II.H.13 University of Nevada, Reno Photo-Electrochemical Project*

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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 incorporation in a single photo anode.
- Improve the durability of the material.
- On-field application.
- 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 band gap: 2.3 eV by 2013.
- Chemical conversion process efficiency: 10% by 2013.
- Plant durability: 1,000 hrs by 2013.

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Approach

In this project, utilization of hybrid metal (Ti, W, Fe, 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 suitable to prepare mixed metal oxide nanotubes e.g. TiFe, TiMn and TiW. In addition to the anodization process, we are 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:

1. Synthesis of visible light active mixed metal oxide photocatalysts.
2. The formation mechanism and kinetics of metal oxide.
3. Reaction kinetics of the water splitting reactions at the interface.
4. Effect of nanotubular wall thickness on electron trapping.
5. Effect of band bending across the nanotube wall.
6. 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 new catalysts for PEC generation of hydrogen using sunlight.

Accomplishments

- The UNR team has developed a novel sonoelectrochemical process to prepare smooth and ultra-thin hematite band gap (2.2 eV) nanotube arrays (Figure 1). We have also developed a process to prepare TaON nanotube arrays (band gap 2.07 eV). These materials showed excellent visible light activity compared to TiO_2 nanotubes (Table 1).
- UNR also designed a PEC cell for on-field hydrogen generation (Figure 2).

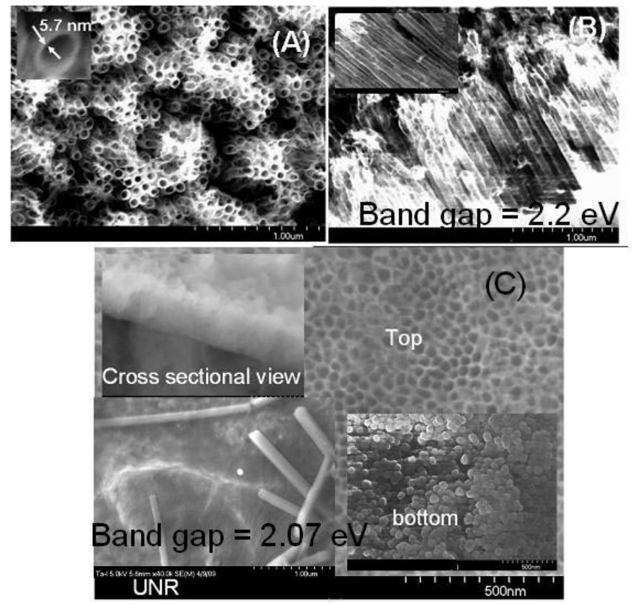

FIGURE 1. Scanning Electron Microscope Images of: (A) & (B) Fe_2O_3 Nanotubes and (C) TaON Nanotube Arrays

TABLE 1. Comparison of Photocurrent Density of TaON Nanotubes with Various other Photocatalysts

Photocatalyst	Photocurrent density (mA/cm^2) at 0.5 $V_{Ag/AgCl}$	Visible Light Contribution (%)
P25/Ti	0.365	0.32
TiO_2 NTs/Ti	0.638	0.39
Fe_2O_3 NTs/Fe	1.4	50
Fe_2O_3 nanoparticle/Fe	0.004	NA
Ta_2O_5 NTs/Ta	0.25	0.28
TaON NTs/Ta	2.6	47

