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

Mano Misra, York R. Smith, Dev Chidambaram
University of Nevada, Reno
Chemical & Materials Engineering Department

DOE Hydrogen Program Review, May 14-18 2012

Project ID # PD076

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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 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 $BiFeO_3$ 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

Combinatorial approach: Coupling with other nanostructured materials

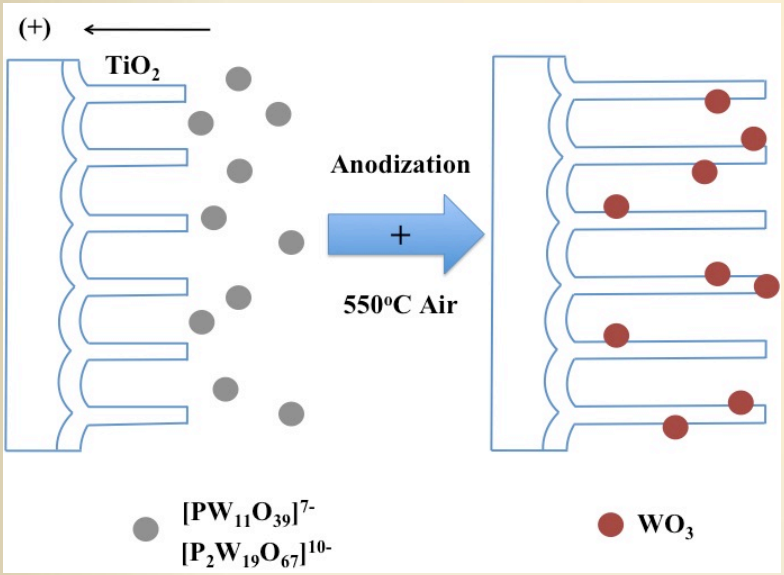
Advantages: Rational design of multi component semiconductor materials with suitable band gaps and reduced charge recombination for enhanced water photoelectrolysis**.** Hybrid photoanodes that contain multiple semiconductors in a single photoanode maintain properties of each components and generally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

Strategy: Design self assembled titania (TiO_2) nanotube array electrode coupled with doped WO_3 or deposited cadmium oxide (CdO) nanocrystals

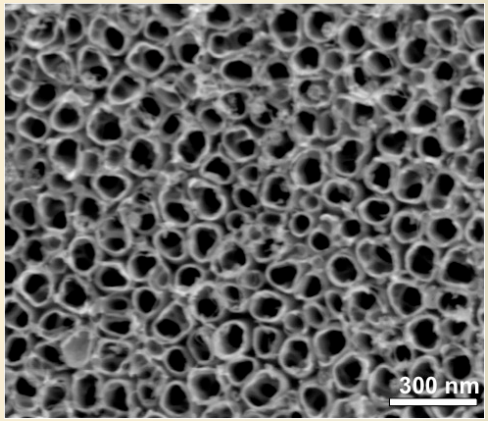
New Approach to Synthesize TiO_2-WO_3 Nanotube Composite

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, $H_3PW_{12}O_{40}$) 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



