesize a semiconducting material or a semiconductor structure with the necessary properties. For the direct PEC decomposition of water to occur, three key energetic conditions and the criteria of stability for the semiconductor must be met. For the energetic conditions, the semiconductor's band gap must be sufficiently large to split water and yet not too large as to prevent efficient absorption of the solar spectrum (ideally 1.8-2.2 eV), the band edges of the semiconductor must overlap the hydrogen and oxygen redox potentials, and the charge transfer across the

semiconductor/liquid interface must be fast enough to prevent band edge migration. In addition, the semiconductor's surface must be stable against corrosion both in the dark and under illumination. Our study of PEC direct-conversion systems involves two areas of research: semiconducting materials and surface treatments. Semiconducting materials can be divided into two types based on their solid state structure: single photon absorbers and multiphoton devices. Surface treatments include coatings to address energetic issues, corrosion problems, and catalysts for the water splitting reactions.

Materials research in this area is progressing on two fronts: 1) working on the high efficiency materials in order to apply basic scientific understanding to lower efficiency, low-cost materials, and 2) working on the durability of low-cost materials in order to apply basic scientific understanding to higher efficiency, lower durability materials. Currently, the highest efficiency systems have the shortest lifetimes, and the lower efficiency systems have the longest lifetimes. The optimal system will likely be a compromise between efficiency and lifetime.

Results

As part of our search for semiconductor materials with inherently greater stability, we have been studying the group III-nitrides for use as PEC materials. Earlier work in our group has shown that GaN can split water and is stable under certain operating conditions. While it is known that GaN is chemically very stable, its band gap is too large (~3.4 eV) to be an efficient PEC device. We have also

shown that adding indium to the material can lower the band gap and that it appears that the composition of $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be adjusted to produce a band gap suitable for solar water-splitting applications. Our best $\text{In}_x\text{Ga}_{1-x}\text{N}$ material currently synthesized has a band gap of 2.71 eV (Figure 1). To be a useful material for water splitting, this band gap must be lowered further by increasing the amount of indium. Work is continuing in this area.

Another material that shows excellent stability in aqueous solution and has a bandgap in the appropriate range for good solar absorption (2.25 eV) is gallium phosphide (GaP). Unfortunately, this is an indirect band gap, leading to low solar absorption efficiency and low conversion efficiency. Recent work has shown that adding a small amount of nitrogen to the GaP lowers the band gap and creates a direct transition. The combination of a smaller band gap and a direct transition would produce a much more efficient system. The $\text{GaP}_x\text{N}_{(1-x)}$ material is being synthesized at NREL as part of their work for the DOE Solar Energy Program, which makes it particularly interesting for an initial study. Figure 2 shows our data on measurement of the band gap. As expected, there is a direct transition and a nearly ideal band gap of 1.9 eV. Further characterizations are necessary to determine if this material can function as a water-splitting device.

Thin-film copper indium gallium diselenide (CIGS) devices are well known for their high conversion efficiency when prepared as polycrystalline thin films. Electrodeposition is a

potentially scalable technique for large area thin film fabrication at reduced costs. In fact, CIGS films have been successfully prepared from electrodeposited precursors to yield solar energy conversion devices with an efficiency of 15.4%. Sulfur incorporation has also been used in CIGS solar energy materials to increase device performance and to provide a graded band gap structure. Our effort in this area was to incorporate sulfur throughout the entire film, to obtain a material exhibiting a higher band gap that is suitable for water splitting. The combination of lower system manufacturing cost (from electrodeposition) and a high efficiency material represents an important area of research for hydrogen production systems. In addition, indium in the film may provide some protection against corrosion. In aqueous solution, indium can form a conducting oxide layer that stabilizes the interface and may protect the underlying material. In this initial effort, $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ thin semiconducting films were made from electrodeposited $\text{Cu}(\text{In,Ga})\text{Se}_2$ precursors, followed by physical vapor deposition of In_2S_3 , Ga, and Se. The band gaps of these materials were found to be between 1.6 and 2.0 eV (Figure 3), which spans the optimal band gap necessary for application for the top junction in PV multijunction devices and unassisted water photolysis. Note also that this research demonstrates the ability to synthesize materials with a full range of band gaps from a single material set.