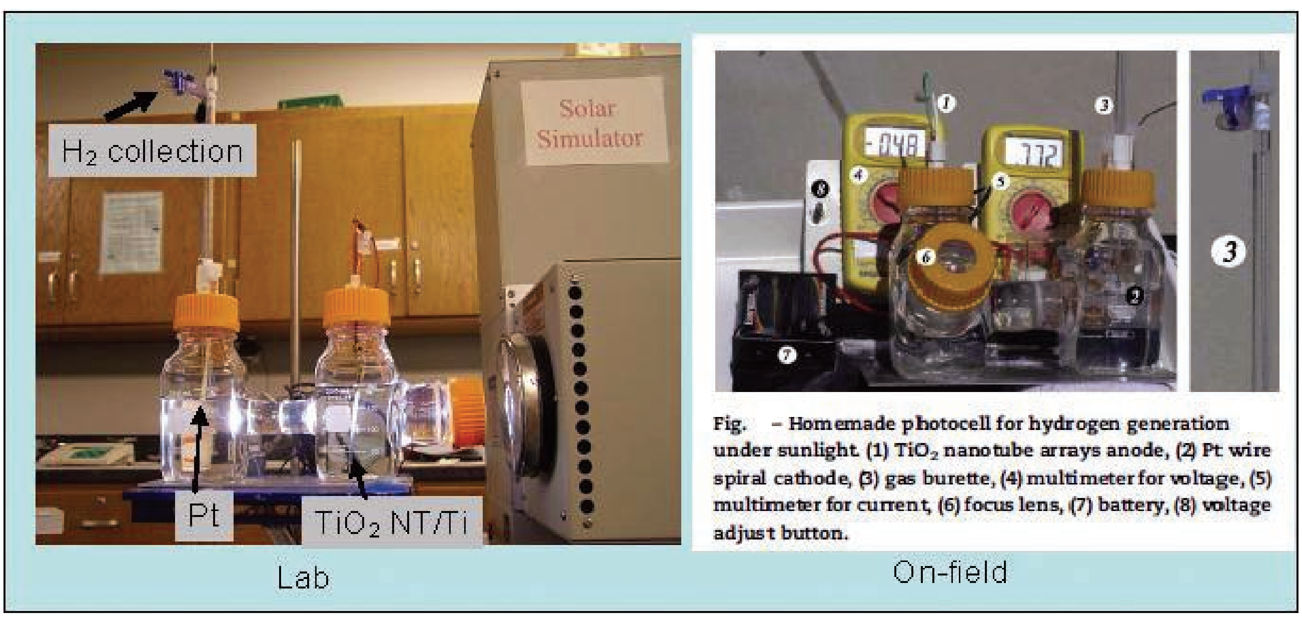

FIGURE 2. Preliminary results indicate that H_2 generation from on-field experiments is comparable to the experiments under simulated solar light conditions (AM 1.5).

Conclusions and Future Actions

- In the last year, we have synthesized photoanodes with low band gap nanotubular materials by sonoelectrochemical anodization techniques. We have also expanded the idea to understand the formation mechanism, crystallization and kinetics of the formation of nanotubes by the sonoelectrochemical anodization method. These nanotubes are found to efficient materials for hydrogen generation by water splitting using visible light. These nanotubular photo-anodes are found to be stable for 30 days (8 h/day). In summary, the following bulleted list is indicative of the areas we will pursue in the coming year of the project:
- Synthesis of one dimensional mixed metal oxide and metal oxynitride nanotubular materials.
- Synthesis of coupled and combinatorial photo-anodes.
- Incident photon to current conversion efficiency measurements.
- Design large PEC system for on-field testing under real solar irradiation.
- Scale-up testing for solar light harvesting.

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 2009 Publications/Presentations

Publications

1. "Photoelectrolysis of water using heterostructural composite of TiO_2 nanotubes and nanoparticles," *J. Physics D: Applied Physics* 2008, *41*, 245103/1.

2. "Electrochemically assisted photocatalytic degradation of methyl orange using anodized TiO_2 nanotubes, *Journal of Applied Catalysis B. Environmental* 2008, *84*, 372.

3. "Synthesis of a carbon nanotube/ TiO_2 nanotube hybrid material and its use for reversible hydrogen storage," *Nanotechnology* 2008, *19*, 445607/1.

4. "Synthesis of coupled semiconductor by filling 1D TiO_2 nanotubes with CdS," *Chem. Mater.* 2008, *20*, 6784.

5. "Functionalization of self-organized TiO_2 nanotubes with Pd nanoparticles for photocatalytic decomposition of dyes under solar light illumination," *Langmuir* 2008, *24*, 11276.

6. "Interfacial Charge Transfer in Photoelectrochemical generation of hydrogen from water," *Proc. ESA Annual Meeting on Electrostatics*, 2008, K1.

7. "Formation and stability of anatase phase of phosphate incorporated and carbon doped titania nanotubes," *Materials Research Bulletin* 2009, *44*, 398.

8. "Enhancement of the photoelectrochemical conversion efficiency of nanotubular TiO2 photoanodes using nitrogen plasma assisted surface modification," *Nanotechnology* 2009, *20*, 075704.

9. "Water photooxidation by smooth and ultra-thin α-Fe_2O_3 nanotube arrays," *Chem. Mater.* (2009 DOI: 10.1021/cm8030208).

10. "Double-wall anodic titania nanotube array for water photoxidation," *Langmuir* (2009 DOI: 10.1021/la900426j).

11. "Hydrogen generation under sunlight by self ordered TiO_2 nanotube arrays" *Int. J. Hydrogen Energy*, 2009, *34*, 3250.

12. "Nanostructured anodic iron oxide film as photoanode for water oxidation" *J.Physics D: Appl. Phys.*, 42 (2009) 135303 (10pp).

Presentations

1. "Photooxidation of Water Using Vertically Aligned Nanotube Arrays: A comparative study of TiO_2, Fe_2O_3 and TaON nanotubes" Material Research Society Meeting 2009, March 16th, San Francisco, CA.

2. "Nanotubular semiconductor photocatalysts for visible light water photooxidation: UNR update" PEC Working Group Meeting 2009, March 17th to March 19th, San Francisco, CA.