II.G.8 Photoelectrochemical Hydrogen Generation from Water Using $TiSi_2$ –TiO_2 Nanotube Core-Shell Structure*

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*Congressionally directed project

Fiscal Year (FY) 2011 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 (3.1.4) of the Fuel Cell 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 metal oxide nanotubes (NTs) 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: 2.0eV by 2018.
- Chemical conversion process efficiency: 10% by 2013.
- Plant durability: 1,000 hr by 2013.

Approach

In this current project, utilization of hybrid metal (Ti, Fe, Ta) oxide nanotubular arrays for generation of hydrogen from water using sunlight is studied. The metal oxide nanotubular arrays are found to be robust, photo-corrosion resistant, and can be used efficiently to generate hydrogen and most importantly active in the visible light portion of the solar spectrum. 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 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. It is found from preliminary work that materials prepared in organic solvents such as ethylene glycol by an ultrasonic assisted process are very 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 found 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. This project is integrating a highly efficient photoanode, a cathode, and a modified electrolyte to design a photoelectrochemical (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 is 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 is determined as a function of time, electrochemical and analytical measurements. The photo-efficiency is determined by measuring current as well as volume of the hydrogen generated by gas chromatograph. 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:

- Synthesize photoanodes that can harvest the full spectrum of sunlight.
- Theoretical investigation on the materials synthesized.
- On-field testing under real solar irradiation.

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 photo-electrochemical generation of hydrogen using sunlight.

FY 2011 Accomplishments

- The UNR team has developed a composite photocatalyst comprising of self-assembled titania (TiO_2) NTs coupled with titanium disilicide ($TiSi_2$) nanoparticles (NPs) for PEC hydrogen generation (Figure 1).
- A new approach is taken to synthesize TiO_2 NTs with bigger pore size and length so that more $TiSi_2$ particles can be loaded. Anodization of Ti to form TiO_2 NTs in the presence of a chelating agent disodium ethylenediamine tetraacetate ($Na_2[H_2EDTA]$) under high voltage (80 V_{DC}) makes the diameter of the NTs bigger than the conventional process (Figure 2). The back side of the TiO_2 NTs is etched with 5% hydrofluorhydric acid to form a TiO_2 nanotubular membrane.
- $TiSi_2$ NPs are produced from commercial bulk particles by a multiple ball milling followed by ultrasonicatation process (Figure 3). The $TiSi_2$ nanoparticles are sintered into the TiO_2 nanotube array to prepare the $TiSi_2/TiO_2$ NTs. This catalyst is then annealed under a nitrogen atmosphere to form a composite of $TiSi_2$ nanorods inside TiO_2 NTs at 500°C for 6 h. The prepared $TiSi_2$-TiO_2 material is then coated on Ti foil using a titanium tetrachloride solution followed by annealing at 500°C for 3 h under nitrogen. This also helped in sintering the $TiSi_2$ nanoparticles inside the TiO_2 nanotubes to form a nanorod array. The TiO_2 nanotubular array is found to be stable after the synthesis of $TiSi_2$ nanorods inside them (Figure 4). The $TiSi_2$ nanostructure is found to be homogeneously distributed throughout the TiO_2