In the area of bandedge engineering, gallium indium phosphide (GaInP_2) surfaces were modified with metallo-porphyrin compounds in order to shift

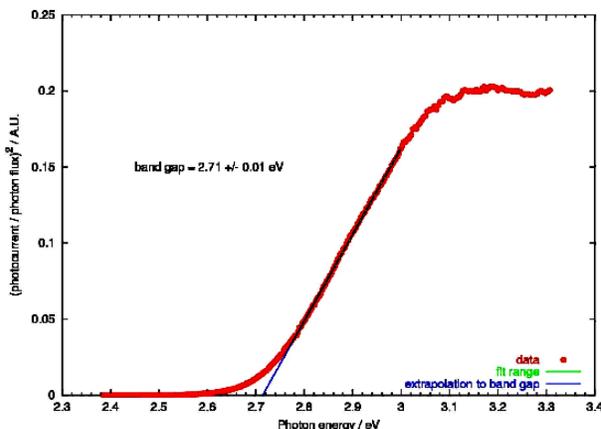


Figure 1. Band Gap Analysis of the Photocurrent Spectrum for Sample $\text{In}_{0.14}\text{Ga}_{0.86}\text{N}$

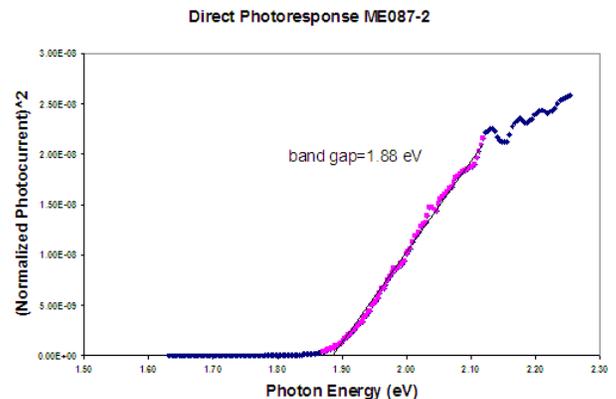


Figure 2. Band Gap Analysis of GaPN Material

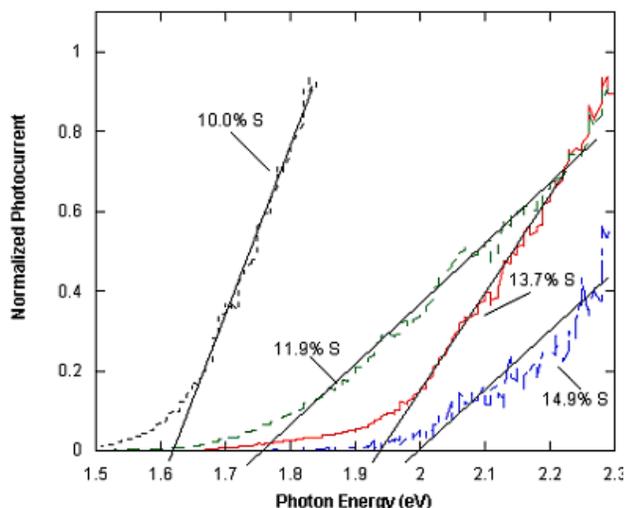


Figure 3. Photoresponse Measurements of Thin Films With Varying Composition (Atomic percent sulfur in each film is shown)

the semiconductor's band edges. Compounds used included Nickel(II)-Tetra(N-Methyl-2-pyridyl) porphyrin chloride [NiTMPyP(2)], Fe(III)TMPyP(2), and VO(IV)TMPyP(4). Sample treatments using these water-soluble compounds were applied by immersion of the semiconductor in a solution of the porphyrin for varying lengths of time. The position and movement of GaInP₂ band edges were monitored by capacitance measurements, and shifts of up to 1 volt were observed after some surface treatments. While a shift of 1 volt should be sufficient to allow GaInP₂ to split water, no water splitting was observed. Work is continuing to determine what is preventing the system from operating as we expected.

