

II.E.4 University of Nevada, Reno Photo-Electrochemical Project*

Dr. Mano Misra

University of Nevada, Reno (UNR)
1664 N. Virginia Street, MS 388
Reno, NV 89503
Phone: (775) 784-1603; Fax: (775) 327-5059
E-mail: misra@unr.edu

DOE Technology Development Manager:
Roxanne Garland

Phone: (202) 586-7260; Fax: (202) 586-2373
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson

Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FC36-06GO 86066

Subcontractors:

- Dr. John A. Turner
National Renewable Energy Laboratory (NREL)
Golden, CO
- Dr. Malay Mazumder
University of Arkansas at Little Rock, Little Rock, AR

Start Date: June 1, 2006

Projected End Date: September 30, 2009

*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 incorporation 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 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

Technical Targets

This project is investigating potential application of hybrid TiO₂ 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 band gap: 2.3 eV by 2013;
- Chemical conversion process efficiency: 10% by 2013; and
- Plant durability: 1,000 hrs by 2013.



Approach

In this current project, utilization of hybrid metal (Ti, W, Fe, Cd and Ta) oxide nanotubular arrays for generation of hydrogen from water using sunlight is studied. The nanotubular arrays are prepared by sonoelectrochemical anodization of the respective metals in optimized synthesis conditions. We have already developed processes to synthesize metal oxide nanotubes in inorganic, organic and ionic liquids as electrolytes. This process is also found suitable to prepare mixed metal oxide nanotubes e.g. TiFe, TiMn and TiW. In addition to the anodization process, we are also developing new mixed metal oxide compounds by electrodeposition, hydrothermal and microwave assisted methods. 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 by 2013. The scale-up and stability of the materials looks highly promising for large-scale hydrogen generation. It is envisioned that the process can be efficient and economical in the production of solar hydrogen.

The hydrogen generation work is conducted using a hybrid metal oxide or mixed metal oxide nanotubes electrode in alkaline solutions in the presence of

simulated and on-field solar light. The photo-efficiency is determined by measuring current as well as volume of the hydrogen generated using water displacement and gas chromatography analysis. The material stability and photo-efficiency is determined as a function of time, electrochemical and analytical measurements.

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

- Synthesis of visible light active mixed metal oxide photocatalysts.
- Synthesis of metal silicides.
- The formation mechanism and kinetics of metal oxide.
- Reaction kinetics of the water splitting reactions at the interface.
- Effect of nanotubular wall thickness on electron trapping.
- Effect of band bending across the nanotube wall.
- Stability of the catalysts for 1,000 hrs.

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

Accomplishments

- The UNR team has developed a novel pulsed electrodeposition technique to synthesize mixed metal oxide nanorods inside one dimensional architecture (Figure 1).
- UNR also designed a bifacial ultrasonically mediated fabrication process to synthesize highly ordered hybrid metal oxide photoanodes to a yield high volume of hydrogen (Figure 2).

Conclusions and Future Actions

In the last year, we have designed bi-facial photoanodes by sonoelectrochemical anodization techniques. This design has the following advantages compared to other systems reported so far: (a) high active surface area in small geometrical area; (b) double efficiency per footprint; and (c) reduced recombination losses due to intermediate metallic contact. This design can be exploited for large scale H₂ production using solar concentrating technology. We have also expanded the idea to understand the formation mechanism, crystallization and kinetics of the formation of nanotubes by the sonoelectrochemical anodization method. The positive effect of this new sonoelectrochemical anodization technique on the photoelectroactivity of the nanotubes is also established (Figure 3). Titania nanotubes prepared by single step

