Photoelectrochemical Generation of Hydrogen Using Heterostructural Titania Nanotube Arrays

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Overview

Timeline

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

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

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

Objectives

Overall	Develop high efficiency hybrid-semiconductor materials for hydrogen generation by water splitting.
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_2O.

- 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.

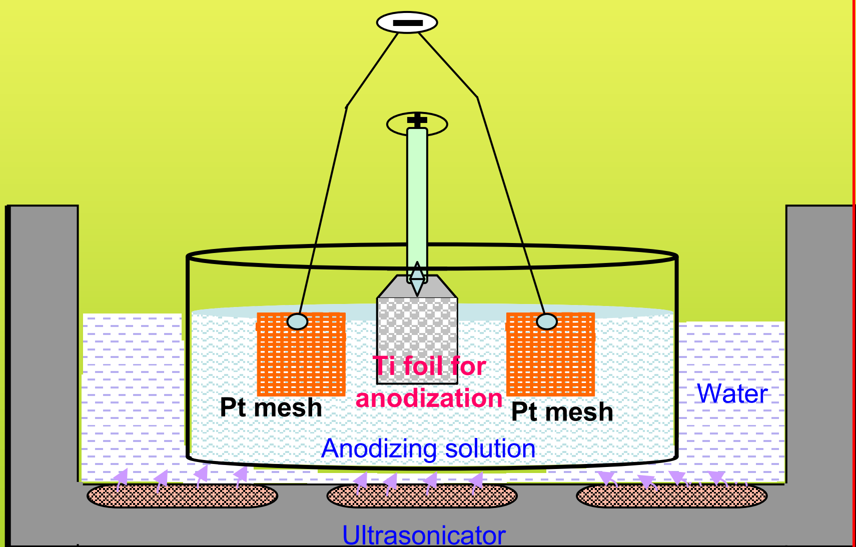


Fig. Experimental set-up for bifacial photoanode

Formation mechanism:

$Ti + 2H_2O \rightarrow TiO_2 + 4H^+$ --- (1)

$TiO_2 + 6\ F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2\ H_2O$ -- (2)

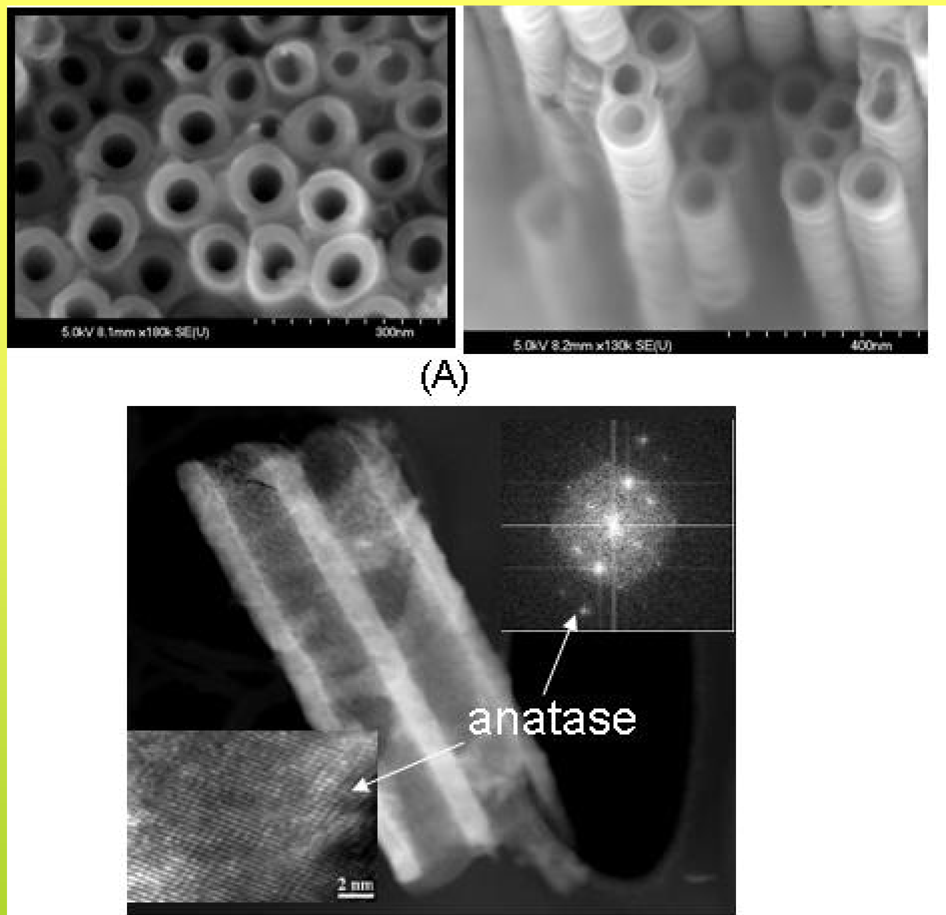
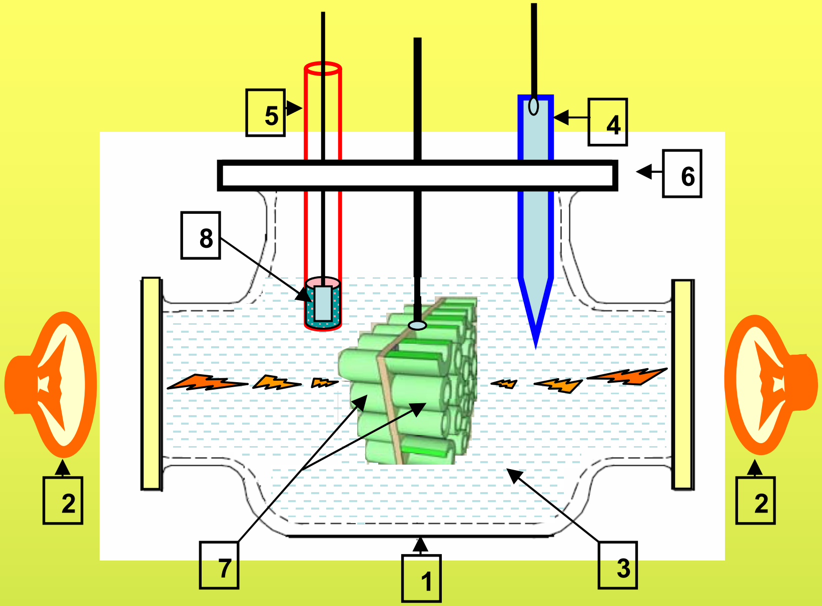


