Photoelectrochemical Generation of Hydrogen Using Heterostructural Titania Nanotube Arrays

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DOE Hydrogen Program Review 2008
## Overview

### Timeline
- Project start date: October, 2006
- Project end date: September, 2009
- Percent complete: 60%

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

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

### Partners
- **John Turner**, National Renewable Energy Laboratory
- **M.K. Mazumder**, University of Arkansas at Little Rock
### Objectives

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<th>Overall</th>
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<td>Develop high efficiency hybrid-semiconductor materials for hydrogen</td>
<td>generation by water splitting.</td>
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<td>generation by water splitting.</td>
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| 2006-2007 | • Develop new anodization technique to synthesize high quality and robust TiO$_2$ nanotubes with wide range of nanotube architecture. |
|           | • Develop single step, low band gap TiO$_2$ nanotubes.                                                              |
|           | • Develop kinetics and formation mechanism of the titanium dioxide nanotubes under different synthesis conditions.     |

| 2007-2008 | • Develop organic-inorganic hybrid photoanodes.                                                                       |
|           | • Develop combinatorial approach to synthesize hybrid photo-anodes having multiple semiconductors in a single photo-anode. |
|           | • 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.                                              |
**Approach**

**Task A. Synthesis and fabrication of metal and mixed metal oxide nanotubular arrays by electrochemical anodization method.**
- Ultrasonic mediated metal (Ti, Fe, W and Ta) oxide nanotube arrays
- Synthesis in organic as well as inorganic medium
- Annealing and characterization of TiO$_2$ nanotubes
- Coupling of nanotubes with low band gap semiconductors

**Task B. Band-gap modification and engineering.**
- Photo-anode (doping with hetero-elements and design composite photoanodes)
- Photo-cathode (Pt and Ni nanoparticles/TiO$_2$)

**Task C. Application of the nanotubular materials for photo-electrochemical generation of H$_2$ from H$_2$O.**
- Test hybrid photoanodes
- Test hybrid cathodes
- Reducing e-h recombination with organics by solution chemistry

**Task D. Materials stability of hybrid TiO$_2$ nanotubular photo-anodes.**
- Electrochemical methods
- Spectroscopic analysis

**Task E. Scale-up and process evaluation.**
- Scale-up (photoanodes and cathodes)
- Photoelectrochemical hydrogen generation under real solar irradiation
Novel methods for the formation of titania nanotubes

**Bi-facial photoanode:**
Organo-fluoride solution in the presence of ultrasonic waves.

![Experimental set-up](image)

**Fig.** Experimental set-up for bifacial photoanode

Formation mechanism:

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ \quad \text{--- (1)}
\]

\[
\text{TiO}_2 + 6 \text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2 \text{H}_2\text{O} \quad \text{-- (2)}
\]

**Characteristics:**
- 20-150 nm diameter
- 0.5 -15 μm length
- Smooth, compact and robust

![TEM images](image)
Advantages:

High surface area in small geometrical area  
Double efficiency per footprint  
Solar concentrating technology can be exploited  
Reduced recombination losses due to intermediate metallic contacts  

Fig. Schematic of PEC test arrangement using bifacial electrodes  

Fig. Potentiodynamic and potentiostatic hydrogen generation using bifacial electrodes (geometrical area=16 cm²)
Stability test of titania nanotubes under PEC conditions: Evaluation of the materials for long term operation

Fig. H₂ generated continuously for (a) 8 h and (b) for 30 days (8h/day). Photoanode consisting of nitrogen annealed titania nanotubes are used (geometrical area = 3.5 cm²) in these experiments.

Fig. XRD of the photoanode before and after the long term test. It shows the photoanode is stable after one month operation. This is also confirmed by DRUV-Vis and SEM measurements.
Organic-inorganic hybrid photoanode: Surface functionalization of titania nanotubes with 2,6-dihydroxyanthraquinone (DHA)

Fig. The hybrid photoanode absorbs visible photons efficiently than titania nanotubes alone.

