

II.E.8 Photoelectrochemical (PEC) Hydrogen Generation

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Objectives

- Improve (a) photo-conversion efficiency to 10% evolving H₂ and O₂ and (b) photo-corrosion resistance of photo-anodes for 5,000 hours of operation generating H₂ from water using photoelectrochemical (PEC) cells.
- Develop surface engineered TiO₂ and TiSi₂ nanostructured photoanodes (nanotubes and nanorods) doped with N, C or F to (1) reduce the effective band gap at the surface by introducing surface states that have energies within the band gap of the bulk semiconductor, (2) straddle photoanode band edges with respect to the electrochemical potentials of (H₂/H₂O) and (H₂O/O₂), (3) minimize Fermi level pinning, and (4) reduce charge carrier traps at the interface for improving light absorption and increasing efficiency of photo-electrolysis of water generating hydrogen.
- Perform fundamental studies on surface energetics such as generation and control of surface states, role of surface states in H₂ generation, minimization of surface states that are responsible for recombination of photo-excited charge carriers at the interface, and on photocorrosion of semiconductor electrode exposed to different wavelength of solar radiation.
- Optimize surface structure for enhancing scattering cross section for improving light absorption.

Technical Barriers

This project addresses the following technical barriers identified in the Hydrogen Production section of the DOE in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AP) Materials Efficiency
- (AQ) Materials Durability
- (AS) Device Configuration Designs

Technical Targets

The primary focus of this project is to achieve high photo-conversion efficiency in generating hydrogen by splitting water. Taking every technical aspect into account, a band gap (E_g) of 2.5 eV is most desirable. 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 has not been found successful. Small band gap electrodes suffer from poor stability, inadequate charge transfer properties and a high charge recombination rates. Finding the right material for high efficiency and durability is of highest importance.

Our technical target is to reach the DOE goals:

- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant solar-to-hydrogen (STH) efficiency: 8% by 2010 and 10% by 2015
- Hydrogen production cost: \$3.00/gge (approximately 1 kg of H₂) by 2018

Accomplishments

- TiO₂ nanorods were synthesized using electrochemical anodization of Ti foil.
- A low-pressure helium, nitrogen, and oxygen plasma was used for modifying surface energetics, surface chemical and physical structures.
- The plasma treated TiO₂ samples were analyzed for their photoelectrochemical activity.
- The photocurrent density of nitrogen plasma treated samples was 80% higher as compared to untreated samples.
- Plasma treated samples were analyzed for determining the surface chemical structure using X-ray photoelectron spectroscopy (XPS); it shows that N atoms substituted O atoms in the surface lattice structure.



Introduction

For efficient generation of hydrogen using a PEC system, it is necessary to understand the fundamental aspects of interfacial charge transfer and recombination of electrons and holes at the semiconductor-electrolyte junction where the light is to be absorbed efficiently generating charge carriers. Rapid charge transfer for electrolysis with a minimal charge recombination is needed. Since surface states dominate these processes in the semiconductor electrolyte interface, our specific targets include both surface modifications of the semiconducting electrodes and chemical control of electrolytes for obtaining the desired surface energy states within the forbidden bulk band gap region, increasing the band bending for rapid charge separation and removal of charge carrier traps from the surface. Since the use of TiO_2 provides a low production cost, a good corrosion resistance, an excellent environmental compatibility, our technical targets are based on using this extensively studied material by the photoelectrolysis communities for fundamental analysis of interface. It appears to us that we should use two or three photoanode systems for covering the solar spectrum from the ultra violet (UV) region to near the infrared region.

For improving durability it is necessary to study the stability of the materials for photo-corrosion resistance at different pH and at both UV and visible wavelengths of incident photons. Structural modification of the anode surface is also needed for improving light absorption. Similarly, enhancement of quantum efficiency of anodic surface may be possible by incorporating nanoparticles of Ag or Pt as co-catalysts in the photoanodes.

Approach

TiO_2 , being the workhorse of photoelectrolysis for the last four decades for its advantages in electrode fabrication, stability, inertness and cost effectiveness, was chosen for our fundamental investigations on interfacial charge carrier generation and transport systems. We will use both TiO_2 photoanodes with n-type dopants and TiSi_2 photoanodes to cover the UV and visible (VIS) regions of the solar radiation spectrum. Since interfacial generation, recombination and transfer of

charge in the PEC system is dominated by the surface states and the surface structures, our research is focused on the control of surface states using TiO_2 photoanodes.

