Photoelectrochemical Generation of Hydrogen from Water Using Nanotube-Based Semiconductor Systems for Improved Visible Light Activity

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## Overview

### Timeline
- Project start date: October, 2006
- Project end date: September, 2012
- Percent complete: 85

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

### Budget
- Total project funding: $ 3,650 K
  - DOE share: $ 2,970 K
  - Contractor share: $ 680 K
- Funding for FY06: $ 3,650 K

### Partners
- National Renewable Energy Laboratory
- University of Arkansas at Little Rock
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 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$_3$ photoanodes based on DFT modeling

2011-2012

• Synthesis of titania nanotubes in mixed acid electrolytes to dope transitional metals
Approach

Task A. Synthesis and fabrication of photocatalysts

• Fabrication of couple semiconductor (TiO$_2$ nanotube-WO$_3$ and TiO$_2$ nanotube-CdO)
• 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 nanotubular oxide composite photoanodes

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
Water Photooxidation by TiO$_2$ Nanotube-Metal Oxide Composite

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

Research Approach

Advantages: Rational design of multi component semiconductor materials with suitable band gaps and reduced charge recombination for enhanced water photoelectrolysis. Hybrid photoanodes that contain multiple semiconductors in a single photoanode maintain properties of each components and generally have greater efficiency

Strategy: Design self assembled titania (TiO$_2$) nanotube array electrode coupled with doped WO$_3$ or deposited cadmium oxide (CdO) nanocrystals
New Approach to Synthesize TiO$_2$-WO$_3$ Nanotube Composite

**Objective:** To obtain TiO$_2$-WO$_3$ nanotubular array composite utilizing tungsten anions species during

**Procedure:** Anodization of titanium in a fluorinated solution of phosphotungstic (PTA, $\text{H}_3\text{PW}_{12}\text{O}_{40}$) acid to form TiO$_2$-WO$_3$ composite nanotube arrays.

PTA forms anionic species in solution which migrate to the Ti anode during anodization and couples with TiO$_2$ to form surface sites of W$^{6+}$ or localized TiO$_2$-WO$_3$ heterojunctions

**Anodizing condition**
- 0.5 wt% NH$_4$F + 2.5 wt% PTA in DI H$_2$O (pH = 4)
- 22 °C, 20 V$_{\text{DC}}$, 60 min, mechanical stirring

90-120 nm diameter
500 nm length
5-10 nm wall thickness
XPS results show a $\text{WO}_3$ loading of 2.91 wt.%

Ti 2p (a) and W 4f (b) peak positions suggest Ti$^{4+}$ and W$^{6+}$

Exact W 4f peaks cannot be determined due to Ti 3p, however
Characterization of the Composite Material

• Absorbance spectra (a) shows increased visible light absorbance for TiO$_2$-WO$_3$ (inset) while still maintaining UV characteristic of TiO$_2$.

• Tauc plot (b) shows a reduction in bad gap from 3 eV to 2.7 eV which suggests some doped tungstate species.
Photoelectrochemical studies under simulated solar light

- Under AM 1.5 illumination in 0.1 M Na$_2$SO$_4$ (pH ~6) with Pt counter electrode
- 46% increase in photocurrent when NT formed in the presence of PTA
- Stable and repeatable photoresponses

Potentiostatic plot under discontinuous illumination at 1.4 V (vs Ag/AgCl).
Improvement in photoelectrochemical activity

- Enhanced activity due to suppression of charge recombination and improved hole transport to electrolyte
  - Lower charge transfer resistance (Nyquist plot)
- Localized TiO$_2$-WO$_3$ heterojunctions or W$^{6+}$ states may account for reduced charge transfer resistance

Photoelectrochemical water splitting reaction efficiency

Nyquist plot under illumination at OCP and 1000 Hz. The data was fit to an equivalent Randle circuit (inset) to obtain charge transfer resistance values ($R_{ct}$).
TiO$_2$ nanotubes synthesized at 40V for 1h in ethylene glycol (0.5 wt% NH$_4$F, 10 wt% DI H$_2$O) and annealed at 500°C for 2h in air

CdO anodically deposited under galvanostatic condition of -0.1 mA/cm$^2$ for various times (200-1,000 s) from a solution of 0.05 M Cd(C$_2$H$_3$O$_2$)$_2$*2H$_2$O + 0.1 M Na$_2$SO$_4$
Morphology of CdO deposits on anodized TiO2 nanotube arrays

- CdO morphology function of deposition time
  - Three morphologies: (i) nano crystallites (15-80 nm); (ii) interconnected layered decoration around nanotube rims; (iii) CdO particle agglomerates
- XPS data shows for deposition form 300-1,000 s the CdO loading marginally increases from 20-24 wt%
• 0.25 M Na$_2$SO$_4$ electrolyte under AM 1.5 irradiation
• Over 70% increase in photocurrent density at 1.4 V (vs Ag/AgCl)
• Stable and reproducible photoresponses
Improvement in photoelectrochemical performance of CdO-TiO$_2$ photoanode

- Enhanced photoelectrochemical performance of TiO$_2$-CdO over TiO$_2$ due to increased charge carrier density ($N_A$) and more negative flat band potential ($E_{fb}$)
  - TiO$_2$ $N_A = 3.3 \times 10^{17}$ cm$^{-3}$
  - TiO$_2$-CdO $N_A = 1.5 \times 10^{18}$ cm$^{-3}$
  - TiO$_2$ $E_{fb} = 0.0$ mV
  - TiO$_2$-CdO $E_{fb} = 10.0$ mV

- Increased band bending and increased life time of charge carriers for TiO$_2$-CdO

Photoelectrochemical water splitting reaction efficiency of 1.64% at 0.08 V for (i) TiO$_2$ nanotubes and 2.2% at 0.17 V for (ii) CdO deposited for 300 s.

Mott-Schottky plot for (i) TiO$_2$ nanotubes and (ii) CdO deposited for 300 s conducted under AM 1.5 irradiation and 1,000 Hz.
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 new coupled semiconductor photo-catalyst through two techniques. A novel method to prepare TiO$_2$-WO$_3$ during anodization resulting in improved photoelectrochemical performance. The use of CdO as a visible light sensitizer and the relationship to morphology of deposits with photoelectrochemical performance has been examined.

- **Technology transfer/collaboration:** Active partnership with NREL and University of Arkansas at Little Rock.

- **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
- Synthesis of other TiO₂ nanotube-transitional metal composites formed via single step anodization from anionic metal species
- Develop electrochemical methods to fill TiO₂ nanotubes with CdO
- 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.