Conclusions

- Nitride materials based on GaInN are possible high-efficiency, water-splitting materials, showing good stability and the correct energetics.
- Initial studies on nitride materials based on GaPN showed that achieving the necessary band gap was possible.
- Surface studies of water-soluble, porphyrin-modified GaInP₂ showed that it is possible to affect the energetic position of the semiconductor band edges.

- Work on the thin-film CuInGaSSe system showed that it is possible to synthesize material with band gaps in the range 1.6-2.0 eV.

FY 2003 Presentations

- Presentation for the Chemistry Department of the Colorado School of Mines entitled "Photoelectrochemical Direct Water Splitting Systems."
- Presentation for North Carolina State University entitled "Photoelectrochemical Systems for Hydrogen Production via Direct Water Splitting."
- Presentation at the American Institute of Chemical Engineers' Spring meeting, speaking in a session on climate change.
- Presentation at the American Physical Society's Spring meeting, speaking in a session on climate change.
- Presentation at the U.S. DOE Hydrogen Program's first Quarterly Program Performance and Results Briefing, for upper DOE management.
- Lecture on renewable energy and hydrogen at the University of Colorado for a class on energy and the environment.
- Banquet speaker at the Northwest regional American Chemical Society meeting in Spokane, Washington.
- Presentation at the California Alternative Energy Retreat in Bishop, California, speaking on the general topic of hydrogen.
- Presentation at the California Hydrogen Business Council, speaking on the NREL Hydrogen Program research.
- Presentation at the Georgia Tech "Blue Skies" symposium speaking on the hydrogen economy.
- Two talks at the XII International Materials Research Congress, Mexico, "Band edge Engineering of p-GaInP₂ Electrodes with Porphyrins, Pthalocyanins and other Organic Molecules," and "Corrosion Studies of Stainless Steels for Bipolar Plate Material in Polymer Electrolyte Membrane Fuel Cells."

- Presentation at the National Hydrogen Association meeting entitled "Hydrogen and Energy Security: Key Issues and Potential" with Jim Ohi.
- Presentation on the hydrogen economy at the ASM International Oak Ridge Chapter, Oak Ridge, Tennessee.
- Two presentations at Ashland University, Ashland, Ohio, one entitled "Renewable Energy Systems, Energy Storage and Hydrogen," and a second one for local high school students entitled "Energy and Hydrogen, Today and Tomorrow."
- Presentation on fuel cells and hydrogen to the Clean Energy States Alliance Spring 2003 Meeting.
- Presentation at GE Central Research on photoelectrochemical water splitting.
- Presentation at the International Electrochemical Society meeting (invited) entitled "Integrated Multijunction Photovoltaic/Electrolyte System for Water Photoelectrolysis."

FY 2003 Publications

1. V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, G. M. Stepanyan, J. A. Turner, and O. Khaselev, "Investigation of Ceramic Fe_2O_3 Photoelectrodes for Solar Energy Photoelectrochemical Converters," *International Journal of Hydrogen Energy*, 27, p 33 (2002).
2. Scott Warren and J. Turner, "Increasing the Efficiency in Photoelectrochemical Hydrogen Production," *USDOE Journal of Undergraduate Research*, p 75 (2002).
3. J. D. Beach, H. Al-Thani, S. McCray, R. T. Collins, and J. Turner, "Bandgaps and Lattice Parameters of 0.9 μm Thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ Films for $0 < x < 0.140$," *J. Appl. Phys.*, Vol 91, No. 9, (2002).
4. X. Mathew, A. Bansal, J. Turner, R. Dhere, N. Mathews and P. Sebastian, "Photoelectrochemical Characterization of Surface Modified CdTe for Hydrogen Production," *J. New Mat. For Electrochemical Systems*, Vol 5 149-154 (2002).

Special Recognitions & Awards/Patents Issued

1. Outstanding Mentor Award from the Office of Science, U.S. Department of Energy.