

## II.G.11 Photoelectrochemical Generation of Hydrogen\*

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\*Congressionally directed project

### Technical Targets

- Solar-to-hydrogen (STH) efficiency: 10% by 2015 by developing photoanodes having efficient light absorption in the visible range and a long-term corrosion resistance.
- Hydrogen production cost: \$3.00/gge (approximately 1 kg of H<sub>2</sub>) by 2018 by optimizing the generation process and the storage of hydrogen.

### Accomplishments

- Plasma treatments of photoanodes for (a) minimizing charge carrier traps and contaminants, (b) doping the photoanode surface with nitrogen, and (c) creating oxygen vacancies for achieving high photocurrent density.
- Optimization of the surface structure of the nanotubes to improve light absorption.
- Use of layered electrodes of titanium disilicide (TiSi<sub>2</sub>) and titanium dioxide (TiO<sub>2</sub>) for light absorption in the visible range.
- Development of processes for synthesizing layered patterned nanotubular electrodes.
- Increased photocurrent density by more than 80% by plasma treatments and enhanced light absorption by 55% with modified nanotubular structure.
- Patent application and publication of papers reporting our work.



### Objectives

- Improve photocatalytic properties of photoanodes by (a) removing contaminants and unwanted surface states, (b) doping the photoanode surface with nitrogen for creating oxygen vacancies and vacant acceptor states to enhance oxidation of water.
- Study interfacial charge transfer process in photoelectrochemical (PEC)-based hydrogen generation.
- Synthesize nanostructured photoanodes.
- Optimize surface structure of nanotubular electrodes for maximizing photocurrent density.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

### Introduction

During the last four decades, PEC production of hydrogen has been intensively investigated due to the advantages of the PEC method: (1) potential for direct conversion of sunlight for generating pure hydrogen, (2) high quantum efficiency of several semiconductors over nearly the entire spectrum of solar radiation, (3) possible application of inexpensive and environmentally safe materials for large scale operation, and (4) relatively low capital and operating costs.

The current barriers that prevent commercialization of the PEC technology for hydrogen production are: (1) lack of semiconducting materials that will have two essential properties: (a) bandgap for harvesting sunlight from 360 to 860 nm in wavelength for splitting water into hydrogen and oxygen and (b) high corrosion resistance of the semiconducting photoanodes during electrolysis of water, and (2) poor transfer efficiency of the photo-generated charge carriers at the interface between the solid electrode and the liquid electrolyte.

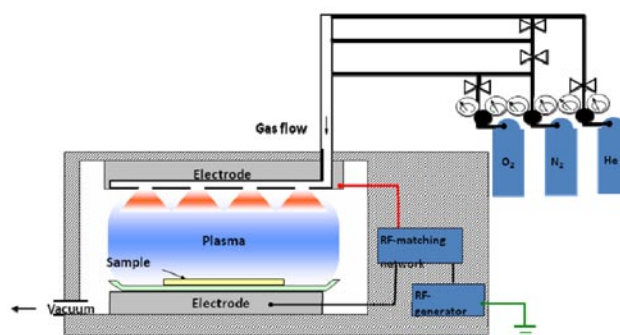
No single or compound semiconductor photoanode has been found which satisfy these critical requirements [1-3]. Several nanostructural designs have emerged as are the choices of materials, but an efficient process with optimal photo-conversion efficiency is yet to be realized for commercialization of the PEC process. The aim of our project is to engineer chemically stable photoanodes which will have a bandgap with high light absorption efficiency and yet straddle the reduction and oxidation chemical potentials of water and meet the DOE goals for hydrogen production.

## Approach

To address the current barriers, our approach is to develop a hybrid nanostructured photoanode comprised of thin-film layers of  $\text{TiO}_2$  covering nanotubes of  $\text{TiSi}_2$ . The latter has a high efficiency in light absorption covering the visible solar spectrum. The layered nanotubular electrodes can be arranged in a patterned array for trapping sunlight, providing large effective area for electrolysis, and corrosion protection by the titania film.

