Photo-electrochemical Hydrogen Generation from Water Using $TiSi_2$ –TiO_2 Nanotube Core-Shell Structure

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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 (TiO_2) nanotubes with wide range of nanotubular architectures

2006-2007

- Develop low band gap TiO_2 nanotubes
- Understand kinetics and formation mechanism of the TiO_2 nanotubes under different synthesis conditions

2007-2008

- Develop organic-inorganic hybrid photo-anodes
- Develop multi-junction photoanodes
- Develop cost-effective cathode materials

2008-2009

- Develop mixed metal oxide nanotubular photoanodes
- 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 $BiFeO_3$ and $TiSi_2$ –TiO_2 hetero nanotubular structures as high efficiency photo anodes.

2011-2012

- **Develop coupled semiconductor systems for visible light activity**

Approach

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

Combinatorial approach: Coupling with other nanostructured materials

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.

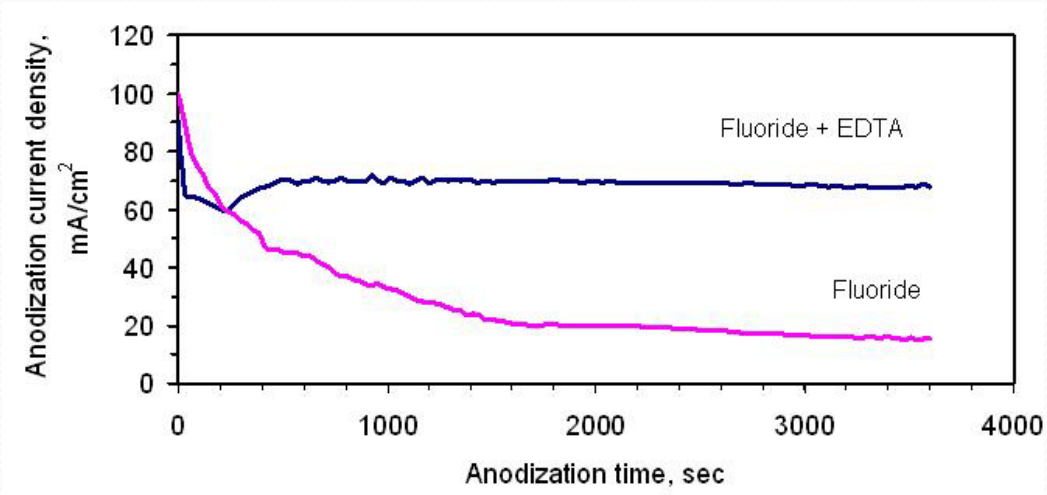
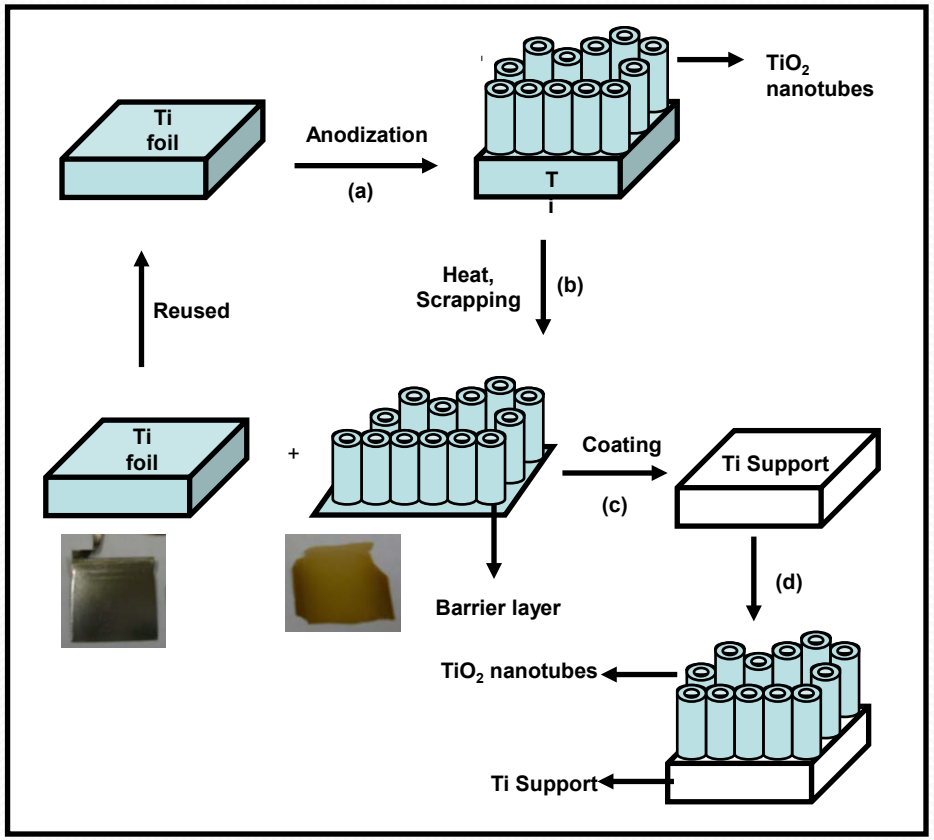


