II.H.12 Photoelectrochemical (PEC) Hydrogen Generation*

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*Congressionally directed project

Objectives

The goal is to produce hydrogen economically using photoelectrochemical (PEC) electrolysis of water directly from sunlight with corrosion resistant semiconductor electrodes for catalytic conversion. The specific objectives are:

- Improve (a) photo-conversion efficiency (solar-to-hydrogen [STH] ratio) to 10 percent evolving H_2 and O_2 and (b) photo-corrosion resistance of photo-anodes for 5,000 hours of operation generating H_2 from water.
- Synthesize photoanodes maximizing both light absorption and photoactive sites for high STH conversion.
- Develop surface engineered TiO_2 and $TiSi_2$ nanostructured photoanodes (nanotubes and nanorods) doped with N, to reduce the effective band gap.
- Develop a hybrid semiconducting photoanode, $TiSi_2$, with a corrosion inhibiting TiO_2 protective layer.
- Use heterogeneous, nanostructured, and hybrid semiconductor photoanodes consisting of layered electrodes made of $TiSi_2$ and TiO_2 for electrolyzing water.
- Perform fundamental studies on surface energetics: (a) control of surface states, (b) minimization of traps that are responsible for recombination of photo-excited charge carriers at the interface, and (c) reduction of photocorrosion of semiconductor electrodes.
- Design and construct a prototype hydrogen generator for demonstration.

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:

(Y) Materials Efficiency
(Z) Materials Durability
(AC) Device Configuration Designs

Technical Targets

Our technical target is to reach the DOE goals:

- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant STH efficiency: 8% by 2010 and 10% by 2015
- Hydrogen production cost: $3.00/gge (approximately 1 kg of H_2) by 2018

The band gap of the semiconductor electrode needed in PEC electrolysis must not be higher than 2.5 eV in order to harvest the bulk of the solar flux which resides within the wavelength range 350 to 800 nm, and the band-edge of the semiconductor must straddle the electrochemical redox potentials of water [1,2]. The semiconducting electrode must be corrosion-resistant in contact with the electrolytes used in the PEC cell for splitting water. However, most stable semiconducting electrodes have large band gaps and hence low efficiency for photo-conversion for the entire spectrum of solar radiation. Reduction of band gap by doping the bulk of the semiconductor has not been found successful since such a process introduces charge carrier traps and compromises electron conduction and

material durability. Small bad gap electrodes suffer from poor stability, inadequate charge transfer properties and a high charge recombination rates.

The primary focus is to develop photoanodes with high photo-conversion efficiency in order to develop PEC-based hydrogen generators that are scalable, financially attractive in the global economy, and environmentally safe.

Accomplishments

- Titanium disilicide ($TiSi_2$) thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation have been synthesized.
- Electrochemical synthesis of patterned TiO_2 nanorods and nanotubes with separations comparable to wavelength of visible light for trapping solar radiation.
- Multi-layered photoanodes for high efficiency photo-conversion and minimization of photocorrosion.
- Plasma treatments of photoanodes for (a) removing charge traps, (b) surface doping with nitrogen, and (c) creating oxygen vacancies for achieving high photocurrent density.
- Design of prototype PEC hydrogen generator with a solar radiation concentrator for optimized operation.

Approach

(1) We used TiO_2, photoanodes for its stability, inertness and cost effectiveness, in our investigations on (a) the development of nanostructred photoanodes, (b) surface doping with N, (c) plasma treatments for removing surface contaminants, (d) reducing traps of interfacial charge carriers, and (e) optimization of photocurrent density.

(2) Since the band gap of $TiSi_2$ semiconductor electrodes varies over a wide range from 1.5 eV to 3.4 eV, our approach during this year has been on the use $TiSi_2$ for electrolyzing water.

(3) A thin layer of TiO_2 semiconductor needs to be applied as a protective cover over the $TiSi_2$ layer for inhibiting corrosion. TiO_2 is one of the most stable semiconductors for PEC application but its wide bandgap allows harvesting photons only in the ultraviolet range.