The photoactive materials from the silicide and titania family have the potential to overcome deficiencies of single metal oxide photoanodes. While the nanostructure greatly improves the reaction surface area and light absorption, the efficiency of the charge carrier transport and the corrosion resistance need to be investigated for different heterostructures including layered films, nanotubes and nanoparticles.

Interfacial charge carrier transfer phenomena govern the PEC-based hydrogen generation process. While the role of surface and interface states in the charge carrier transport and the necessity for matched lattice structure in using heterostructured semiconductors (such as  $\text{TiO}_2$  and  $\text{TiSi}_2$ ) have been reported in the literature, the chemical and physical control mechanisms for mitigating the losses due to the presence of charge carrier traps and minimization of photocorrosion of the electrodes are yet to be established. Fundamental studies are needed in the design of the PEC process, including the synthesis of nanostructured photoanodes to provide the desired bandgap, surface structure, and corrosion resistance. Optimization of operational parameters such as the optical system for collecting sunlight, collection, storage of hydrogen, and the control system for monitoring the safety and production efficiency of the process needs to be pursued. Our experimental studies are aimed to: (1) remove surface contaminants [3-8] and surface states that act as charge carrier traps, (2) apply plasma surface modification [9-11], using a reactor as shown in Figure 1, for surface cleaning as well as for surface doping of the photoanodes with n-type dopants (N), (3) optimize the structure of the nanotubes by varying anodization voltage for increasing light absorption, (4) use layered electrodes of  $\text{TiSi}_2$  and  $\text{TiO}_2$ , and



**FIGURE 1.** Schematic of Low-Pressure Plasma Reactor used for Surface Modification

(5) evaluate surface-modified nanostructured layered photoanodes for photoelectrochemical generation of hydrogen.

## Experimental Studies

$\text{TiO}_2$  semiconductor has been extensively used for PEC-based hydrogen production. It has an ionic crystal structure and its surface lattice oxygen ions are not surrounded by Ti cations on a clean surface. These surface oxygen atoms act as donor surface states in the gap region above the valence band edge. These gap states can increase the production of photogenerated electrons in the visible range but the donor states at the surface act as efficient traps for the holes and reduces the PEC oxidation of water. Similarly, the adsorbates on the electrode surface can form chemical bonds with the atoms of surface contaminants forming extrinsic surface states. We have used helium plasma treatment for minimizing the density of these extrinsic surface states which improved the charge carrier transport significantly.

As the surface adsorbates [9-13] were removed by helium plasma cleaning, the surface atoms of  $\text{TiO}_2$  are exposed. The dangling bonds of the metal and the oxygen atoms on the surface give rise to acceptor and donor states respectively. For an n-type semiconductor like  $\text{TiO}_2$ , it is desirable to have vacant acceptor states to increase the barrier height  $\phi$ . Nitrogen plasma treatment was used to increase vacant acceptor states and the barrier height enhancing the migration of holes from the electrode surface to the electrolyte for oxidizing water.

A self-assembled vertically ordered nanotubular  $\text{TiO}_2$  array, which has been considered to be an ideal architecture for photoelectrolysis, was synthesized and used in this study. The development of nanotubular electrode structure resulted in a significant improvement of electron conduction, rapid diffusion of holes for oxidation, and an increase of the effective surface area of the photoanodes. The nanotubular structure increases the effective surface area for light absorption

as well as for photocatalysis, however, nanostructured surface increases the density of surface states which can affect photoactivity either positively or negatively depending upon if these sites are electron traps or hole traps. Minimizing the surface density of the hole traps is essential for oxidizing water with n-type photoanodes. We used nitrogen plasma for minimizing the hole traps.

