Photo-electrochemical Hydrogen Generation from Water Using TiSi$_2$ –TiO$_2$ Nanotube Core-Shell Structure

Mano Misra
Principal Investigator
Chemical and Materials Engineering
University of Nevada, Reno
Reno, Nevada, 89557
Phone: 775-784-1603
Email: misra@unr.edu

DOE Hydrogen Program Review 2011, May 9-13, 2011

Project ID # PD076
## Overview

### Timeline
- Project start date: September, 2006
- Project end date: September, 2012
- Percent complete: 86

### Barriers
- Barriers addressed:
  - AP. Materials efficiency
  - AQ. Materials durability
  - AR. Bulk material synthesis
  - AS. Device configuration and scale up

### Budget
- Total project funding: $ 3,400 K
  - DOE share: $ 2,720 K
  - Contractor share: $ 680 K

### Partner
- *John Turner*, National Renewable Energy Laboratory
Objectives

Overall
Develop high efficiency hybrid-semiconductor nanotubular materials for hydrogen generation by water splitting

- Develop new anodization techniques to synthesize high quality and robust titanium dioxide (TiO₂) nanotubes with wide range of nanotubular architectures

2006-2007
- Develop low band gap TiO₂ nanotubes
  - Understand kinetics and formation mechanism of the TiO₂ nanotubes under different synthesis conditions
- Develop organic-inorganic hybrid photo-anodes

2007-2008
- Develop multi-junction photoanodes
- Develop cost-effective cathode materials

2008-2009
- Develop multi-junction photoanodes
- Design PEC systems for on-field testing under real solar irradiation

2009-2010
- Develop semiconductors which absorb in the visible region of the solar spectrum

2010-2011
- Develop visible light sensitive ferroelectric BiFeO₃ and TiSi₂ – TiO₂ hetero nanotubular structures as high efficiency photo anodes.

2011-2012
- Develop coupled semiconductor systems for visible light activity
Task A. Synthesis and fabrication of photocatalysts

- Ultrasonic mediated TiO$_2$ nanotube arrays (NTs)
- Low cost sol-gel based synthesis of BiFeO$_3$ ferroelectric photo catalysts
- Fabrication of couple semiconductor (TiSi$_2$ nanorod-TiO$_2$ nanotube)
- Characterization and fundamental understanding of the materials prepared

Task B. Application of the nanotubular materials for photoelectrochemical generation of H$_2$ from Water

- Evaluate photoelectrochemical behavior of TiO$_2$-TiSi$_2$ photoanodes
- Evaluate photocatalytic and photoelectrochemical behavior of BiFeO$_3$

Task C. Materials stability of hybrid oxide nanotubular photo-anodes

- Electrochemical methods
- Spectroscopic and Electron Microscopic analyses

Task D. Scale-up and process evaluation.

- Scale-up of photoanodes
- Photoelectrochemical hydrogen generation under real solar irradiation

Task E. First Principle Modeling of Semiconductors for harvesting visible light
Photo Electrochemical Water Splitting by TiSi$_2$ Nanorod-TiO$_2$ Nanotubes

TiSi$_2$: Band gap varies from 3.4 eV (ca. 360 nm) to 1.5 eV (ca. 800 nm)
Ideal material for PEC applications

Major challenges for TiO$_2$ NTs for PEC application
- Large band gap of 3.1-3.2 eV; absorbs solar light only in the UV region
- Only about 4-5% of the solar spectrum falls in this UV range

Managing the challenge: Options
- Changing electrical properties of the TiO$_2$:
  - Varying the crystallite size
- Doping with other metal/non-metal ions:
  - Induce red shift to the band gap
- Coupling with other nanostructured materials

UNR Approach

Advantages: Results in hybrid photoanodes that contain multiple band gap materials in a single photo anode with appropriate band edge positions leading to enhanced light absorbance in visible spectrum and high photo conversion efficiency.

Strategy: Design self-assembled titania (TiO$_2$) nanotube array electrode filled with titanium disilicide (TiSi$_2$) nanoparticles
New Approach to Synthesize TiO$_2$ Nanotubes (NTs)

**Objective:** To obtain a TiO$_2$ nanotubular membrane with bigger pore size and length so that more TiSi$_2$ particles can be loaded (compared to conventional synthesis).

