II.G.3 University of Nevada, Reno Photo-Electrochemical Project*

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Dr. John A. Turner, National Renewable Energy Laboratory (NREL), Golden, CO

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*Congressionally directed project

Objectives

- Develop high efficiency metal oxide nanotubular array photo-anodes for generating hydrogen by water splitting.
- Develop density functional theory to understand the effect of morphology of the nanotubes on the photo-electrochemical properties of the photo-anodes.
- Develop kinetics and formation mechanism of the metal oxide nanotubes under different synthesis conditions.
- Develop combinatorial approach to prepare hybrid photo-anodes having multiple hetero-atoms incorporated in a single photo anode.
- Improve the durability of the material.
- Scale-up the laboratory demonstration to production unit.

Technical Barriers

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

(Y) Materials Efficiency
(Z) Materials Durability

Technical Targets

This project is investigating potential application of hybrid TiO_2 nanotubes for hydrogen generation by water photoelectrolysis. Insights gained from these studies will be applied toward the design and synthesis of high efficiency materials for hydrogen generation from water splitting that meet the following DOE targets:

- Usable semiconductor bandgap: 2.0 eV by 2018
- Chemical conversion process efficiency: 10% by 2013
- Plant durability: 1,000 hrs by 2013

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Approach

In this current project, utilization of hybrid titania nanotubular arrays for generation of hydrogen from water using sunlight is studied. The titania nanotubular arrays are robust, photo-corrosion resistant, and can be used in different electrolyte systems to generate hydrogen. It is envisioned that the process can be efficient and economical in the production of solar hydrogen. The nanotubular arrays are prepared by electrochemical anodization of solid titanium metal in different inorganic and organic electrolytes in the presence of fluoride ions. The effect of voltage, time, and solution chemistry on the size, uniformity, and self-assembly of nanotube formation is studied. Preliminary work has shown that an ultrasonic assisted process can generate a stable and efficient pattern of nanotubes that have excellent photo-efficiency. Materials prepared by organic solvents such as ethylene glycol and diethylene glycol also show enhanced activity for this purpose. In addition to the preparation of a TiO_2-based photoanode, we also show that these nanotubes can work efficiently as a cathode by nanoparticles modification. This project is integrating a highly efficient photoanode, a cathode, and a modified electrolyte to design a photoelectrochemical cell (PEC) to generate hydrogen with at least 10% efficiency (Figure 1) by 2013. The scale-up process looks highly promising for large scale hydrogen generation.

The photoelectrochemical hydrogen generation work is conducted using arrays of a hybrid titania nanotubular electrode in alkaline solutions in the presence of simulated solar light. The photo-efficiency is determined by measuring current as well as volume of the hydrogen generated by gas chromatograph. The

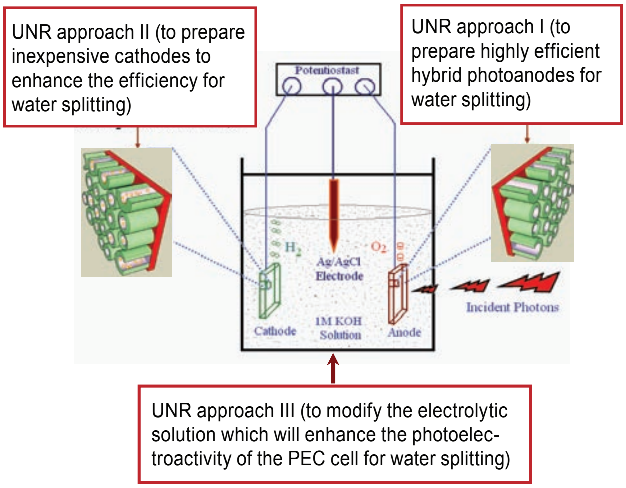

FIGURE 1. A schematic view of the approaches adopted by UNR to develop a highly efficient PEC cell for water splitting. The combination of the three approaches (I + II + III) are expected to give >12% efficiency to generate H_2 from water using sunlight.

material stability and photo-efficiency is determined as a function of time. The photo conversion efficiency (η) is given by the relation η (%) = [(Total power output – electrical power output) / light power input] x 100

$$(\%) = J_p \, [(E^0_{rev} - E_{app}) / I_0] \times 100$$

Where, J_p = photocurrent density (mA/cm^2); $J_pE^0_{rev}$ = total power output; J_pE_{app} = electrical power input; and I_0 = power density of incident light (mW/cm^2).