Recent studies report that  $\text{TiSi}_2$  (a) has a significant absorption of light over most of the AM 1.5 solar energy spectrum ranging from 1.4 eV ( $\lambda=860$  nm) to 3.4 eV ( $\lambda=360$  nm), (b) is photoactive in generating hydrogen by splitting water, but (c) has a low photocorrosion resistance. Our experiments showed light absorption of  $\text{TiSi}_2$  micro-particles in the visible range of the solar spectrum providing a photocurrent density of  $3.0 \text{ mA/cm}^2$  when we used  $\text{TiSi}_2$  particles along with  $\text{TiO}_2$  nanotubular photoanode. We are investigating different structures of  $\text{TiSi}_2$  photoanodes covered by a thin  $\text{TiO}_2$  film to maximize light absorption while protecting the electrodes against photocorrosion.

The test photoanodes prepared for evaluating the photoelectrolytic properties were annealed under both oxygen and nitrogen atmospheres achieve crystallization of  $\text{TiO}_2$  in its anatase form.

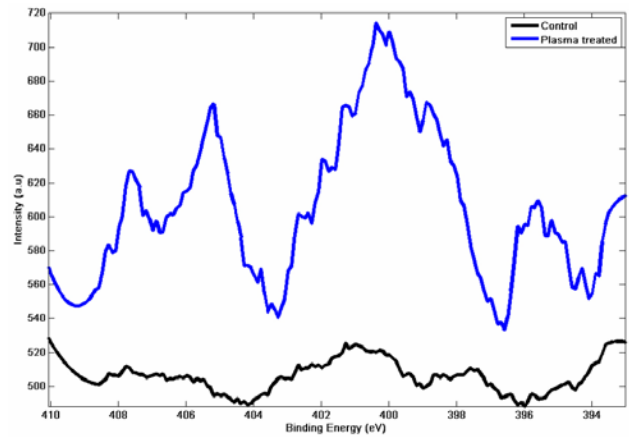
The PEC apparatus used for measuring photocurrent density of the test photoanodes under dark and illuminated conditions consisted of (1) a potentiostat/galvanostat electrochemical instrument model 283, (2) a Xenon lamp (30 mW), (3) a 60 mm-diameter quartz optical window, and (4) a reference electrode ( $\text{Ag}/\text{AgCl}$ ) placed close to the photoanode. The electrolyte used was 1M potassium hydroxide ( $\text{pH} \sim 14$ ) + deionized water solution.

**Results**

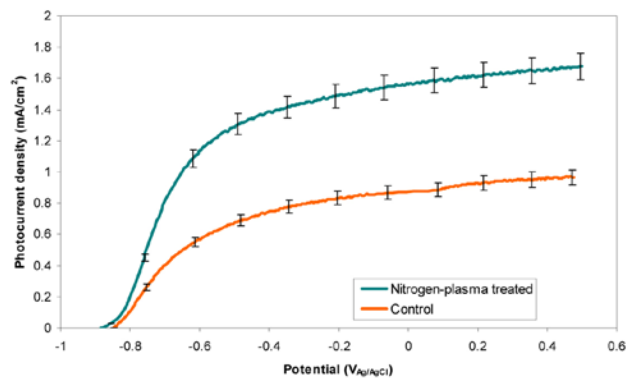
X-ray photoelectron spectroscopy (XPS) analysis indicated the incorporation of N in titania lattice structure of the photoanode surface. As shown in Figure 2, the narrow scan N 1s spectrum is demonstrated at 400 and 396 eV, which has been ascribed to the presence of nitrogen in the lattice structure either as substitutional dopants for O, or as interstitial dopants in the  $\text{TiO}_2$  crystal structure.

Nitrogen plasma treatment of titania photoanodes resulted in 80% increase in photocurrent density as shown in Figure 3. Plasma surface cleaning with helium plasma and surface doping by nitrogen plasma increased photocurrent density of titania nanotubular electrodes.