Figure: Current transient plot of anodization of TiO_2 in fluoride + EDTA and only fluoride solutions (conventional way). The anodization current decreases continuously when only fluoride is used. Addition of EDTA increases the steady state anodization current. This may be due to the release of free F^- in the ($EDTA+F^-$) solution. This leads to the extremely fast kinetics when ($EDTA+F^-$) solution is used for anodization

Anodizing condition:

5% water in ethylene glycol + 0.5 wt% NH_4F + 0.25 wt% $Na_2[H_2EDTA]$, pH = 6.4-6.5,15 ^oC, 80 V_{DC}, 30 min, mechanical stirring

TiO_2 Nanotubular Membrane synthesis



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)

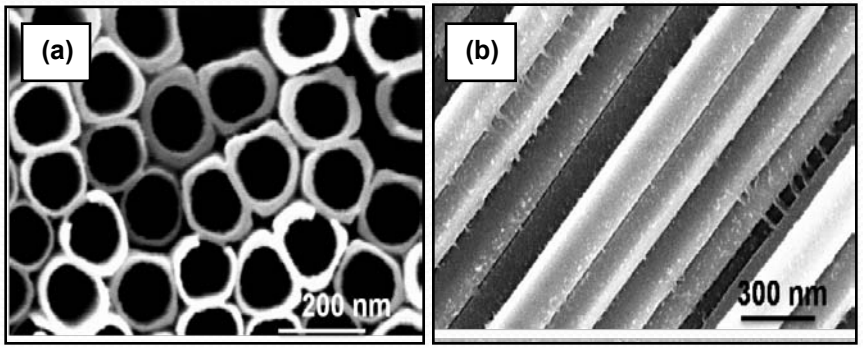


Figure: FESEM images of TiO_2 NTs prepared in organic medium at 80 V_{DC} for 30 min. **(a)** Top view and **(b)** cross sectional view (close-up) view of the NTs

Results of anodization: TiO_2 NTs of length: 22 μm; pore diameter :122 nm; wall thickness: ~30 nm

As-purchased large particles of $TiSi_2$ (<44 μm)

Multi-step ball milling

Ultrasonication in methanol

Nanoparticles (~50-60 nm)

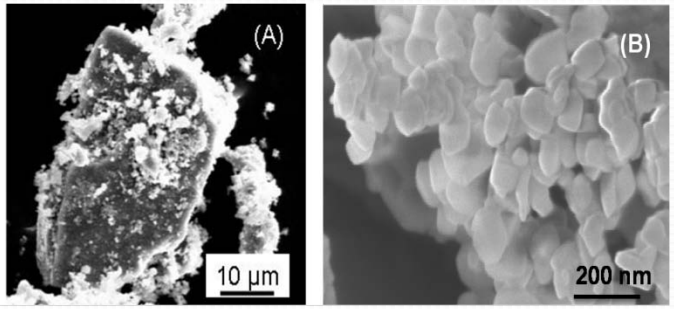


Figure: FESEM images of (A) as-received $TiSi_2$ particles (<44 μm), (B) ball milled $TiSi_2$ particles (~50-60 nm)