(4) The interfacial charge transfer process between the layered semiconductors will be optimized by controlling the thickness of the films to match the width of the charge depletion layers and by plasma surface treatments. Both $TiSi_2$ and TiO_2 are good electron conductors; hence minimal recombination losses are expected when penetration depth is made equal to the film thickness and the width of the charge depletion layer.

(5) Our approach has been to use patterned nanotubular electrodes that maximizes both light absorption efficiency and interfacial sites for oxidizing water. Based on our studies, we are synthesizing triple layer nanotubular arrays with wall thickness comparable to the diffusion length of the holes. The outer surface of the nanotubular electrodes is to be plasma treated with nitrogen in order to create oxygen vacancies at the outer surface layer forming TiN and to increase the height of the charge depletion layer.

(6) We are currently testing the photo-corrosion resistance of TiO_2 and $TiSi_2$ photoanodes using electrochemical impedance spectroscopy under ultraviolet and visual radiation exposures. We will test and evaluate the prototype hydrogen generator following the standard test protocol developed by the DOE PEC working group.

(7) Our approach has been focused on the design and construct of an integrated laboratory scale self-standing PEC-based hydrogen generators using heterogeneous, nanostructured hybrid layered electrodes made of $TiSi_2$ and TiO_2 semiconductors with solar concentrators (Figure 1).

Results

- Development of titanium disilicide thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation (Figures 2, 3).
- Deposition of thin layer of $TiSi_2$ (Figure 2).

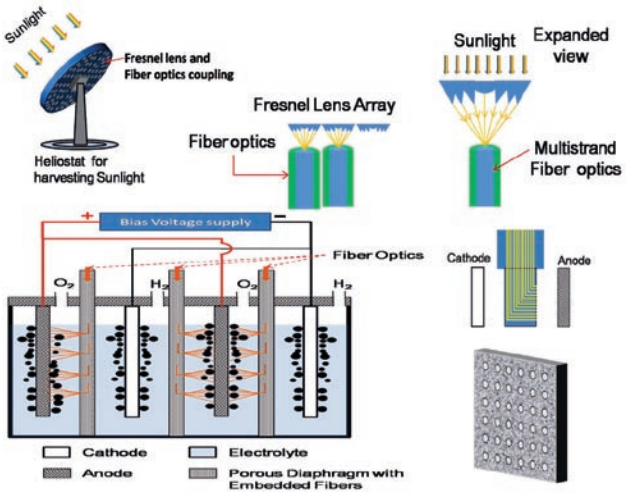

FIGURE 1. Design of an Integrated Laboratory Scale Hydrogen Generator using Stacked PEC Cells and Solar Concentrator

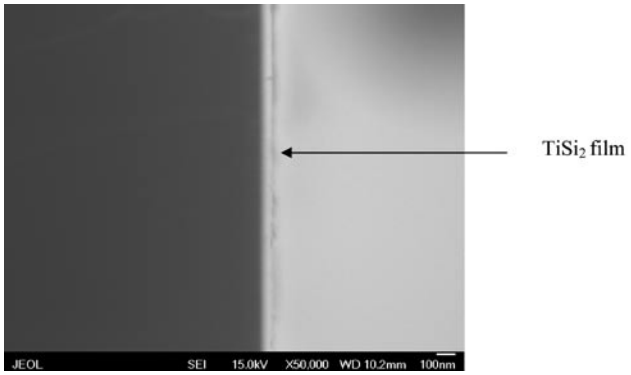

FIGURE 2. Scanning Electron Microscope Image of a Titanium Silicide Film on a Silicon Substrate

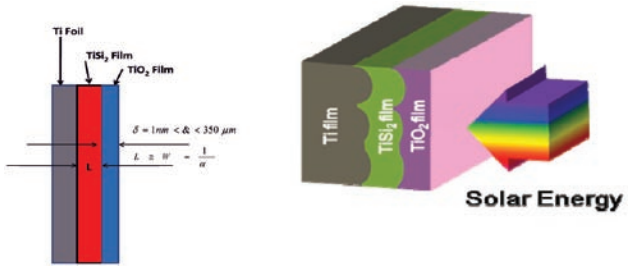

FIGURE 3. Application of layered photoanodes using $TiSi_2$ and TiO_2 semiconductors. $TiSi_2$ electrode with coating of a transparent TiO_2 electrode to be used for studying the PEC activities.