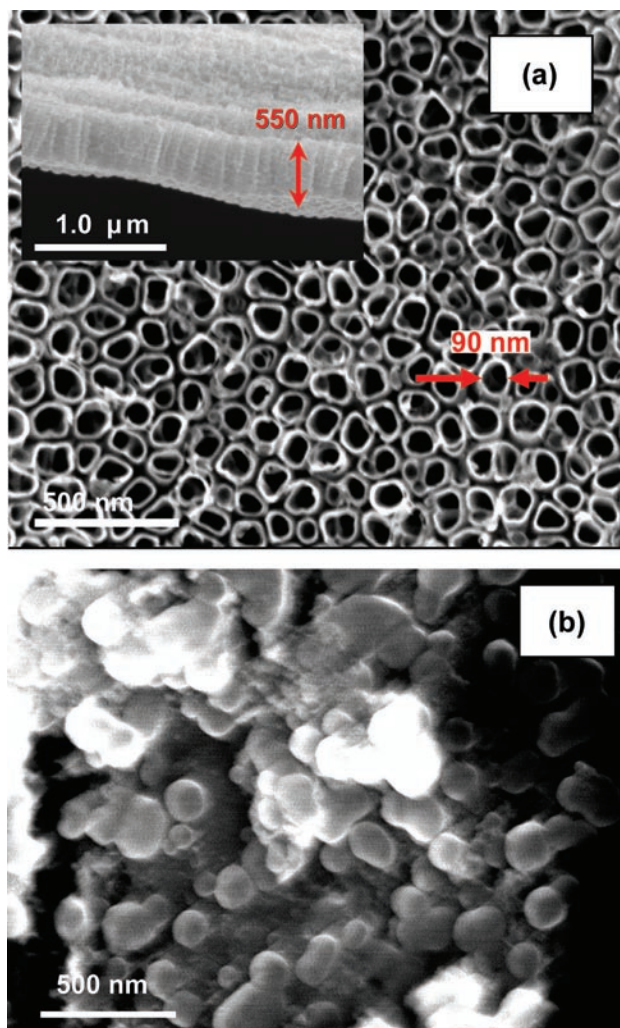


FIGURE 1. Scanning electron microscope (SEM) images of: (a) TiO₂ nanotube arrays and (b) single crystalline Fe₂O₃ (hematite) nanorods prepared inside the one dimensional nanotube architecture.

carbon doping are found to be efficient for hydrogen generation by water splitting using solar spectrum. The TiO₂ nanotubes are prepared in a glycol solution using the sonoelectrochemical anodization method which leads to functionalization of organic compounds with Ti-OH groups present in the nanotubes. These functionalized TiO₂ nanotubes are then annealed under reduced atmosphere to produce carbon doped TiO₂ nanotubes (TiO_{2-x}C_x). The prepared low band gap TiO_{2-x}C_x catalysts show ~4% solar-to-hydrogen conversion efficiency which is in line with DOE's goal to achieve "Hydrogen Economy". There are few carbon-doped TiO₂ nanotubular catalysts which have been reported in the last few years using external carbon sources. These external carbon sources generally form graphitized carbon on the surface of the nanotubes. The surface-deposited carbon does not alter the band structure of the material and is not stable. We have also

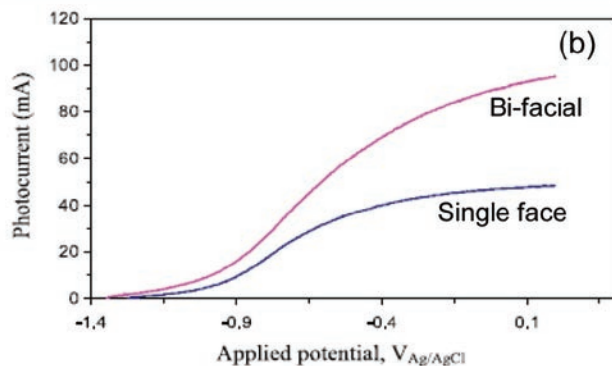
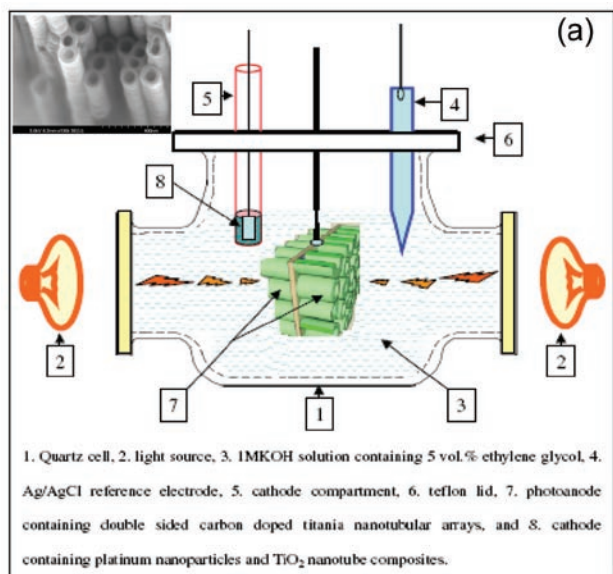