Fabrication of $TiSi_2$NP/TiO_2NT Electrode

Fabrication of $TiSi_2$ NP/TiO_2 NT Heterostructure: 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 nitrogen (N_2) atmosphere to form a composite of $TiSi_2$ nanorods inside TiO_2 NTs at 500 ^oC for 6h. Annealing converts the material to a crystalline one and also removes the organics

Fabrication of $TiSi_2$ NP/TiO_2 NT electrode: The prepared $TiSi_2$-TiO_2 material is then coated on Ti foil using titanium tetrachloride ($TiCl_4$) solution followed by annealing at 500 ^oC for 3 h under N_2. This also helped sinter the $TiSi_2$ nanoparticles inside the TiO_2 nanotubes to form nanorod array. The TiO_2 nanotubular array is found to be stable with the growth of $TiSi_2$ nanorods within the nanotubes

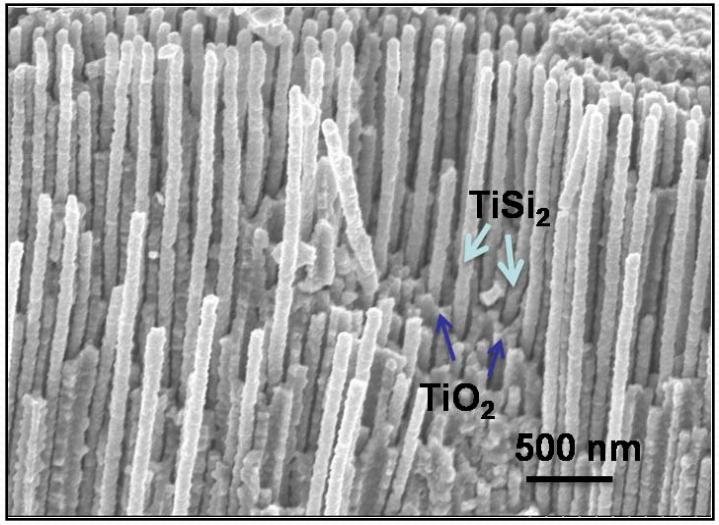


Figure: FESEM images of $TiSi_2$ particles sintered into the TiO_2 NT array

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 $TiSi_2$

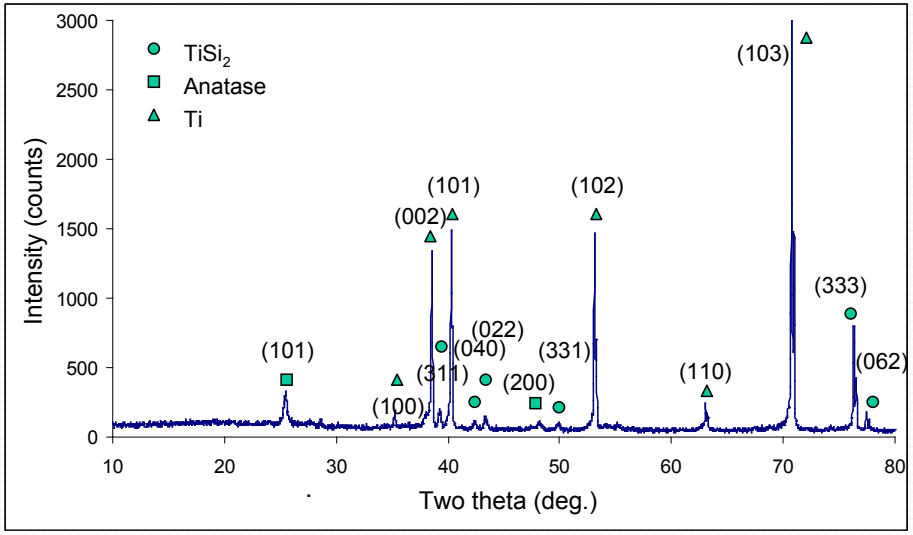


Figure : GXRD pattern of $TiSi_2$ NP/TiO_2NT. Orthorhombic $TiSi_2$ and anatase TiO_2 are observed in the heterostructure. A peak for the Ti base is also noticed