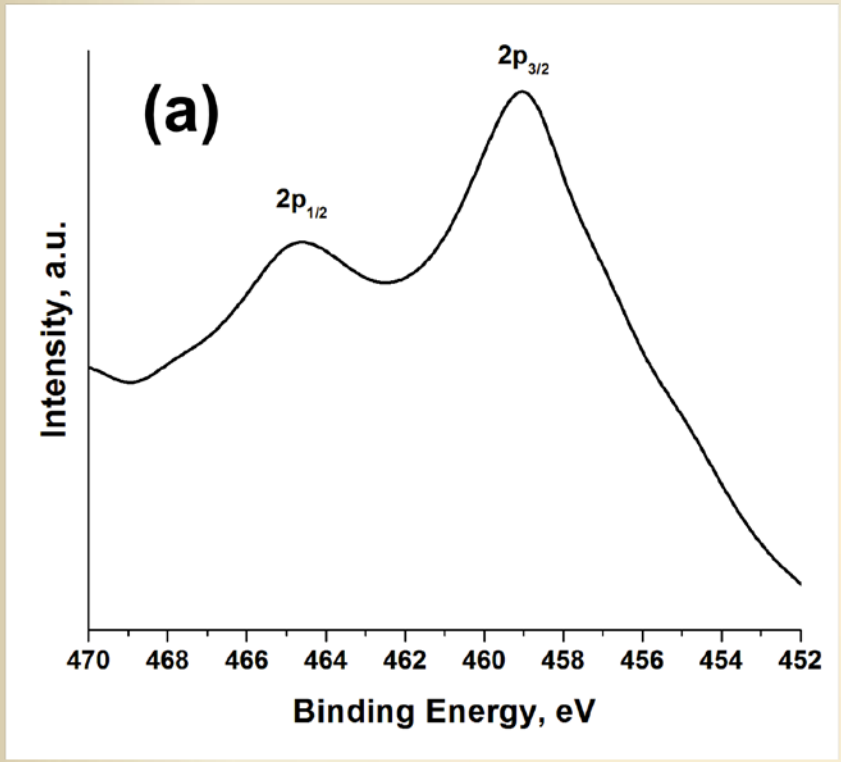
TiO_2-WO_3 nanotube composite formed

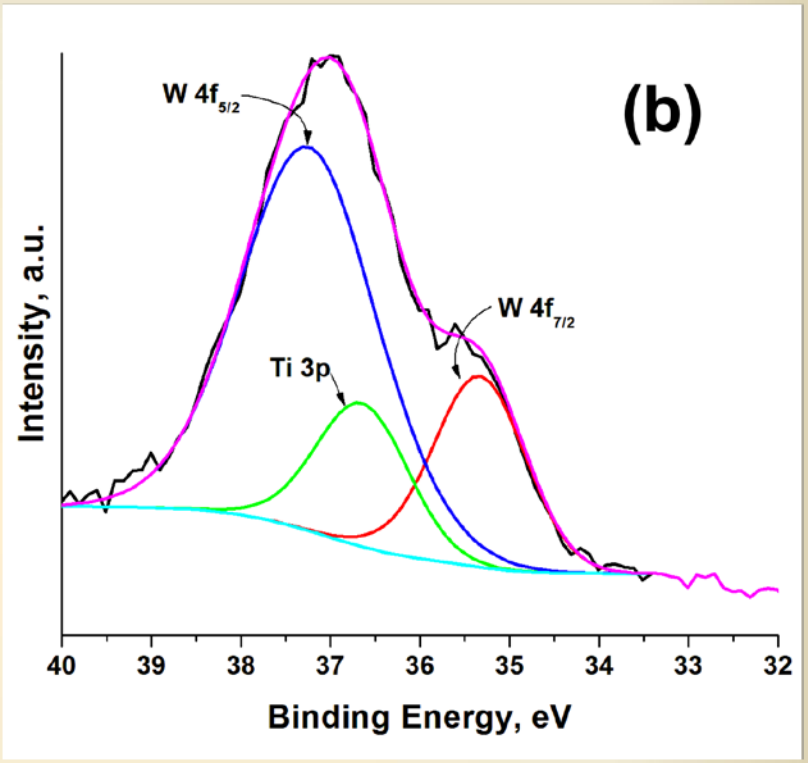
Anodizing condition

0.5 wt% NH_4F + 2.5 wt% PTA in DI H_2O (pH = 4)
22 °C, 20 V_{DC}, 60 min, mechanical stirring