We are using plasma surface treatment (1) to remove surface contaminants and unwanted surface states caused by uncontrolled chemisorption of gases and vapors on the dangling bonds of surface atoms that act as charge carrier traps and (2) for surface doping of TiO_2 photoanodes with n-type dopants (N, C, Si, ...) on annealed TiO_2 nanotubes and nanorods. The plasma surface modified TiO_2 anodes are tested for their photocurrent density when illuminated by artificial solar radiation. Results are compared to examine the improvement in photocurrent density with surface modification. We now plan to use TiSi_2 photoanodes to examine similar improvements of photocurrent density under visible portion of the solar radiation. We are currently testing the photo-corrosion resistance of TiO_2 and TiSi_2 photoanodes using electrochemical impedance spectroscopy under UV and VIS radiation exposures.

Our studies are being performed in close cooperation with other PEC centers, as we are working closely with the University of Nevada at Reno and the DOE PEC group.

Results

Surface modification was performed using low-pressure oxygen, nitrogen and helium plasma, operating at 13.56 MHz rf 200 W applied power at a pressure of 150 mtorr. Figure 1 shows the schematic of the plasma reactor used in this study. Samples were exposed to plasma for 10 minutes in each test run. Plasma treated samples were tested for photocurrent density, optical absorbance and surface chemical structure.

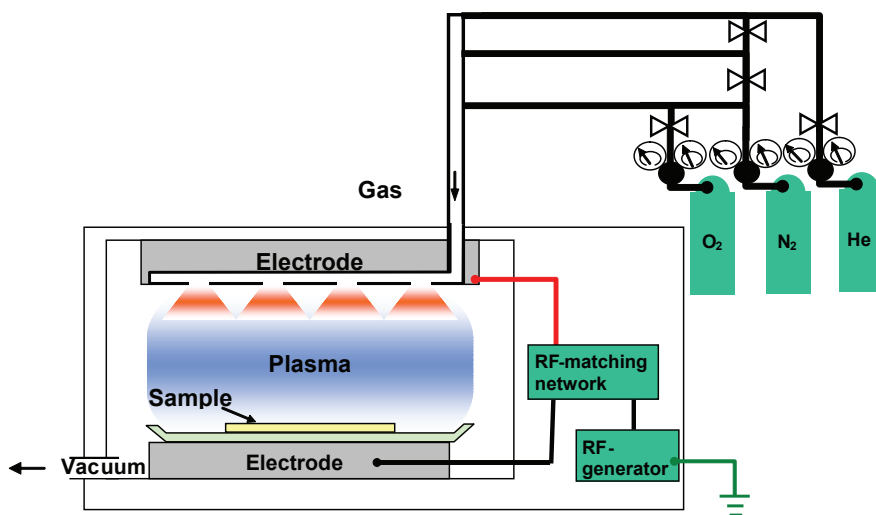


FIGURE 1. Schematic of Low-Pressure Plasma Reactor used for Surface Modification

Figures 2 and 3 show the photocurrent density obtained from as-anodized and oxygen annealed photoanode samples, with and without plasma surface treatments. The current density for the nitrogen plasma treated samples (0.21 mA/cm^2) was higher as compared to the as-anodized sample (0.08 mA/cm^2) at 0.2 V (Figure 2). In case of oxygen annealed samples (annealed at 500°C for 6 h in oxygen) the nitrogen plasma treated sample again demonstrated higher photocurrent densities (1.68 mA/cm^2 at 0.2 V) as compared to untreated sample (0.93 mA/cm^2 at 0.2 V) (Figure 3).

Table 1 summarizes the open circuit potentials (OCPs) and photocurrent density values for the oxygen annealed plasma treated samples. The OCPs values under the dark condition ranged from -0.3 to -0.4 V . The OCP decreased from -0.85 V to -0.97 V for N_2 plasma treated sample. This negative shift in OCP values after illumination indicates an increase in band bending after plasma treatment. Since the OCP values reflect the difference between the Fermi level of semiconductor and redox potential of the electrolyte, a more negative value of OCP is preferred.

TABLE 1. Summary of Photocurrent Density and the OCP Slope Values of Oxygen Annealed and Plasma Treated Samples Compared with the As-Anodized Samples

Sample Description	OCP (Light), $V_{\text{Ag/AgCl}}$	Current at -0.2 V (mA/cm^2)	Current at 0.2 V (mA/cm^2)
Control	-0.85	0.83	0.93
N_2 plasma treated	-0.97	0.94	1.68

The experimental results show that the nitrogen plasma treatment of oxygen annealed samples increased photocurrent density and band bending which manifests into increasing photopotential and thus increasing photocurrent. The increase in photocurrent density after plasma treatment could be ascribed to combination of several factors including removal of surface contaminants, change in surface physical structure and modification of surface chemical structure causing change in surface energetics.