Absorption Studies of $TiSi_2$ NP/TiO_2 NT Composite Material

Diffuse reflectance ultraviolet and visible (DRUV-Vis) results

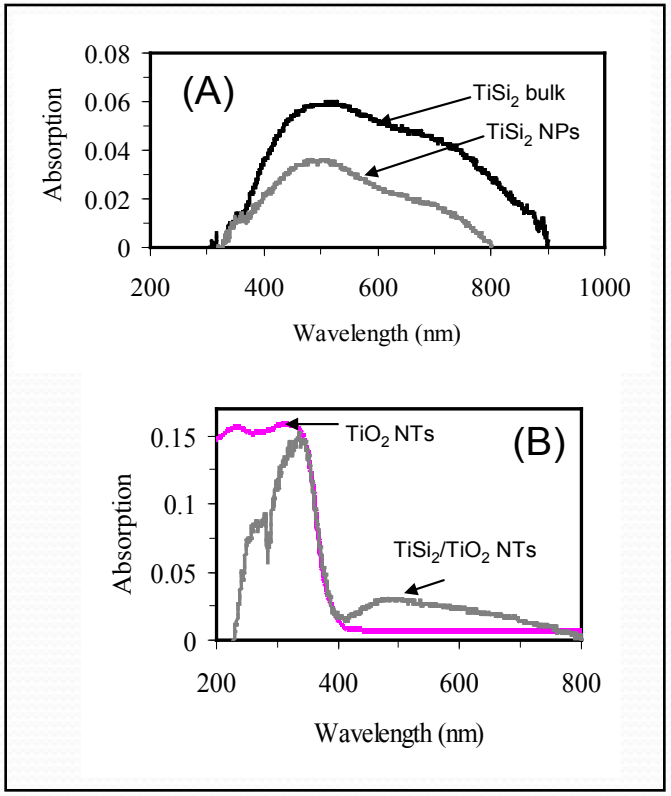


Figure: DRUV-Vis spectra of (A) $TiSi_2$ bulk and nanoparticles and (B) TiO_2 NTs and $TiSi_2/TiO_2$ NTs catalyst. $TiSi_2$ particles showed absorption in the visible light region and $TiSi_2/TiO_2$ NTs absorb light in both UV and visible region.

- The bulk $TiSi_2$ 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 TiO_2 NTs is observed only in the UV region (< 400 nm; band gap, E_g = 3.1 eV).

- The spectrum of $TiSi_2/TiO_2$ 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 TiO_2 NTs as well as in the visible light region due to the $TiSi_2$ particles. DRUV-Vis show that the $TiSi_2/TiO_2$ NT photocatalyst is prepared by combining the absorption properties of the TiO_2 NTs in the UV region and $TiSi_2$ in the visible region.

Photoelectrolysis of water using $TiSi_2$NP/TiO_2NT anode and Pt cathode

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.