90-120 nm diameter
500 nm length
5-10 nm wall thickness

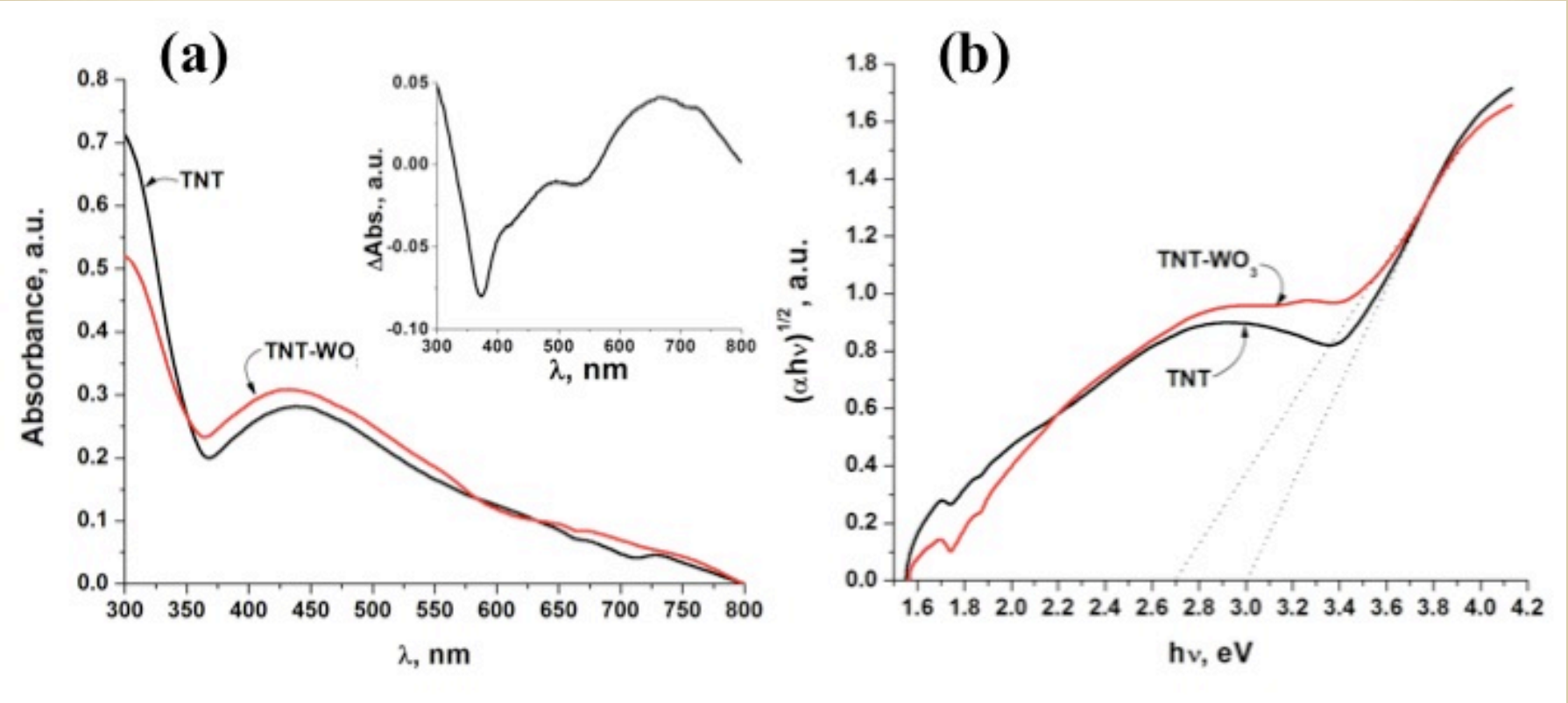
Characterization of the Composite Material





