II.G.13 Photoelectrochemical Generation of Hydrogen from Water Using Visible Light Sensitive Ferro-Electric $BiFeO_3$ and Semiconductor Nanotubes*

Dr. Mano Misra
University of Nevada, Reno (UNR)
1664 N. Virginia Street, MS 388
Reno, NV 89500
Phone: (775) 784-1603
E-mail: misra@unr.edu

DOE Technology Development Manager:
Eric Miller
Phone: (202) 287-5829
E-mail: eric.miller@hq.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956
E-mail: David.Peterson@go.doe.gov

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

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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 photoelectrochemical (PEC) 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

(Z) Materials Durability

Technical Targets

This project investigates 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: 2.3 eV by 2013
- Chemical conversion process efficiency: 10% by 2013
- Plant durability: 1,000 h by 2013

Approach

In this current project, utilization of hybrid metal (Ti, W, Fe, Ta) oxide nanotubular arrays for generation of hydrogen from water using sunlight is being studied. The metal oxide nanotubular arrays have been found to be robust, photo-corrosion resistant, and can be used efficiently to generate hydrogen and most importantly are active in the visible light portion of the solar spectrum. It is envisioned that the process will be efficient and economical in the production of solar hydrogen. The nanotubular arrays were prepared by electrochemical anodization of solid 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 was studied. It was found that materials prepared in organic solvents such as ethylene glycol by an ultrasonic assisted process were stable and form an efficient pattern of nanotubes that have excellent photo-efficiency. We have already developed processes to synthesize metal oxide nanotubes in inorganic, organic and ionic liquids as electrolytes. This process is also suitable to prepare mixed metal oxide nanotubes e.g. TiFe, TiMn and TiW. In addition to the preparation of metal oxide-based photoanodes, we have also shown that these nanotubes can work efficiently as a cathode by nanoparticle modification. In addition to the anodization process, we have also developed new mixed metal oxide compounds by sol-gel method. In this project, a highly efficient photoanode, a cathode, and a modified electrolyte will be integrated to design a PEC cell to generate hydrogen with at least 10% efficiency by 2013. The scale up process looks highly promising for large-scale hydrogen generation.

The hydrogen generation work was conducted using a hybrid metal oxide nanotubular or mixed metal oxide photoanode in alkaline solutions in the presence of simulated solar light. The material stability and photo-efficiency was determined as a function of time, electrochemical and analytical measurements. The photo-efficiency was determined by measuring current as well as volume of the hydrogen generated by gas chromatograph.

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

- The formation mechanism and kinetics of metal oxide nanotubes prepared by various anodization methods and electrochemical solutions.
- Synthesis of visible light active metal oxide nanotubular photocatalysts for PEC applications and analysis of their various phases while annealing by X-ray diffraction (XRD) measurements followed by density functional theory (DFT) calculations.
- Synthesis of visible light active mixed metal oxide photocatalysts for PEC applications.
- Develop quantum dot sensitized nanotubular oxide hybrid photo-anodes based on DFT modeling.
- Stability of the catalysts for 1,000 h.

On the basis of fundamental and applied research, a scaled-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 designed a low-cost process for synthesis of nanostructured bismuth iron oxide ($BiFeO_3$) as a multiferroic material for PEC applications. The experimental band gap of $BiFeO_3$ was found to be 2.1 eV (Figure 1(I)). The synthesis conditions were optimized and it was found that a highly crystalline nanostructured material could be obtained when $BiFeO_3$ is annealed under N_2 at 600°C for 2 h (Figure 1(II)).
- $BiFeO_3$ was found to be an efficient photocatalyst generating hydrogen under AM 1.5 light illumination conditions in 1 (M) KOH as electrolyte (Figure 2).