**Procedure:** Anodization of titanium at potentials > 60 V in the presence of a chelating agent (EDTA) in fluoride containing ethylene glycol electrolyte forms large diameter TiO$_2$ nanotubes.

**Anodizing condition:**
- 5% water in ethylene glycol
- + 0.5 wt% NH$_4$F +
- 0.25 wt% Na$_2$[H$_2$EDTA], pH = 6.4-6.5, 15 °C, 80 V$_{DC}$,
- 30 min, mechanical stirring

**Figure:** Current transient plot of anodization of TiO$_2$ in fluoride + EDTA and only fluoride solutions (conventional way). The anodization current decreases continuously when only fluoride is used. Addition of EDTA increases the steady state anodization current. This may be due to the release of free F$^-$ in the (EDTA+F$^-$) solution. This leads to the extremely fast kinetics when (EDTA+F$^-$) solution is used for anodization.
1. **Preparation of TiO$_2$ thin film:** The anodized samples are properly washed with distilled water to remove the occluded ions, dried in an air oven to take out the TiO$_2$ layer as a thin film.

2. **Obtaining membrane:** This film is etched with aqueous hydrofluoric acid (HF) (5%) from the back side whereby the barrier layer is dissolved.
Fabrication of Titania Nanotubes (NTs) with Nanoparticles (NPs)
(Synthesis of NP/NT Heterostructure Photoanode)

Results of anodization: TiO$_2$ NTs of length: 22 μm; pore diameter: 122 nm; wall thickness: ~30 nm

Figure: FESEM 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: FESEM images of (A) as-received TiSi$_2$ particles (<44 μm), (B) ball milled TiSi$_2$ particles (~50-60 nm)

As-purchased large particles of TiSi$_2$ (<44 μm)

Multi-step ball milling

Ultrasonication in methanol

Nanoparticles (~50-60 nm)
Fabrication of TiSi₂ NP/TiO₂ NT Electrode

**Fabrication of TiSi₂ NP/TiO₂ NT Heterostructure:** The TiSi₂ nanoparticles are sintered into the TiO₂ nanotube array to prepare the TiSi₂/TiO₂ NTs. This catalyst is then annealed under nitrogen (N₂) atmosphere to form a composite of TiSi₂ nanorods inside TiO₂ NTs at 500 °C for 6h. Annealing converts the material to a crystalline one and also removes the organics.

**Fabrication of TiSi₂ NP/TiO₂ NT electrode:** The prepared TiSi₂-TiO₂ material is then coated on Ti foil using titanium tetrachloride (TiCl₄) solution followed by annealing at 500 °C for 3 h under N₂. This also helped sinter the TiSi₂ nanoparticles inside the TiO₂ nanotubes to form nanorod array. The TiO₂ nanotubular array is found to be stable with the growth of TiSi₂ nanorods within the nanotubes.

**Figure:** FESEM images of TiSi₂ particles sintered into the TiO₂ NT array.
### Characterization of the Composite Material

- **Field emission scanning electron microscopy (FESEM):** Analyze the nanotube-nanoparticle composite formation and morphology.

- **The TiSi$_2$ nanostructure is found to be homogeneously distributed throughout the TiO$_2$ nanotubular array.** Energy Dispersive Spectroscopy (EDS) analysis showed ~25 wt% TiSi$_2$ in the TiSi$_2$/TiO$_2$ NTs photocatalyst.

- **Glancing angle X-ray diffraction (GXRD) pattern shows peaks corresponding to both TiSi$_2$ and TiO$_2$ (anatase).** It can be seen that in this work single phases of TiSi$_2$ (C54) and TiO$_2$ (anatase) are observed. The peaks (311), (040), (022), (331), (333) and (062) all correspond to C54, orthorhombic structure of TiSi$_2$.

---

**Figure:** GXRD pattern of TiSi$_2$ NP/TiO$_2$NT. Orthorhombic TiSi$_2$ and anatase TiO$_2$ are observed in the heterostructure. A peak for the Ti base is also noticed.
Absorption Studies of TiSi₂ NP/TiO₂ NT Composite Material

Diffuse reflectance ultraviolet and visible (DRUV-Vis) results

- The bulk TiSi₂ particles (<44 μm) have an absorption range from 350–800 nm (band gap range $E_g = 3.4$ eV to 1.5 eV. These particles absorb very little in the UV region.