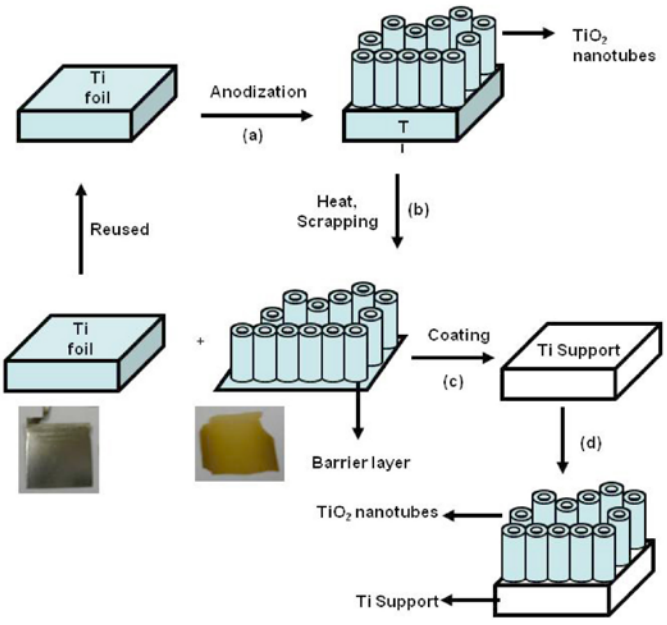

FIGURE 1. Schematic Showing the Formation of $TiSi_2/TiO_2$ NT Composite Structure

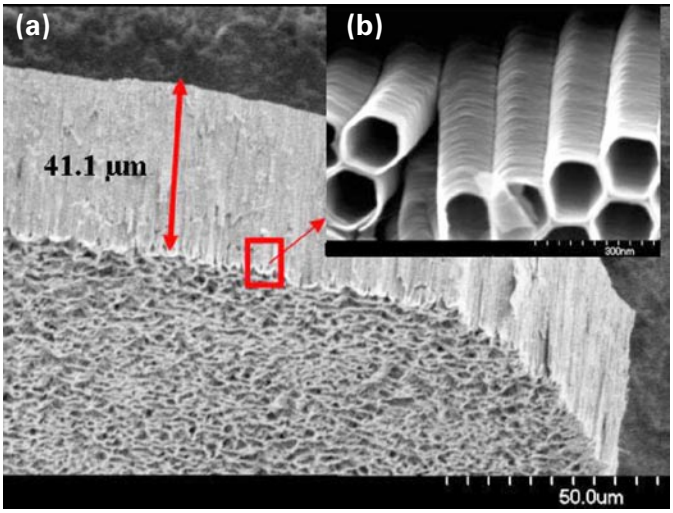

FIGURE 2. Field emission scanning electron microscope images of TiO_2 NTs prepared in organic medium at 80 V_{DC} for 30 min. (a) top view and (b) cross sectional view (close-up) view of the NTs.

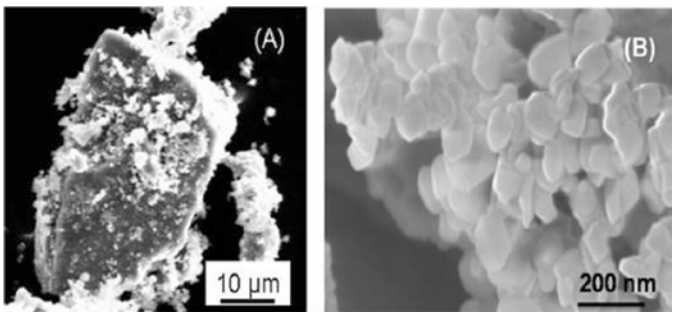

FIGURE 3. Field emission scanning electron microscope images of (A) as-received $TiSi_2$ particles (<44 µm), (B) ball-milled $TiSi_2$ particles (~50-60 nm).

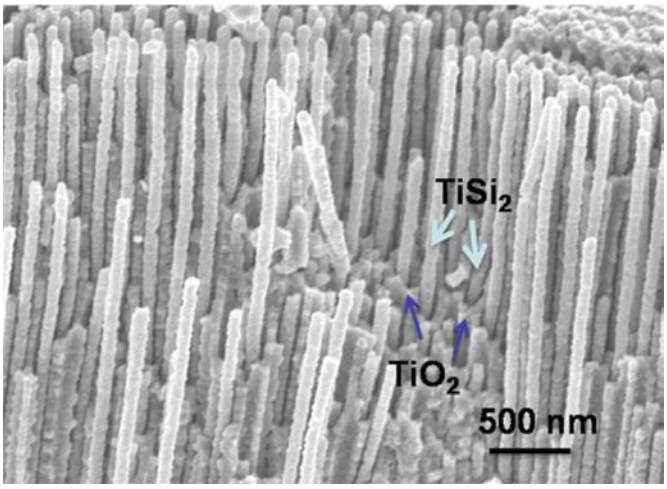

FIGURE 4. Field emission scanning electron microscope images of $TiSi_2$ particles sintered into the TiO_2 NT array.