FIGURE 2. (a) A schematic diagram of the designed double sided photoanode and (b) hydrogen generation from the double-sided nanotubular photoanode. The inset of (b) shows the scanning electron microscope image of a section of the photoanode used for hydrogen generation by water splitting.

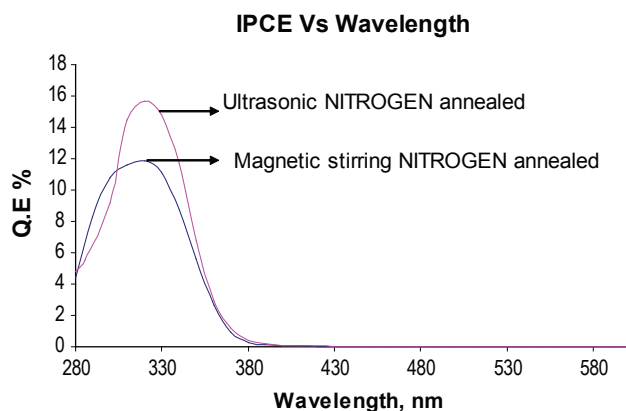


FIGURE 3. A comparison of quantum efficiency of TiO₂ nanotubes prepared under magnetic stirring and ultrasonic irradiation.

developed techniques to synthesize organic-inorganic hybrid nanotubular materials. This is carried out by functionalizing TiO₂ nanotubes with a ligand (e.g., 2,6-dihydroxyanthraquinone). This hybrid material harvests solar light more efficiently than the intrinsic TiO₂, and thus increases the photoactivity of the material by more than 30%. UNR has also developed pulsed electrodeposition (PED) techniques to prepare multi-junction band gap metal oxide electrodes. The vertically aligned nanotubes are selectively filled with other metal oxides to develop a new class of core-shell metal oxide materials. This technique can be useful to design 1-dimensional (1D) metal oxide catalysts with variable band gap energies. We have also shown that these nanotubular photoanodes are stable (few of them are found stable for 240 hours without much change in photoactivity) and can be scaled-up without losing the integrity and activity of the catalysts.

In addition to development of new photoanode materials to harvest solar light, the UNR group is also working to reduce the cost of the H₂ production system. We have developed new cathode materials by functionalizing Pt and Ni nanoparticles (1–2 wt%) into TiO₂ nanotubes. This cathode reduces the cost of the system considerably (the cost of Ni and Ti is more than 200 times lower than Pt) by keeping the activity of the photoanode intact. In summary, UNR has contributed some significant technologies in the last couple of years to achieve DOE's various goals such as: (1) highly efficient photocatalyst; (2) low cost system; and (3) stable and scalable technologies.

To continue our effort to achieve DOE's target for 2013, we would like to propose (based on preliminary results) the following research areas:

- Synthesis of mixed metal oxide photoanodes. We would like to develop our earlier designed PED technique to synthesize mixed metal oxide nanostructure materials. This process grows one metal oxide (low band gap material) inside another porous metal oxide (with good charge transport properties). These types of 1D semiconductor materials not only harvest solar light efficiently; but also fasten the transport of photogenerated electrons. This can lead to a highly efficient photoelectrode.
- Synthesis of metal (core)-metal oxide photoanodes. Even though DOE has identified Fe₂O₃ as one of the best semiconductor materials, still its activity is far below other metal oxides (e.g. TiO₂). This is due to its low charge transport (CT) properties. To improve the CT properties of Fe₂O₃, the UNR group has developed a technique to synthesize Fe₂O₃ nanofibers (~4–5 nm diameter) and cubic nanoparticles (with Fe core) on ITO support. The photogenerated electrons generated by Fe₂O₃ can be transferred to the back contact (ITO) through

the Fe metal (the core of the nanostructure). The second approach is to grow CNTs inside etched TiO₂ nanotubes and then functionalize CNTs with low band gap metal oxides (e.g., Fe₂O₃ nanoparticles). This reduces the conduction band (CB) miss-match between TiO₂ and Fe₂O₃, and enhances the photoactivity (ultraviolet light is harnessed by TiO₂ and visible light by Fe₂O₃) of the composite photoanode. These processes will eliminate the highly expensive techniques and use of precious metals currently being used to enhance the conductivity of the Fe₂O₃ based catalysts.