Stepped-voltage anodization was used to synthesize titania nanotubes of variable diameters. Photocurrent density vs bias voltage plotted for samples anodized at different voltages. Annealing of the photoanodes was modified. The results (Figure 4) showed enhanced light absorption and increased photocurrent density

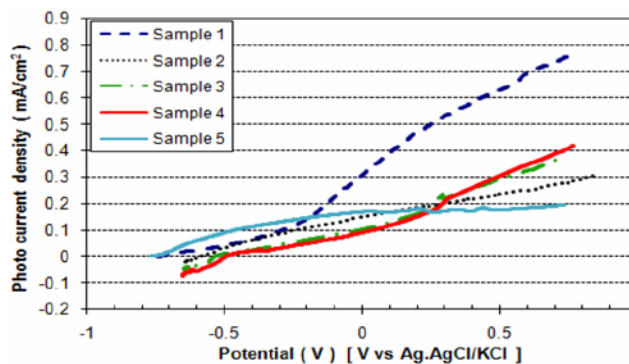


**FIGURE 2.** XPS Spectrum (a) Control and (b) Nitrogen-Plasma treated  $\text{TiO}_2$  Photoanodes



Sample description	OCV (bright), $V_{\text{Ag}/\text{AgCl}}$	Current at $-0.2 \text{ V}$ ( $\text{mA cm}^{-2}$ )	Current at $0.2 \text{ V}$ ( $\text{mA cm}^{-2}$ )
Control	-0.85	0.83	0.93
$\text{N}_2$ plasma treated	-0.97	0.94	1.68

**FIGURE 3.** Photocurrent Density Measurements for Control and Nitrogen Plasma-Treated Titania Photoanodes



**FIGURE 4.** Photocurrent Density vs. Stepped Voltage Anodization

by 55%. Several deposition processes for developing heterojunction  $\text{TiO}_2/\text{TiSi}_2$  photoanodes have been

studied; an e-beam deposition system has been installed for depositing thin films of different photoanode materials. An electrospray system has been designed and constructed for electrostatic coating of  $\text{TiSi}_2$  particles with nanoparticles of  $\text{TiO}_2$ .

## Conclusions and Future Directions

Our experimental studies with plasma surface treatments with helium and nitrogen gas show clearly an increase of photoanode current density compared with the untreated surface of the electrodes. The nitrogen plasma treatment increased acceptor surface states and improved performance of the  $\text{TiO}_2$  photoanodes. Surface cleaning of the photoanode by low-temperature helium plasma treatment removed a major fraction of the contaminants (adsorbates) from the surface.

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma treatment process for surface doping of  $\text{TiO}_2$  nanotubular photoanode with N for increasing oxygen vacancies and (3) annealing process for crystallization for improving photocatalytic generation of hydrogen from water. The test results show promising aspects of tuning several parameters involved in PEC processes in improving conversion efficiency.

## Plan for Future Studies

- Develop patterned nanotubular layered  $\text{TiSi}_2$  and  $\text{TiO}_2$  photoanodes.
- Study methods for (1) optimizing the film thickness (in the nm range, to improve tunneling) of  $\text{TiO}_2$ , (2) matching the crystalline structures of the layered semiconductors and (3) reducing the interface states in the heterojunction semiconductors and the electrolyte by passivating the surfaces involved.
- Characterize interfacial states between the  $\text{TiSi}_2/\text{TiO}_2$ /electrolyte junction by determining the optical absorption spectrum, durability and photocurrent density.
- Develop multi-junction ( $\text{TiSi}_2$  and  $\text{TiO}_2$ ) nanotubular electrodes to enhance the absorption of solar radiation in the visible range. Measure light absorption vs.  $\lambda$ .
- Measure photocurrent conversion efficiency (incident photon conversion efficiency vs  $\lambda$ ), corrosion resistance, and photo-generated carrier concentration decay rate by using a radio frequency conductivity probe.
- Optimize the PEC process for developing layered photoanodes and minimize the density of interfacial charge carrier traps by hydrogen plasma passivation followed by nitrogen plasma treatments.

## FY 2010 Publications/Presentations

### Patent Application

1. “Plasma Treated Nanostructured Titania Photo-anode for Hydrogen Generation” Rajesh Sharma, Alexandru Biris, Malay Mazumder, US Provisional patent application, 2010.