- Pure TiO₂ NTs is observed only in the UV region (< 400 nm; band gap, $E_g = 3.1$ eV).

- The spectrum of TiSi₂/TiO₂ NTs catalyst shows sharp edge ~ 550 nm (band gap, $E_g = 2.25$ eV) and has strong absorption in the UV region due to the TiO₂ NTs as well as in the visible light region due to the TiSi₂ particles. DRUV-Vis show that the TiSi₂/TiO₂ NT photocatalyst is prepared by combining the absorption properties of the TiO₂ NTs in the UV region and TiSi₂ in the visible region.

**Figure:** DRUV-Vis spectra of (A) TiSi₂ bulk and nanoparticles and (B) TiO₂ NTs and TiSi₂/TiO₂ NTs catalyst. TiSi₂ particles showed absorption in the visible light region and TiSi₂/TiO₂ NTs absorb light in both UV and visible region.
The maximum photocurrent density ($J_p$) obtained from TiO$_2$ NTs photoanode is 0.9 mA/cm$^2$ at 0.2 V$_{Ag/AgCl}$.

Under the same illumination conditions, TiSi$_2$/TiO$_2$ NTs photoanode showed ~3.49 mA/cm$^2$ photocurrent density.

The superior activity of the coupled photocatalyst is due to good charge separation as well as efficient solar light harvesting.

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>TiO$_2$-TiSi$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 mA</td>
<td>3.4 mA</td>
</tr>
</tbody>
</table>

Figure: 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.
The evaluation of the stability of the photoanode material is carried out by potentiostatic (current vs. time, I-t) measurements.

The photocurrent value goes down to almost zero as soon as the illumination of light on the photoanode is stopped, and the photocurrent comes back to the original value as soon as light is illuminated again on the photoanode.

Photocurrent value remained almost a constant for more than a hour

The results indicate that the photoanode is stable under photoelectrochemical splitting of water and the current observed is mostly due to the photo activity of the catalyst.

Figure: Potentiostatic (I-t) plot of TiO$_2$-TiSi$_2$ at 0V vs. Ag/AgCl reference electrode. The photocurrent became zero when the light is switched off (illumination stopped) and the original photocurrent again came back after illumination.

Conclusion: The composite photocatalyst is having potential for long term operation with good photoactivity
In order to appreciate the photocurrent results obtained from the TiSi\textsubscript{2}NP/TiO\textsubscript{2}NT photoelectrode, we compare the results with the photocurrent densities of other photoelectrode systems: TiO\textsubscript{2} NTs/Ti, Degussa P25 NPs coated on Ti (P25/Ti) and TiSi\textsubscript{2} NPs coated on Ti (TiSi\textsubscript{2}/Ti).

<table>
<thead>
<tr>
<th>Catalyst\textsuperscript{b}</th>
<th>Photocurrent density (mA/cm\textsuperscript{2}) at 0.2 V\textsubscript{Ag/AgCl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi\textsubscript{2}/TiO\textsubscript{2} NTs</td>
<td>3.49</td>
</tr>
<tr>
<td>TiO\textsubscript{2} NTs</td>
<td>0.90</td>
</tr>
<tr>
<td>TiSi\textsubscript{2}/Ti</td>
<td>0.26</td>
</tr>
<tr>
<td>P25/Ti</td>
<td>0.63</td>
</tr>
</tbody>
</table>

\textsuperscript{a} under AM 1.5 illumination conditions

\textsuperscript{b} annealed under similar conditions

Pt cathode is used in all the experiments
Summary

- **Relevance:** Develop a stable and efficient photoelectrochemical cell for solar hydrogen generation by water splitting

- **Approach:** Synthesize visible light sensitive hybrid nanotube arrays as photoanode material by coupling with other nanostructured materials through combinatorial approach

- **Technical accomplishments and process:** 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 the TiO$_2$ 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.

- **Technology transfer/collaboration:** Active partnership with NREL

- **Proposed future research:** (a) Synthesize photoanodes that can harvest the full spectrum of sunlight, (b) theoretical investigation on the materials synthesized (c) scale-up the PEC system, and (d) on-field testing under real solar irradiation.
Future Work

- Synthesize of visible light sensitive photoanodes
- Kinetics studies of nanotubes formation by titration using spectrophotometric analysis
- Theoretical Investigation of BiFeO₃ by DFT
- 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.