In the future our main focus for the research will be to understand:

1. The formation mechanism and kinetics of TiO_2 nanotubes prepared by various anodization methods and electrochemical solution;
2. How TiO_2 nanotubes are different from TiO_2 nanoparticles with respect to charge transport characteristics and stability;
3. The electronic properties and photoelectroactivity of various titania nanotubes (smooth ridged, branched, etc.);
4. Reaction kinetics of the water splitting reactions at the interface;
5. Effect of nanotubular wall thickness on electron trapping;
6. Effect of band bending across the nanotube wall;
7. Electron and hole mobility and their lifetime;
8. Stability of the nanotubes; and
9. The effect of solution chemistry and cathode on the photoelectroactivity of the photoelectrochemical cell.

The methods to be adopted are as follows:

1. Colorimetric titration

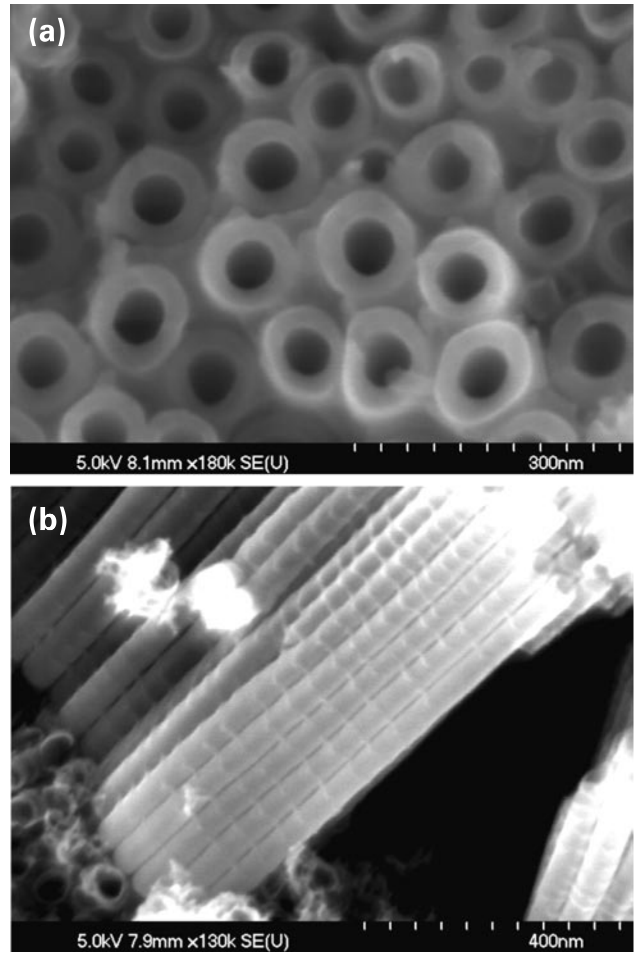

FIGURE 2. Highly Ordered and Compact TiO_2 Nanotube Arrays Prepared by Sonoelectrochemical Anodization Method Developed at UNR; (a) top view and (b) side view of the nanotubular array

2. Electron and hole titration
3. Intensity modulated electrochemical impedance spectroscopy (EIS)

On the basis of fundamental and applied research, a scale-up experiment in the laboratory will be performed to elucidate the viability of titania nanotubes for photo-electrochemical generation of hydrogen using sunlight.