- Development of patterned nanotubular structure by ramping voltage during electrochemical anodization process (Figure 4).
- Design of two-layer nanotubes of TiO_2 and $TiSi_2$ (Figure 4).
- Nanotube fabrication with stepped voltage anodization (Figure 5).
- Optimization of nitrogen plasma treatment process for maximizing photocurrent density.
- Optimization of the annealing process for nanotubular electrodes.
- Plasma surface modifications have shown to minimize the presence of hole traps at the interface and provide remarkable increase in photocurrent density.
- Design of PEC-based hydrogen generator with photoanodes consisting of layered electrodes made of $TiSi_2$ and TiO_2 for electrolyzing water (Figure 6).

Conclusions and Future Directions

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma process for surface doping of TiO_2 nanotubular photoanode

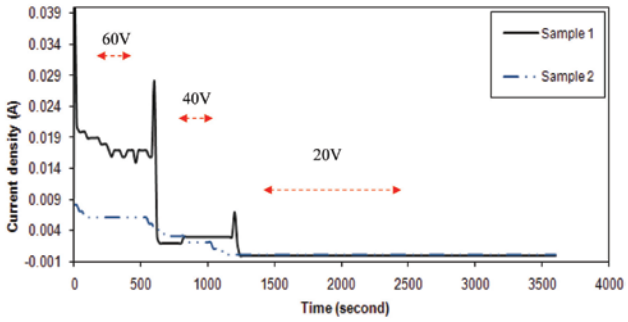

FIGURE 4. Current transient during anodization of Ti while ramping the voltage from 60 V to 20 V.

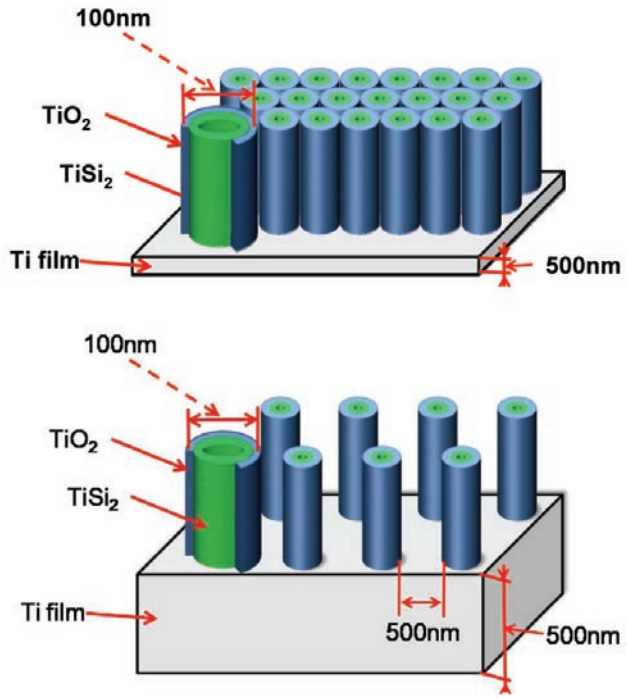

FIGURE 5. Design of two-layered nanotubes in packed form with their outer walls in contact with each other (top) and two-layered nanotubes with their walls separated from each other with spacing equal to the wavelength of incident light (bottom). The separation between the walls traps incident light for improved absorption.

with N for decreasing surface bandgaps and (3) annealing process for crystallization for improving photocatalytic generation of hydrogen by splitting water. TiO_2 nanotubular photoanodes can be prepared by anodization of a titanium foil in an electrolyte containing ethylene glycol, ammonium fluoride, and distilled water. The diameters of the nanotubes were varied by adjusting the anodization voltage and the length of the nanotubes were varied by varying the time period of anaodization. Conical shaped nanotubes with their bases larger than the diameter of their tips were prepared by anodizing at stepped voltages