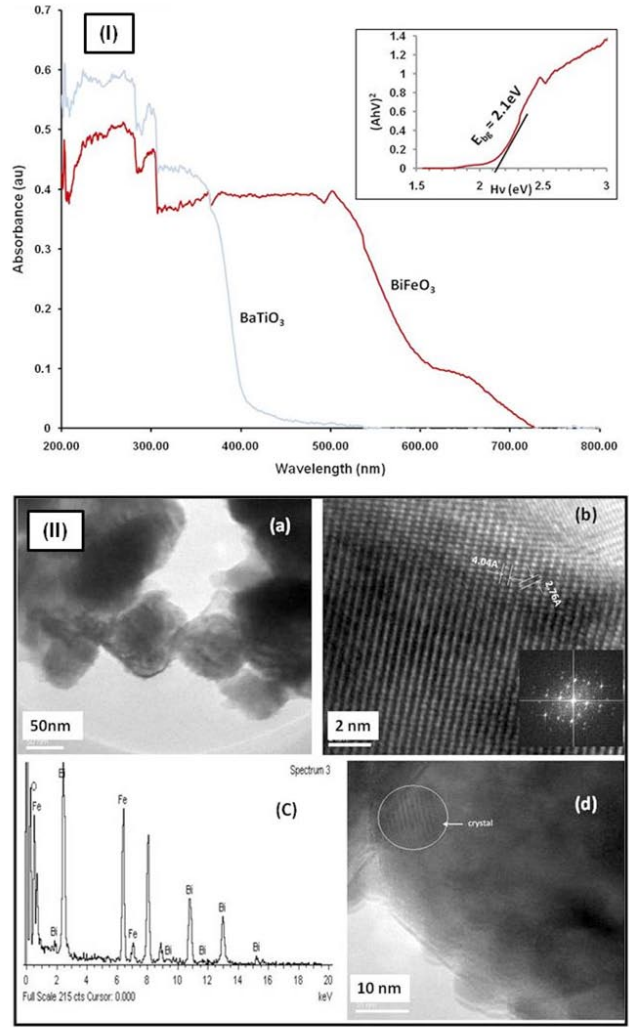

FIGURE 1. **(I)** Ultraviolet-visible absorption spectrums of $BiFeO_3$ and $BaTiO_3$. The inset shows the $BiFeO_3$ plot of $(\alpha h\nu)^2$ as a function of photon energy. **(II)** Transmission electron microscope images and XRD pattern of $BiFeO_3$ calcined at 600°C for 2 h under N_2 atmosphere.

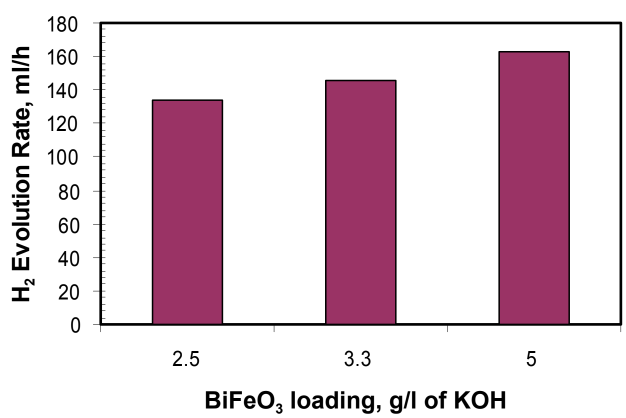

FIGURE 2. Hydrogen generation using $BiFeO_3$ as a multiferroic material for PEC applications in 1 (M) KOH under AM 1.5 light Illumination conditions.

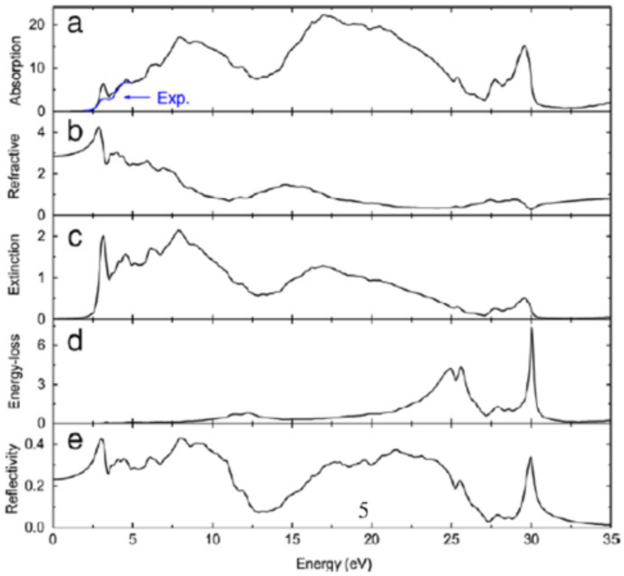

FIGURE 3. The band structure and optical properties of $BiFeO_3$ were estimated using GGA+U-SP approximation considering the unoccupied Fe *3d* orbital state. The calculated band gap was 1.61 eV.