- Synthesis of metal silicides for hydrogen generation. Metal silicides are a new class of semiconductor materials which harness most parts of the solar spectrum, and most of them are stable in the basic solution. We are developing technology to synthesize 1D composites of metal silicides and metal oxides to improve the photoconversion efficiency.
- Incident photon to current conversion efficiency measurements.
- Design PEC system for on-field testing under real solar irradiation.
- Scale-up testing.

Special Recognitions & Awards/Patents Issued

1. "Preparation of nanotubular titania substrate with oxygen vacancies and their use in photo-electrolysis of water", US patent, PCT/US2006/035252.
2. "Preparation of nano-tubular titania substrates having gold and carbon particles deposited thereon and their use in photo-electrolysis of water", US patent PCT/US2008/060293.

FY 2008 Publications/Presentations

Publications

1. "Enhanced photoelectrochemical generation of hydrogen from water by 2,6-dihydroxyanthraquinone functionalized titanium dioxide nanotubes," *J. Phys. Chem. C* 111 (2007) 11506-11510.
2. "Double side illuminated titania nanotubes for high volume hydrogen generation by water splitting," *Nanotechnology* 18 (2007) 445705.
3. "Sonochemical synthesis of low band gap titania nanotubes for photoelectrochemical generation of hydrogen," Proceedings of SPIE-The International Society for Optical Engineering (2007), 6650 (Solar Hydrogen and Nanotechnology II).

4. "Synthesis of Y-branched TiO₂ nanotubes by sonochemical anodization method," *Materials Letter* 62 (2008) 1772.
5. "Self-organized TiO₂ nanotubular arrays for photoelectrochemical hydrogen generation: Effect of crystallization and defect structures," *Journal of Physics D* 41 (2008) 125307.
6. "Efficient photoelectrolysis of water using TiO₂ nanotube arrays by minimizing recombination losses with organic additives," *J. Phys. Chem. C* 112 (2008) 11007.
7. "Synthesis of heterostructure Fe₂O₃-TiO₂ nanorod-nanotube arrays," *Nanotechnology* 19 (2008) 315601.
8. "Stability of TiO₂ nanotube arrays in photoelectrochemical studies," *International Journal of Hydrogen Energy* (in press).
9. "Formation and stability of anatase phase of phosphate incorporated and carbon doped titania nanotubes," *Materials Research Bulletin* (in press, doi:10.1016/j.materresbull.2008.05.004).
10. "Production of renewable solar hydrogen using semiconductor metal oxides by water photoelectrolysis," *Proceedings of Clean Technology 2008* (Fuel Cell & Hydrogen Technologies) p. 331-334.

Presentations

1. "Hybrid titanium dioxide nanotube arrays for photoelectrochemical hydrogen generation by water splitting," The 10th IUMRS international conference on advanced materials (*Energy Materials*), 8–13 October 2007, Bangalore, India.
2. "A novel low-cost photoelectrochemical cell for solar hydrogen generation," *NHA national hydrogen conference*, Sacramento, March-April 2008.
3. "High capacity photoelectrochemical hydrogen generation using hybridized nanotubular arrays of TiO₂ photoanode and cathode," Paper No 085, Proceedings of the *ISFL Conference*, New Delhi, March 2008.
4. "Production of renewable solar hydrogen using semiconductor metal oxides by water photoelectrolysis," *Clean Technology Conference 2008*, Boston, June 2008.
5. "Photoelectrochemical generation of hydrogen using coupled titania nanotube semiconductors," *PEC Working Group Meeting*, Phoenix, AZ, May 2008.