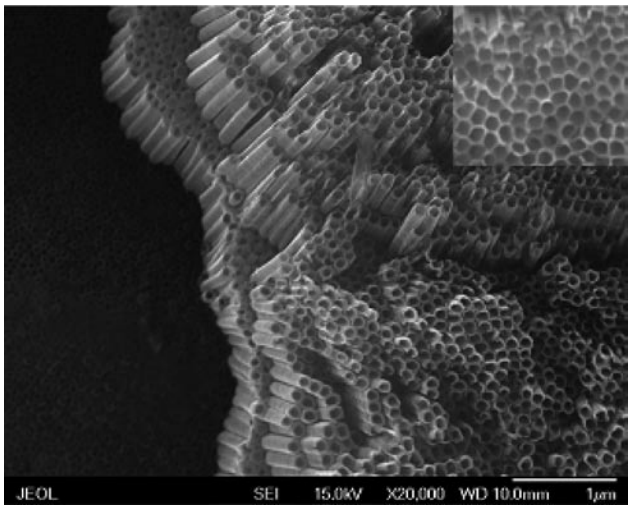

FIGURE 6. Scanning electron microscope image showing the three layer of TiO_2 nanorods formed when the anodization was carried out by ramping the voltage from 60 to 20 Volts.

60 V–40 V–20 V volts for a total time period of 60 min. Nanotubular structure of TiO_2 photoanodes prepared at stepped voltages showed 55% improved photocurrent density compared to the anodic structures prepared by constant voltage anodization.

The present studies also showed that plasma surface doping in nitrogen atmosphere is very effective for improving photocurrent density. Plasma surface doping of TiO_2 nanotubular photoanodes for 20 min showed 80% improvement of photocurrent density measured under the same condition but without plasma treatment process. In sum, the test results show promising aspects of tuning several parameters involved in photoelectrochemical processes in improving conversion efficiency. The structural aspects and surface chemistry both influence greatly the efficiency of solar energy conversion in photocatalytic and photovoltaic processes.

FY 2009 Publications and Presentations

1. 2009 DOE Hydrogen Program Review - Washington, D.C. – May, 2009. Presentation # PDP08.

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3. Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma, Franklin Hardcastle, Alexandru S Biris, and Malay K Mazumder, "Electrochemical synthesis of titania nanotube array for photoelectrochemical hydrogen production," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16–19, 2009.

4. Franklin D. Hardcastle, Hidetaka Ishihara, Rajesh Sharma, and Alexandru S. Biris, "The Structure of Titanium Oxide in Titania (TiO2) Photoactive Water-Splitting Catalysts by Raman Spectroscopy," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16–19, 2009.

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6. R. Sharma, P.P. Das, V. Mahajan, J. Bock, S. Trigwell, A.S. Biris, M.K. Mazumder, M. Misra, "Enhancement of Photoelectrochemical Conversion Efficiency of Nanotubular TiO2 Photoanodes using Nitrogen Plasma Assisted Surface Modification," Nanotechnology, Vol. 20, 2009, 075704.

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8. R. Sharma, P.P. Das, M. Misra, V. Mahajan, J. Bock, S. Trigwell, A.S.Biris, and M.K. Mazumder, "Photo electrochemical performance of Plasma treated Titanium-di-oxide nanostructures," *Materials Research Society Fall Meeting, Boston, MA, 2008.*

9. R. Sharma, M. Misra, V. Mahajan, P. Das, J. Bock, A.S.Biris, M.K. Mazumder, "Application of atmospheric-pressure plasma for enhancing photoelectrochemical properties of TiO_2 electrodes," *IEEE Industry Applications Society 43rd Annual Meeting*, Edmonton, Canada, 2008.

10. M.K. Mazumder, R. Sharma, P.P. Das, M. Misra, "Interfacial Charge Transfer in Photo-electrochemical Generation of Hydrogen from Water," *in Proc. Electrostatic Society of America Annual Meeting*, Minneapolis, MN, 2008.

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