- The band structure and optical properties of $BiFeO_3$ were estimated using generalized gradient approximation with Hubbard-type interaction parameter and spin polarized approach (GGA+U-SP) approximation considering the unoccupied Fe 3d orbital state. The calculated band gap was 1.61 eV (Figure 3).
- UNR has developed an innovative ultrasonically mediated fabrication process to synthesize crystalline tantalum oxynitride (TaON) nanotube (NT) arrays (Figure 4). TaON NTs have been synthesized by a two-step process, firstly by forming Ta_2O_5 NTs (anodizing Ta foil) followed by heating them in an atmosphere of flowing NH_3 at 700ºC for 6 h. It should be mentioned here that TaON nanoparticles (NPs) are not formed when Ta_2O_5 NPs are heated at 700ºC for 6 h under identical synthesis conditions as TaON NTs.
- TaON NTs have a band gap 2.07 eV (Figure 5(A)) and show excellent visible light activity (47%) compared to TiO_2 nanotubes (0.39%) (Figure 5(B)).
- The first principle computational calculations of Ta_2O_5 and TaON have been carried out based on DFT using plane wave assumption (Figure 6). The calculated band gaps are smaller than the experimentally determined values. In our current simulation, the calculated band gap of Ta_2O_5 is 3.6 eV, while the experimental value is 4 eV. The calculated band gap of TaON is about 1.9 eV.

Conclusions and Future Actions

In the past year, we have developed new metal oxide based mixed nanotube arrays. We have also got an expanded idea on the formation conditions of metal oxynitride NTs and metal oxynitride NPs. TaON NTs prepared by single nitridation and annealing step are found to be efficient photocatalysts for hydrogen generation by water splitting using visible part of the solar spectrum. Preliminary studies on $BiFeO_3$ as a multiferroic material for photocatalysis has shown positive results. Theoretical studies on bandgap calculations are in accordance with the experimentally determined values. 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 materials for PEC applications.
- Synthesis of photoanodes composed of multiferroic materials.

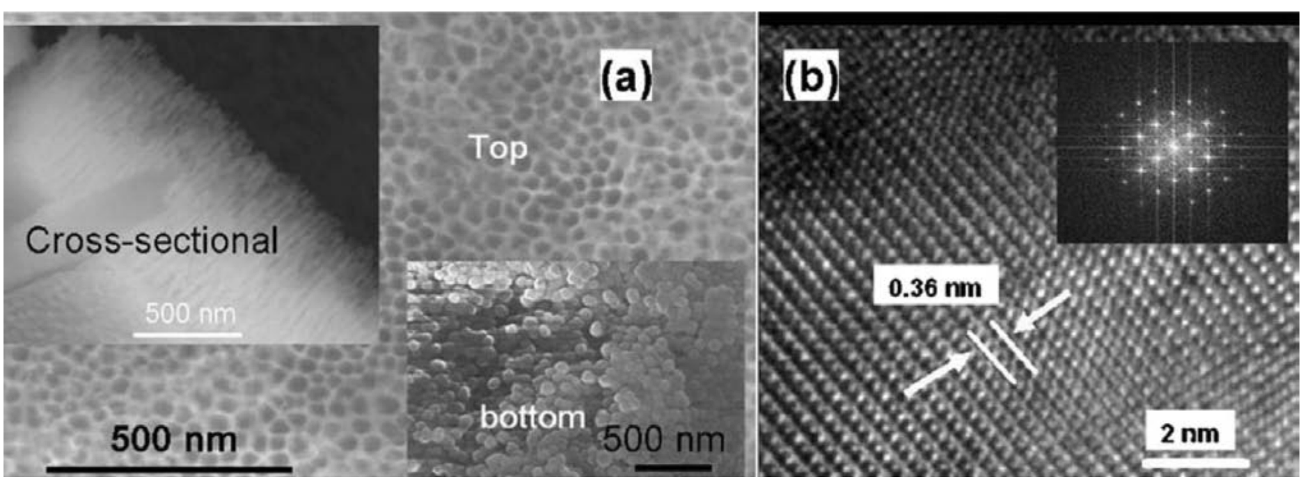

FIGURE 4. **(a)** Field emission scanning electron microscopy images of TaON nanotube arrays on Ta foil. The insets show the cross sectional image of Ta_2O_5 NT arrays. **(b)** High-resolution transmission electron microscope and fast Fourier transformation pattern of TaON NTs.