### Publications

1. Rajesh Sharma, Hidetaka Ishihara, Alexandru S. Biris, Malay K. Mazumder, “Development of surface engineered nanostructured photoanodes for enhanced photo electrochemical processes,” *IEEE Industry Applications Society 43<sup>rd</sup> Annual Meeting*, Houston, 2010.
  2. Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma, Franklin Hardcastle, Ganesh K Kannarpady, Malay K Mazumder, “Electrochemical Synthesis of Titania Nanostructural Arrays and their Surface Modification for Enhanced Photoelectrochemical Hydrogen Production,” *Chemical Physics Letters*, Volume 489, Issues 1-3, 1 April 2010, Pages 81-85, 2010.
  3. Rajesh Sharma, Jacob P. Bock, Alexandru S. Biris, Malay K. Mazumder, Prajna P. Das, Manoranjan Misra, Vishal K. Mahajan, “Evaluation of atmospheric-pressure plasma for improving photo electrochemical response of titania photoanodes,” *IEEE Transactions on Industry Applications*, Vol. 45, No. 4, pp. 1524-1529, 2009.
  4. 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. ESA Annual Meeting on Electrostatics, 2009.
  5. Jeremy Stark, Hidetaka Ishihara, Rajesh Sharma, and Malay Mazumder, “Role of Optics in Optimizing Photoelectrochemical Activity of Semiconductor Anodes,” in Proc. ESA Annual Meeting on Electrostatics, 2009.
  6. Franklin D. Hardcastle, Hidetaka Ishihara, Rajesh Sharma, and Alexandru S. Biris, “The Structure of Titanium Oxide in Titania ( $\text{TiO}_2$ ) Photoactive Water-Splitting Catalysts by Raman Spectroscopy,” in Proc. ESA Annual Meeting on Electrostatics, 2009.
  7. 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  $\text{TiO}_2$  Photoanodes using Nitrogen Plasma Assisted Surface Modification,” *Nanotechnology*, Vol. 20, 2009, 075704.
- ### Conference Abstracts
1. M.K. Mazumder, R. Sharma, S. Banerjee, S. Mahapatra, I. Hidetaka, A.S. Biris, and M. Misra, “ Interfacial Charge Transfer Process in Photoelectrochemical (PEC) Generation of Hydrogen using Layered Semiconductors as Photoanodes,” Materials Research Society Spring Meeting, San Francisco, CA, 2009.

## References

1. Yamashita H, Honda M, Harada M, Ichihashi Y, Anpo M, Hirao T, Itoh N., and Iwamoto N 1998 *J. Phys. Chem.* B**102** 10707.
2. Park JH, Kim S and Bard A J 2006 *Nano Lett.* **6** 24.
3. Umebayashi T., Yamaki T., and Itoh H., 2002 *Appl. Phys. Lett.* **81** 454.
4. Sakai N, Wang R, Fujishima A, Watanabe T and Hashimoto K 1998 *Langmuir* **14** 5918.
5. Yu JC, Lin J, Lo D and Lam S K 2000 *Langmuir* **16** 7304.
6. Chiba Y, Kashiwagi K and Kokai H 2004 *Vacuum* **74** 643.
7. Jun J, Shin J H and Dhayal M 2006 *Appl. Surf. Sci.* **252** 3871.
8. Nakamura I, Negishi N, Kutsuna S, Ihara T, Sugihara S and Takeuchi K 2000 *J. Mol. Catal. A* **161** 205.
9. Negishi N, Takeuchi K and Ibusuki T 1998 *J. Mater. Sci.* **33** 5789.
10. Garbassi F, Morra M and Occhiello E 1996 *Polymer Surfaces: From Physics to Technology* (New York: Wiley) p 223.
11. Chan C M 1994 *Polymer Surface Modification and Characterization* (Munich: Hanser Publications) p 225.
12. Changsheng L, Zhibin MA, Li J and Weihong W 2006 *Plasma Sci. Technol.*
13. Grimes C A 2007 *J. Mater, Chem.* **17** 1451.