- XPS results show a 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

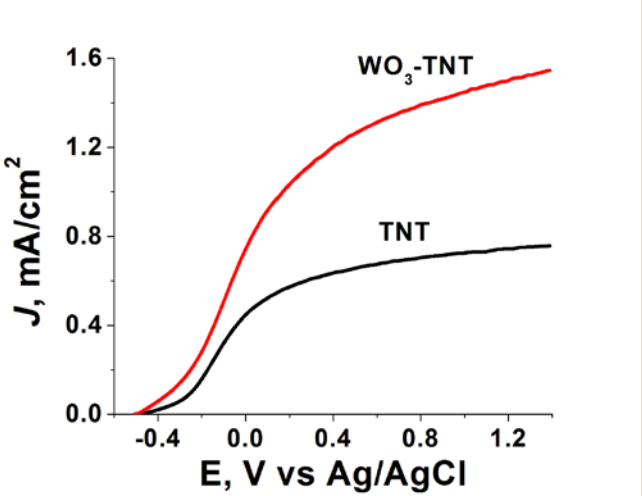


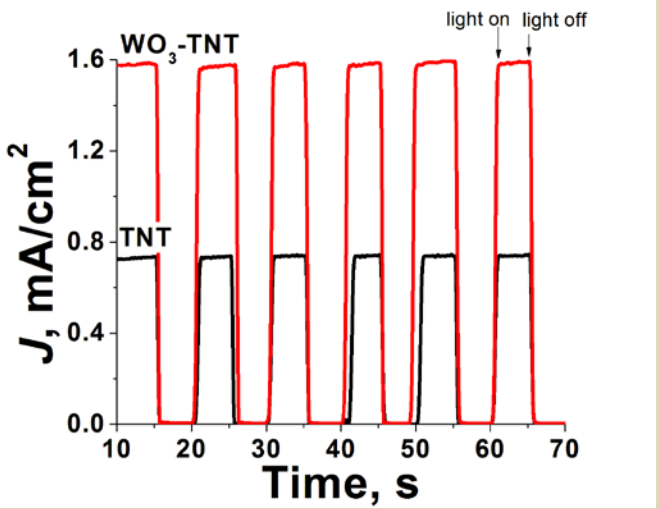
• Absorbance spectra (a) shows increased visible light absorbance for TiO_2-WO_3 (inset) while still maintaining UV characteristic of TiO_2

•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

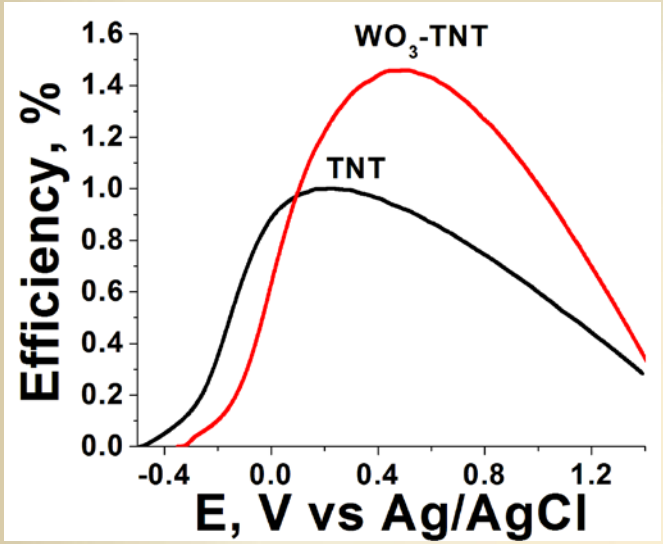
- Under AM 1.5 illumination in 0.1 M Na_2SO_4 (pH ~6) with Pt counter electrode
- 46% increase in photocurrent when NT formed in the presence of PTA
- Stable and repeatable photoresponses



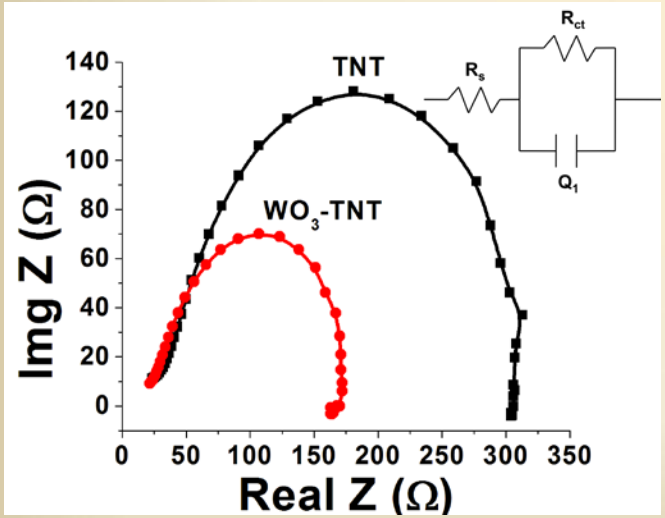


Potentiostatic plot under discontinuous illumination at 1.4 V (vs Ag/AgCl).

Improvement in photoelectrochemical activity



Photoelectrochemical water splitting reaction efficiency

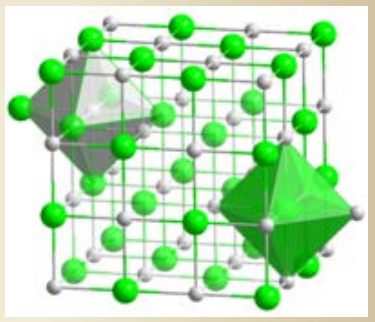


Nyquist plot under illumination at OCP and 1000 Hz. The data was fit to an equivalent Randle circuit (inset) to obtain charge transfer resistance values (R_{ct}).