TiO_2	TiO_2-$TiSi_2$
0.9 mA	3.4 mA

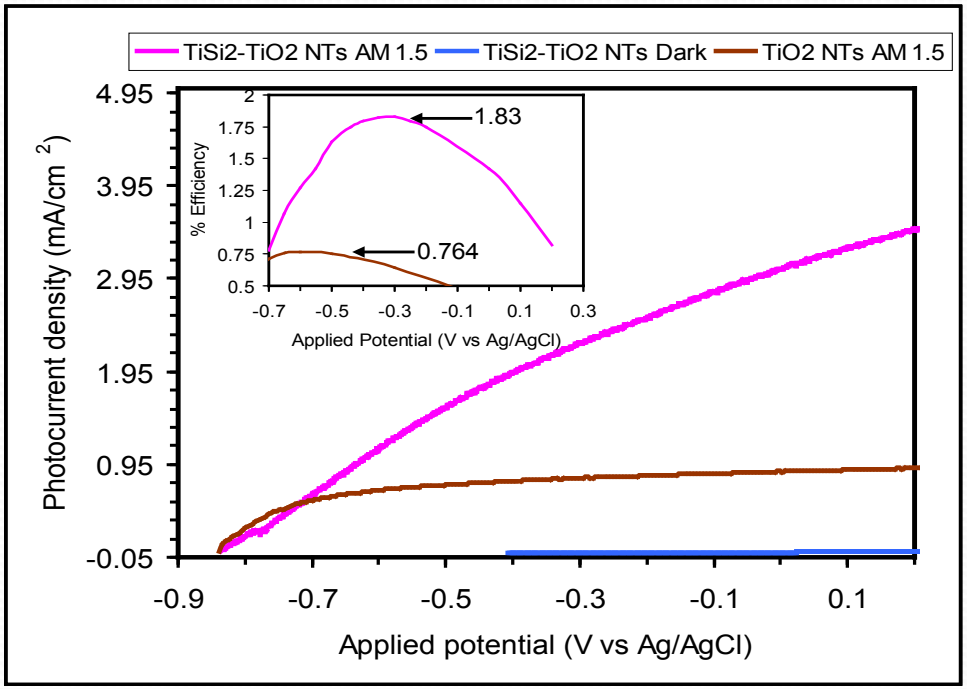


Figure: Potentiodynamic plot of annealed $TiSi_2/TiO_2$ NTs and TiO_2 NTs. Inset shows the solar-to-hydrogen conversion efficiency of $TiSi_2$-TiO_2 NTs and TiO_2 NTs under AM 1.5 illumination

Stability of $TiSi_2NP/TiO_2NT$ Photoelectrode

- 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 photo anode is stable under photo electrochemical splitting of water and the current observed is mostly due to the photo activity of the catalyst.

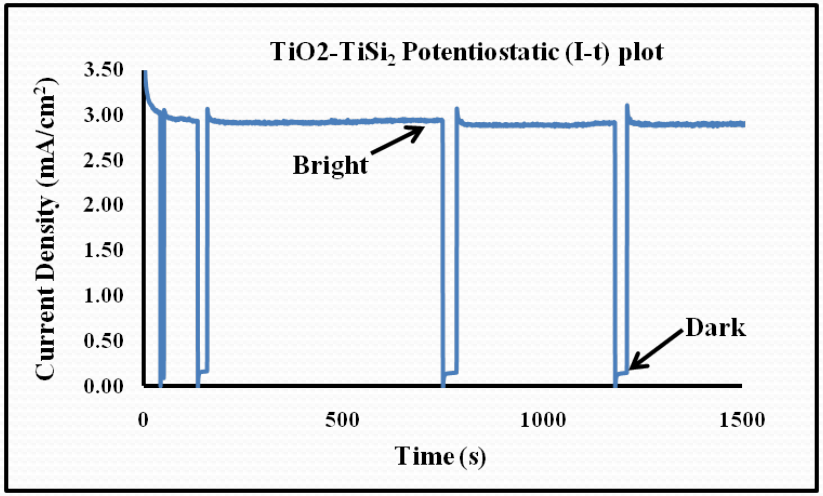


Figure: Potentiostatic (I-t) plot of TiO_2-$TiSi_2$ at 0V vs. Ag/AgCl reference electrode. The photocurrent became zero when the light is switched off (illumination stopped) and the original photocurrent again came back after illumination.

Conclusion: The composite photocatalyst is having potential for long term operation with good photoactivity

Photoelectrolysis of water using various $TiSi_2$ and TiO_2 nanocatalysts[a]

Comparative Results

In order to appreciate the photocurrent results obtained from the $TiSi_2$NP/TiO_2NT photoelectrode, we compare the results with the photocurrent densities of other photoelectrode systems: TiO_2 NTs/Ti, Degussa P25 NPs coated on Ti (P25/Ti) and $TiSi_2$ NPs coated on Ti ($TiSi_2$/Ti).

Catalyst[b]	Photocurrent density (mA/cm^2) at 0.2 $V_{Ag/AgCl}$
$TiSi_2/TiO_2$ NTs	3.49
TiO_2 NTs	0.90
$TiSi_2$/Ti	0.26
P25/Ti	0.63

[a] under AM 1.5 illumination conditions
[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 $BiFeO_3$ 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.