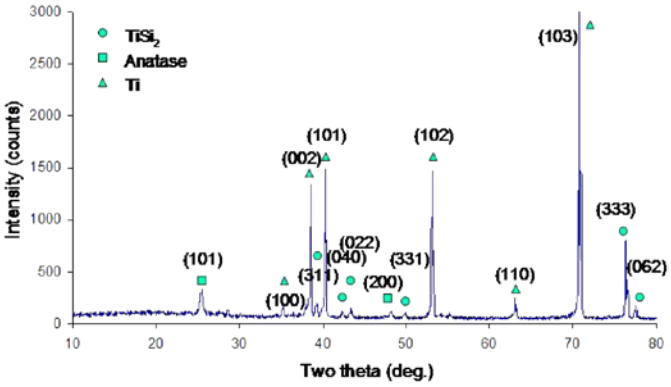

FIGURE 5. Glancing angle X-ray diffraction pattern of $TiSi_2$ NP/TiO_2NT. Orthorhombic $TiSi_2$ and anatase TiO_2 are observed in the heterostructure. A peak for the Ti base is also noticed.

nanotubular array. Energy dispersive spectroscopy analysis showed ~25 wt% $TiSi_2$ in the $TiSi_2/TiO_2$ NTs photocatalyst. Glancing angle X-ray diffraction pattern shows peaks corresponding to both $TiSi_2$ and TiO_2 (anatase) (Figure 5).

- The diffuse reflectance ultraviolet and visible spectrum of $TiSi_2/TiO_2$ NTs catalyst shows a sharp edge ~550 nm (band gap, $E_g = 2.25$ eV). The strong absorption peaks in both the ultraviolet and visible regions suggest that the $TiSi_2/TiO_2$ NT photocatalyst is prepared by combining the absorption properties of the TiO_2 NTs in the ultraviolet region and $TiSi_2$ in the visible region (Figure 6).
- The heterostructural composite photoanode exhibited an enhanced photocurrent density of 3.49 mA/cm^2 at 0.2 $V_{Ag/AgCl}$ compared to TiO_2 nanotubes alone (0.9 mA/cm^2) and can be considered as a potential possible candidate for water splitting reaction using visible light (Figure 7).

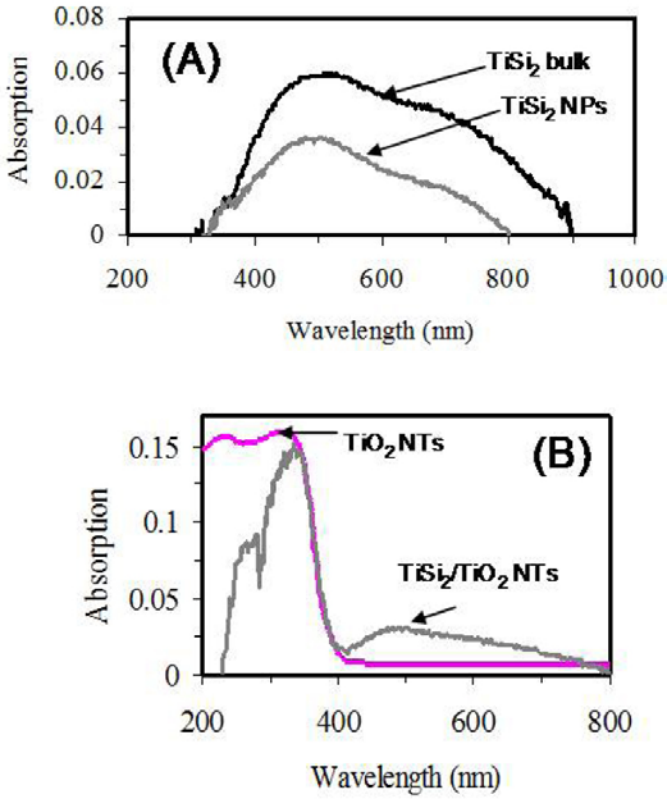

FIGURE 6. Diffuse reflectance ultraviolet and visible spectra of (A) $TiSi_2$ bulk and nanoparticles and (B) TiO_2 NTs and $TiSi_2/TiO_2$ NTs catalyst. $TiSi_2$ particles showed absorption in the visible light region and $TiSi_2/TiO_2$ NTs absorb light in both ultraviolet and visible region. Band gap = 2.25 eV.