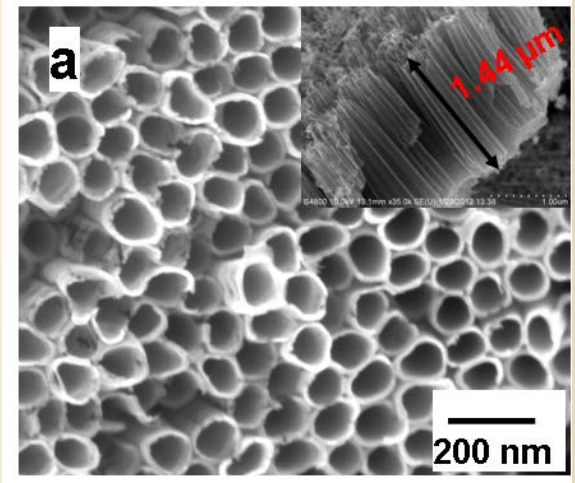
- Enhanced activity due to suppression of charge recombination and improved hole transport to electrolyte
  - Lower charge transfer resistance (Nyquist plot)
- Localized TiO_2-WO_3 heterojunctions or W^{6+} states may account for reduced charge transfer resistance

Electrochemical deposition of CdO on anodized TiO2 nanotube arrays

- CdO band gap 2.3 eV direct, 1.7 eV indirect
  - Comparable to bulk CdS (2.4 eV) making it suitable for visible light sensitization



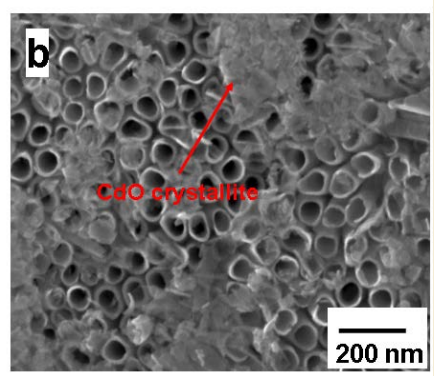
TiO_2 nanotubes synthesized at 40V for 1h in ethylene glycol (0.5 wt% NH_4F, 10 wt% DI H_2O) and annealed at 500^oC for 2h in air



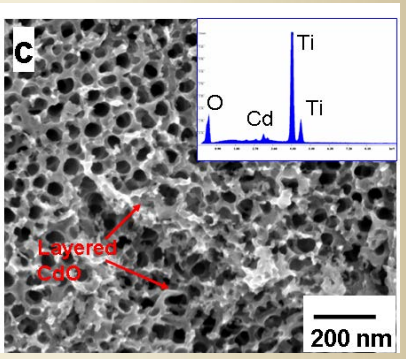
CdO anodically deposited under galvanostatic condition of -0.1 mA/cm^2 for various times (200-1,000 s) from a solution of 0.05 M $Cd(C_2H_3O_2)_2$*$2H_2O$ + 0.1 M Na_2SO_4

Morphology of CdO deposits on anodized TiO2 nanotube arrays

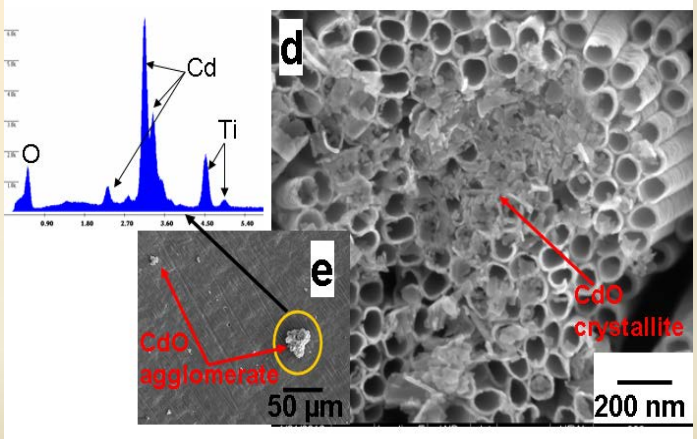
- CdO morphology function of deposition time
  - Three morphologies: (i) nano crystallites (15-80 nm); (ii) interconnected layered decoration around nanotube rims; (iii) CdO particle agglomerates
- XPS data shows for deposition form 300-1,000 s the CdO loading marginally increases from 20-24 wt%