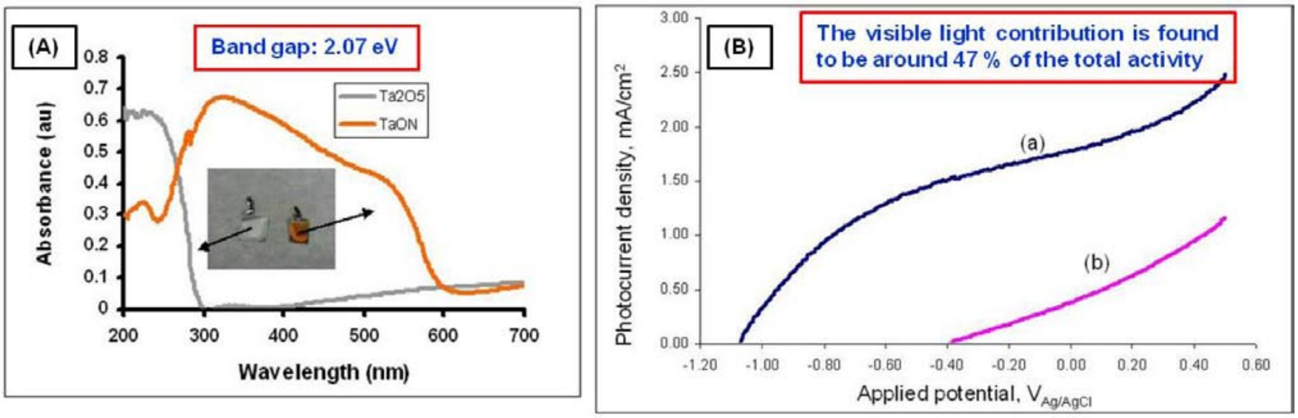

FIGURE 5. **(A)** Diffuse reflectance ultra violet -visible photo spectrometry spectra of Ta_2O_5 and TaON NTs on Ta foil. Inset shows the digital image of Ta_2O_5 and TaON NT arrays. **(B)** Potentiodynamic plot of TaON NTs under global AM 1.5 solar light (a) and visible light (≥420 nm) illumination. Nanotubes of 50 nm internal diameter and 525 nm long are used. Sample is: 1 cm^2. (The dark current density is ~90 mA/cm^2).

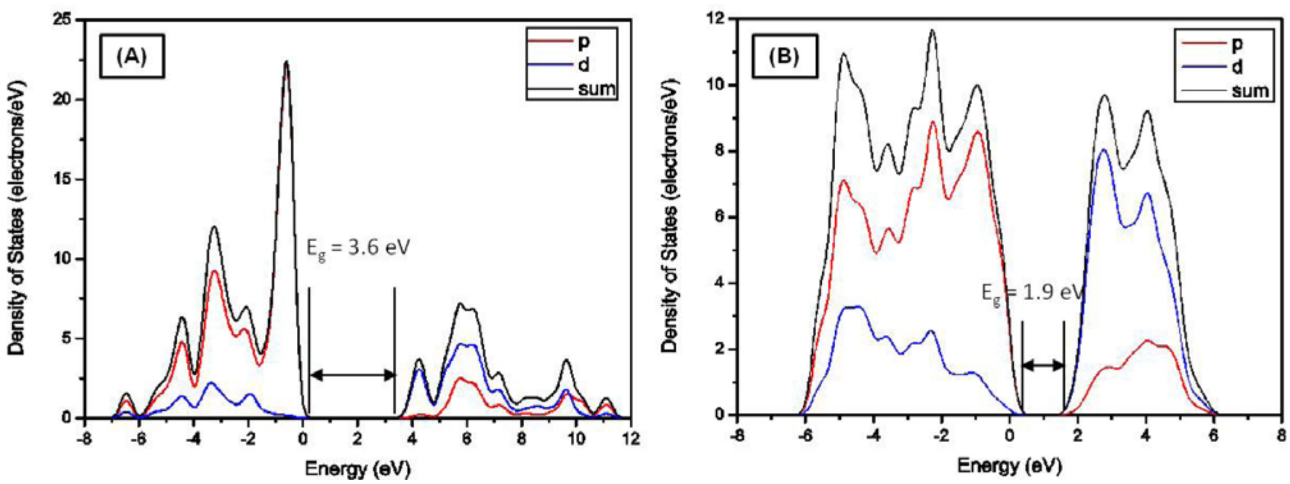

FIGURE 6. Partial density of states as a function of energy level of **(A)** Ta_2O_5 and **(B)** TaON. The calculated band gaps are smaller than the experimentally determined values.

- 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. "Titanium dioxide nanotubes and their use in photovoltaic devices", U.S. Patent, filed May 2010.

FY 2010 Publications/Presentations

1. "Dye-Sensitized Photovoltaic Wires Using Highly Ordered TiO_2 Nanotube Arrays", *ACS Nano* 2010, *4*, 2196.

2. "Bifacial dye-sensitized solar cells based on vertically oriented TiO_2 nanotube arrays", *Nanotechnology* 2010, *21*, 125703.

3. "Formation of chelating agent driven anodized TiO_2 nanotubular membrane and its photovoltaic application", Nanotechnology 2010, *21*, 145201.

4. "Ordered Titanium Dioxide Nanotubular Arrays As Photo Anodes for Hydrogen Generation", Chapter 9, Solar Hydrogen and Nanotechnology, Edited by Lionel Vayssieres, 2010, Published by John Willey and Sons.