Accomplishments

- The UNR team has developed an innovative ultrasonically mediated fabrication process to synthesize highly ordered hybrid titania nanotubes (Figure 2).
- UNR has designed a PEC cell by using carbon doped titania nanotube arrays as photoanode and metal nanoparticles modified titania nanotubes loaded with Pt nano-particles as cathode. This PEC cell is also found to be highly efficient for generating

hydrogen by water splitting (efficiency = 8.5% for visible light and 13.3% for ultraviolet (UV) light), Figure 3. The preliminary results show that the process can be scaled-up by keeping the rate of hydrogen generation intact (Figure 4).

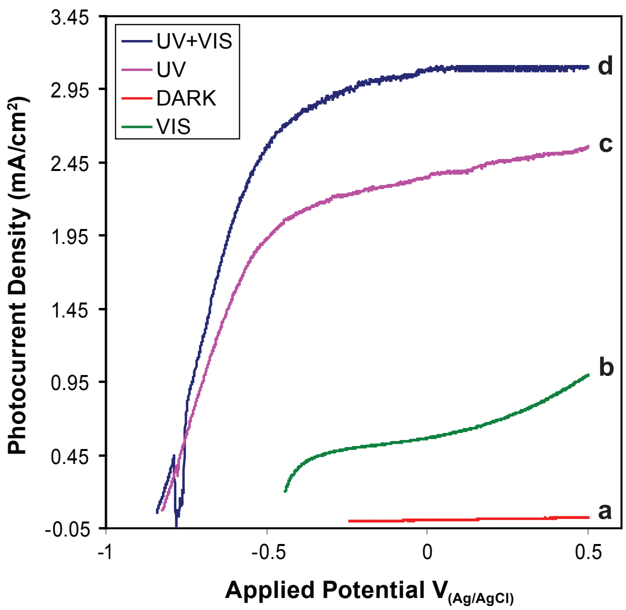

FIGURE 3. Variation of photocurrent density vs. applied potential of the $TiO_{2-x}C_x$ nanotubular arrays in (a) dark, and (b) illumination of visible (520 ± 46 nm), (c) UV (330 ± 70 nm) and (d) complete solar spectrum. The efficiency for the above photoelectrochemical cell is calculated as 13.3% using UV light source and 8.5% using visible light source. (Please see Mohapatra et al., *Journal of Physical Chemistry*: C 111 (2007) 8677-8685 for a detailed discussion on efficiency calculation.)

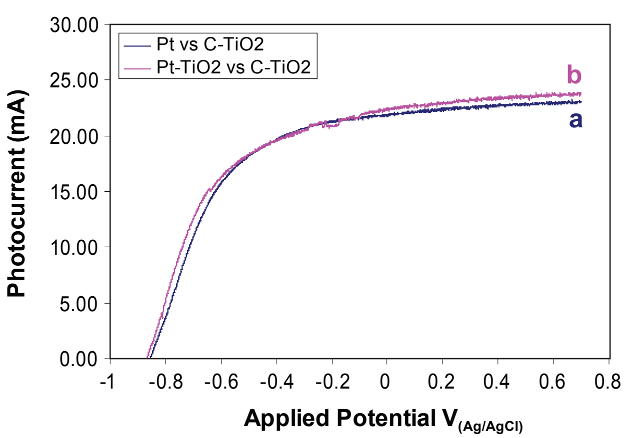

FIGURE 4. Variation of photocurrent obtained from the PEC cell using an 8 cm^2 photoanode containing $TiO_{2-x}C_x$ nanotubular arrays (prepared using the condition earlier mentioned for Figure 2B and annealed under reduce atmosphere) vs. (a) Pt foil and (b) platinum nanoparticles containing titania (Pt/TiO_2) nanotubular arrays as a cathode.