CdO deposition for 300s, forming CdO crystallites

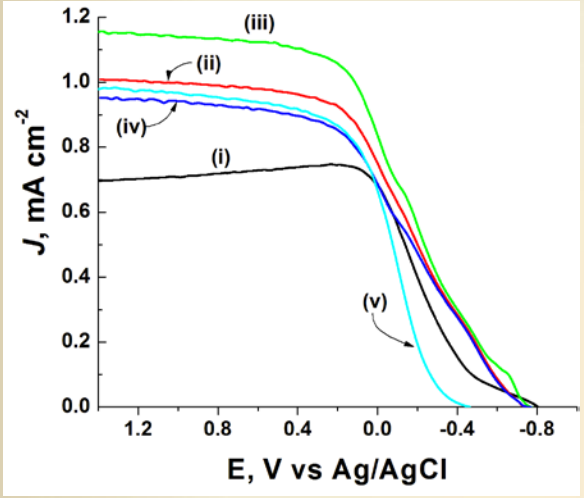


CdO deposition for 500s, forming layered CdO deposits

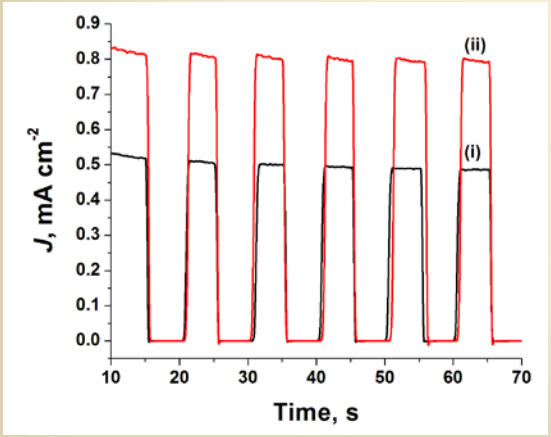


CdO deposition for 1,000s, forming all three CdO deposit morphologies

Photoelectrochemical performance of CdO-TiO_2 photoanode



(i) TiO_2 nanotubes, (ii) 200 s, (iii) 300 s, (iv) 500 s, and (v) 1,000 s CdO deposition time

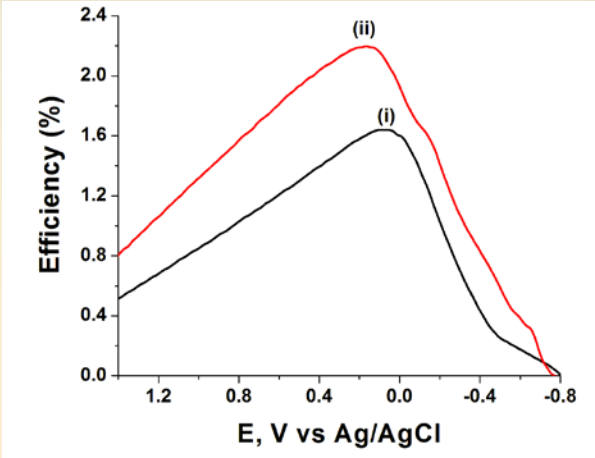


(i) TiO_2 nanotubes, (ii) 300 s CdO deposition time at 0 V vs Ag/AgCl

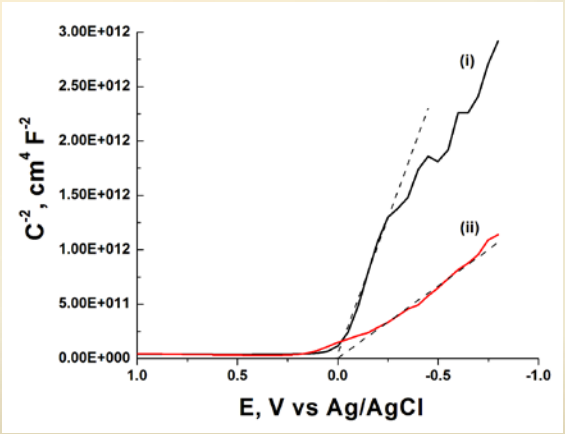
- 0.25 M Na_2SO_4 electrolyte under AM 1.5 irradiation
- Over 70% increase in photocurrent density at 1.4 V (vs Ag/AgCl)
- Stable and reproducible photoresponses

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 x 10^{17} cm^{-3}
  - TiO_2-CdO N_A = 1.5 x 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 TiO_2 nanotube-transitional metal composites formed via single step anodization from anionic metal species
- Develop electrochemical methods to fill TiO_2 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.