Fig. (A) The hybrid photoanode showed better photoactivity than titania nanotubes alone. (B) Potentiostatic measurements showed that the material is stable for long operation.
Fabrication of titania nanotubes with nanoparticles
(Synthesis of nanoparticle/nanotube heterostructure photoanode)

Fig. Schematic of TiO$_2$ nanoparticle/nanotube heterostructural photoanode preparation with (A) SEM image and (B) TEM image of the particles
Nanoparticle/nanotube heterostructure photoanode

**Fig.** Increase in the absorption spectrum was observed in the TiO$_2$ nanotube/nanoparticle hybrid material.

**Fig.** H$_2$ generation using the TiO$_2$ nanotube/nanoparticle hybrid material. A three fold enhancement in the photocurrent density was observed using the hybrid photoanode.
Fabrication of titania nanotubes using low band gap semiconductors: CdS/TiO$_2$ core-shell photoanode

Fig. SEM image showing the CdS/TiO$_2$ core-shell particles on the top of the TiO$_2$ nanotube arrays

Fig. CdS/TiO$_2$ core shell photoanode absorb better visible light compared to TiO$_2$ nanotubes alone
Fig. Potentiodynamic plot of (a) CdS/TiO₂ nanotubes under dark conditions, and (b) ING-TiO₂, (c) ORG-TiO₂, (d) CdS-TiO₂ (ORG) nanotubes under illumination (87 mW/cm²). The measurements are carried out in sulfide-sulfite electrolyte.

Fig. A comparison with past results. CdS/TiO₂ nanotube photoanode showed more than 60% visible light contribution. The results are calculated using AM 1.5 filter (solar spectrum) and band pass filter (λ ≥ 420 nm; visible spectrum).
Photoelectrolysis of water using CdS/TiO$_2$ core/shell photoanode (Contd.)

Fig. Contribution of various wavelength regions to the photoactivity of CdS/TiO$_2$ (ORG) nanotube composite material. It shows that most of the activity is contributed from the solar spectrum of wavelengths in the range of 400-550 nm. Interference filters with CWL of ±15 nm and FWHM of 50 nm are used for the potentiodynamic measurements.

Fig. Potentiostatic (I-t) graph obtained using CdS/TiO$_2$ (ORG) nanotubes as photoanode in sulfide-sulfite electrolyte at -0.8 V$_{Ag/AgCl}$ (under the illumination of 87 mW/cm$^2$ solar light). The photocurrent becomes zero when the light is off and the original current comes back as soon as the light is illuminated.
Photoelectrolysis of water using CdS/TiO$_2$ core/shell photoanode: Tentative mechanism

Fig. A schematic showing the thermodynamic favorable energy bands for CdS and TiO$_2$. The photogenerated electrons transfer from the CdS CB to the TiO$_2$ and the holes transfer from the CB of the CdS to the solution.

e$_1$ = photoelectrons generated from the thin film coated on the CdS particles

Fig. A schematic view to show the effectiveness of core-shell-nanotube approach to harvest sunlight
Development of UNR easy-$H_2$© PEC cell to be used under solar light irradiation (on-field H$_2$ generation)

Preliminary results indicate that H$_2$ generation from on-field experiments is comparable to the experiments under simulated solar light conditions (AM 1.5)
Future Work

• Synthesis of heterostructural photoanodes:
  ◦ Synthesis of mixed metal oxide nanotubes (sputtering-anodization, pulsed electrodeposition-oxidation, electrochemical deposition-anodization).
  ◦ Synthesis of metal oxide and compound semiconductors (electrodeposition, incipient wetness method and spin rotor coatings)
• Synthesis of low-cost cathodes:
  ◦ Preparation of inexpensive and robust cathode by fabricating TiO₂ with Ni.
• Investigation of the photoanode and cathode by microstructural and electrochemical techniques.
• Kinetics studies of the titania nanotubes formation by the H₂O₂ titration and ICP analysis.
• Stability studies of photoanodes by various characterization techniques and Kelvin-Probe measurements.
• Incident photon to current conversion efficiency (IPCE) measurements
• Scale-up the system
• Design PEC system for on-field testing under real solar irradiation.
Summary

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

•  **Approach**: Synthesize hybrid nanotubular TiO₂ composite arrays as photoanode and nanoparticles decorated cathodes for improved photo conversion process.

•  **Technical accomplishments and process**: Developed a hybrid composite photoanode comprising of TiO₂ nanotubes and CdS core-shell configuration having more than 6% solar-to-hydrogen conversion efficiency under AM 1.5 conditions.

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

•  **Proposed future research**: (a) Mixed oxides (oxides of Fe, Ta and W) and composite photoanodes to harvest full spectrum of sunlight, (b) develop inexpensive cathodes using Ni nanoparticles (c) scale-up the PEC system and (d) on-field testing under real solar irradiation.