Conclusions and Future Actions

In the last year, we have developed new sonoelectrochemical anodization techniques to synthesize high quality titania and titania-based mixed oxide nanotube arrays. We have developed a better understanding of the formation mechanism and kinetics of these nanotubes and realized the positive effect of the ultrasonic mediated anodization technique on the photoelectroactivity of the nanotubes. The titania nanotubes prepared by a single step carbon doping are found to be efficient for hydrogen generation by water splitting using solar spectrum. The preliminary studies on the synthesis of the cathode and modification of the electrolytic solution show that it is highly possible to increase the photo conversion efficiency if improvements in all three areas are implemented to design a photoelectrochemical cell. The following bulleted list is indicative of the areas we will pursue in the coming year of the project:

- Develop new doping methods to further reduce band gap of TiO_2 nanotubes.
- Synthesize inorganic-organic hybrid materials for better electron transport.
- Synthesize mixed oxide photoanodes to harvest full spectrum of sunlight.
- Develop inexpensive cathodes using nanowires/nanoparticles of compound semiconductors.
- Scale-up testing for solar light harvesting.

Special Recognitions & Awards/Patents Issued

1. Development of methods and devices for photo-electrochemical generation of hydrogen using hybrid titanium oxide nanotubes, US Patent, filed Sept. 2005.

FY 2006-2007 Publications/Presentations

Publications

1. "Determination of photo conversion efficiency of nanotubular titanium oxide photo-electrochemical cell for solar hydrogen generation," *J. Power Sources*, 159 (2006) 1258-1265.

2. "Photo-electrochemical hydrogen generation using band-gap modified nanotubular titanium oxide in solar light," *J. Power Sources*, 161 (2006) 1450-1457.

3. "Photo-electrochemical generation of hydrogen using hybrid titanium dioxide nanotubular arrays," Proceedings of SPIE-The International Society for Optical Engineering (2006), 6340 (Solar Hydrogen and Nanotechnology), 634001/1-634001/12.

4. "A novel method for the synthesis of titania nanotubes using sono-electrochemical method and its application

for photo-electrochemical splitting of water," *Journal of Catalysis*, 246 (2007) 362-369.

5. "Effect of water content of ethylene glycol as electrolyte for synthesis of ordered titania nanotubes" *Electrochemistry Communication*, 9 (2007) 1069-1076.

6. "Synthesis of self-organized mixed oxide nanotubes by sonoelectrochemical anodization of Ti-8Mn alloy," *Electrochimica Acta*, 2007 (in press).

7. "Design of a highly efficient photo-electrolytic cell for hydrogen generation by water splitting: Application of $TiO_{2-x}C_x$ as a photoanode and Pt/TiO_2 as a cathode," *Journal of Physical Chemistry: C* 111 (2007) 8677-8685.

Presentations

1. "Hydrogen generation from water using solar light," Invited Lecture, Indian Institute of Science, Bangalore, India, July 2nd, 2006.

2. "Photo-electrochemical generation of hydrogen using hybrid titanium dioxide nanotubular arrays," SPIE-The International Society for Optical Engineering Conference, August 14–17, 2006, San Diego, California, USA.

3. "Modification of energy levels of photo electrodes for hydrogen generation by splitting water using solar light," Materials Science & Technology (MS&T) Conference, October 15–19, 2006, Duke Energy Center, Cincinnati, OH, USA (Abstract p. 82).

4. "Ultrasonic assisted electrochemical synthesis of ordered TiO_2 nanotubes and their electronic properties," Materials Science & Technology (MS&T) Conference, October 15–19, 2006, Duke Energy Center, Cincinnati, OH, USA (Abstract p. 209).

5. "Photoelectrochemical generation of hydrogen using sonic mediated hybrid titania nanotubes," 35th AVS Technology Symposium (Renewable energy session), Orlando, Florida, March 11–16th, 2007.

6. "Stable photo-electrochemical generation of hydrogen using ultrasonically formed large area hybrid titanium dioxide nanotubular arrays," NHA Annual Hydrogen Conference 2007, March 19–22, 2007, San Antonio, Texas, USA (Abstract p. 30).