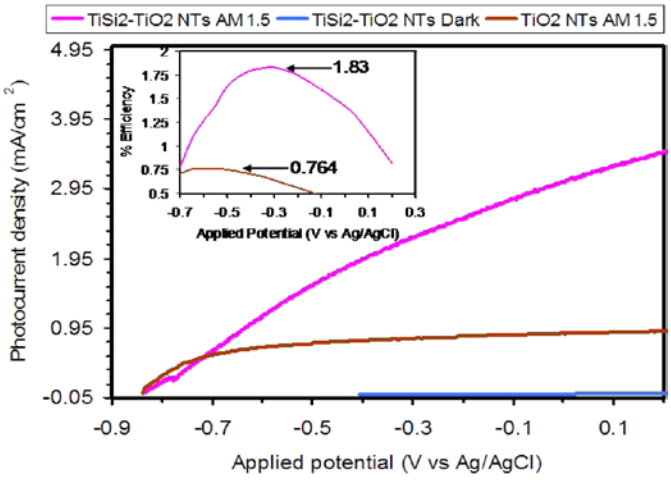

FIGURE 7. Potentiodynamic plot of annealed $TiSi_2/TiO_2$ NTs and TiO_2 NTs. Inset shows the solar-to-hydrogen conversion efficiency of $TiSi_2$-TiO_2 NTs and TiO_2 NTs under AM 1.5 illumination.

Conclusions and Future Actions

In the last year, we have developed a new type of coupled semiconductor photo-catalyst by coupling $TiSi_2$

nanoparticles and TiO_2 NTs by simple sintering method. A unique architecture, $TiSi_2$ nanorods inside $TiSi_2$ nanotubes, is prepared by this process. It showed four-fold enhancement in the amount of hydrogen generated compared to only TiO_2 NTs and ten times compared to P25 TiO_2 nanoparticles. The following bulleted list is indicative of the areas we will pursue in the coming year of the project:

- Synthesize visible light sensitive photoanodes.
- Kinetics studies of nanotube formation by titration using spectrophotometric analysis.
- Theoretical investigation of $BiFeO_3$ by density functional theory.
- To understand the ordering of oxygen vacancies and their role on charge transport properties and recombination losses in oxide and oxynitride semiconductors.
- Scale up the system.
- Design PEC system for on-field testing under real solar irradiation.
- Synthesize quantum dots incorporated inside TiO_2 NTs for PEC.

FY 2011 Publications/Presentations

Publications (2010-2011)

1. "Bismuth Iron Oxide Nanoparticles as Photocatalyst for Solar Hydrogen Generation from Water" *Journal of Fundamentals of Renewable Energy and Applications (JFREA)* (**2011**, *1*, Article ID R101204, 10 pages). **(INVITED)**

2. "Water Photooxidation by $TiSi_2$-TiO_2 Nanotubes" **S. Banerjee**, S.K. Mohapatra, M. Misra *J. Phys. Chem. C* **2011**, *115*,12643-12649.

3. "Morphology-Controlled ZnO Nanomaterials for Enhanced Photoelectrochemical Performance" *Mater. Express* **2011**, *1*, 59-67.

4. "Easy synthesis of bismuth iron oxide nanoparticles as photocatalyst for solar hydrogen generation from water" Master's Thesis by Deng, Jinyi, **2010**, 85 pages; AAT 1484020.

5. Quantum Dot Sensitized Nanotubes for Full Solar Spectrum Photovoltaic Cell Master's Thesis by *Khanal, Sohana*, **2010**, 104 pages; AAT 1484059.