XPS analysis showed that O/Ti ratio of the photoanode decreased from 3.32 in control to 2.80 eV after nitrogen plasma treatment. This decrease suggests removal of oxygen atoms from the surface, which could be due to desorption of water and physisorbed oxygen from the surface or from the lattice or both. XPS analysis also showed that the N-concentration increased from 0.24 to 1.21 atomic percent after plasma treatment. The significant increase in N concentration after plasma treatment suggests the introduction of N in lattice structure either as substitutional dopant replacing O, or as interstitial dopant. This hypothesis is supported

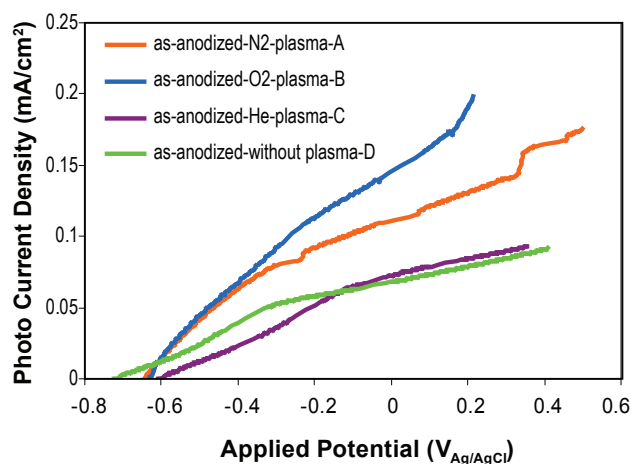


FIGURE 2. Photocurrent Density Data for As-Anodized and Plasma Surface Treated Samples Prepared in Acidic Solution

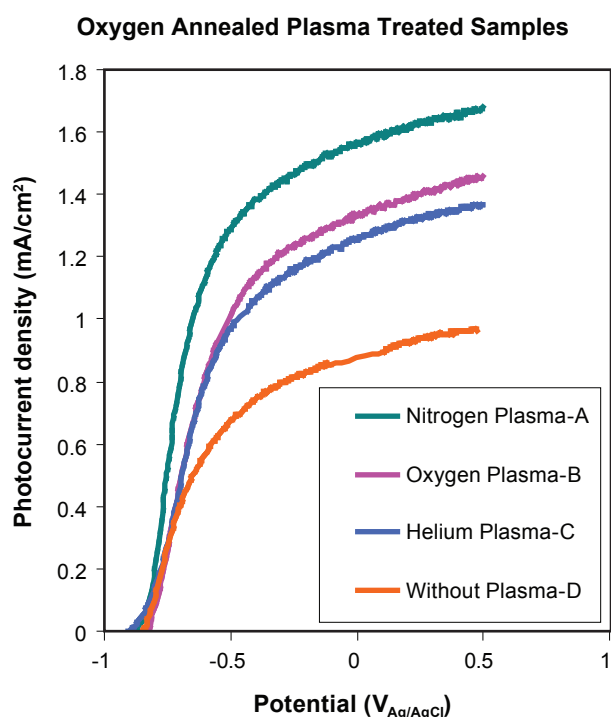


FIGURE 3. Photocurrent Density Data for Oxygen Annealed and Plasma Surface Treated Samples Prepared in Acidic Solution

by several recent studies where N doping has shown a reduction in bandgap of TiO_2 .

Conclusions and Future Directions

Our experiments with plasma-treated TiO_2 photoanodes have shown encouraging results. We will optimize the effective bandgap by plasma doping and measure the photocurrent generation efficiency as a function of incident radiation wavelength. We will

determine the optimum plasma treatment methods for surface modification of TiO₂ photoanodes. Optimization of surface properties with composite micro- and nanostructured surface could enhance both light absorption and photo-conversion.

The surface states of TiO₂ photoanodes will be characterized by determining density of states, surface bandgaps and work function, optical absorption spectrum, photoconductivity, and durability. We will perform comprehensive experimental studies on the improvement of photo-conversion efficiency by modifying surface states and surface structures with the addition of nanoparticles of Au, Pt, and other materials for improved photo-catalytic activity of TiO₂. A multi-dimensional analysis will be performed which will include cost, durability, efficiency and environmental factors. Partnerships with private enterprise are being explored.

FY 2008 Publications/Presentations

1. 2008 DOE Hydrogen Program Review - Washington, D.C.- June, 2008. Presentation # PDP21.
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3. 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.
4. M. K. Mazumder, R. Sharma, P. Das, A. S. Biris, and M. Misra, "Photo-electrochemical Generation of Hydrogen using Plasma Assisted Self-assembled Titania Nanotubes," CTSI Clean Technology and Sustainable Industries Conference and Trade Show, Boston, MA, June 2-4, 2008.
5. 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*, 2008.

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2. Y. Chiba, K. Kashiwagi, H. Kokai, "Plasma surface treatment effect of TiO₂ thin film," *Vacuum*, 2004, 74, 643-646.