II.G.8 Photoelectrochemical Hydrogen Generation from Water Using TiSi$_2$–TiO$_2$ Nanotube Core-Shell Structure*

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, photocorrosion 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 photoefficiency. We have already developed processes 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 photoelectrochemical 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$_2$EDTA]) 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 ultrasonication 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).
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).

**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)