Fig. (A) SEM and (B) TEM images of titania nanotubes

Characteristics:

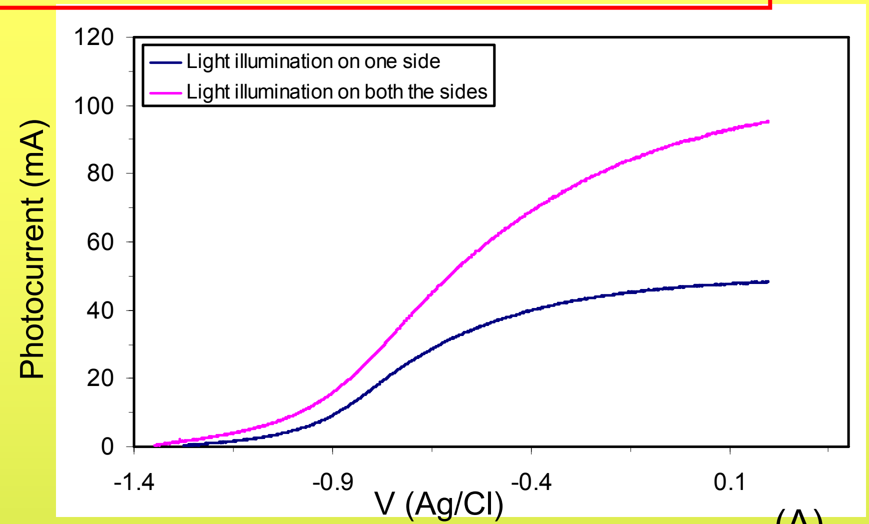
- 20-150 nm diameter
- 0.5 -15 μm length
- Smooth, compact and robust

Photoelectrolysis using bi-facial photoanode and Pt/TiO_2 cathode

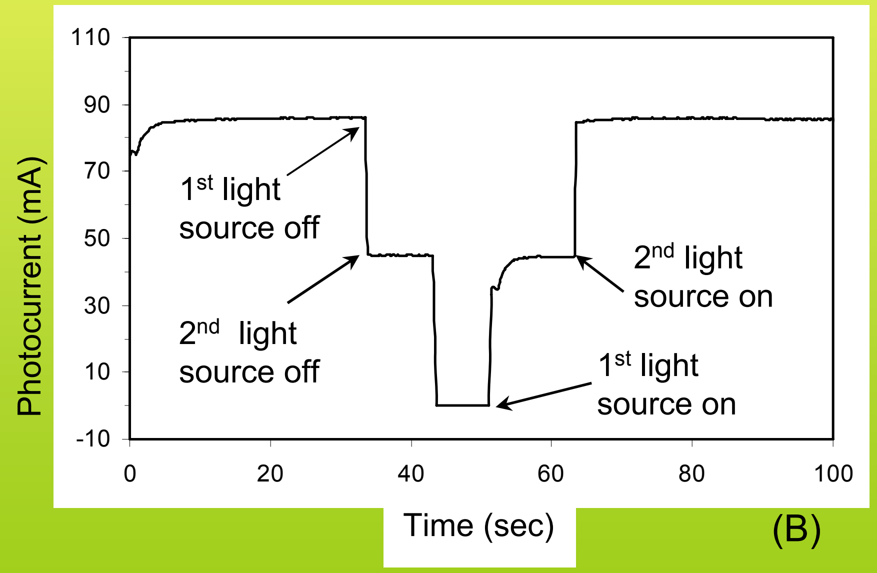


1. Quartz cell, 2. light source,
3. 1MKOH solution,
4. Ag/AgCl electrode,
5. cathode, 6. teflon lid,
7. photoanode, and
8. cathode.

Fig. Schematic of PEC test arrangement using bifacial electrodes



(A)



(B)

Fig. Potentiodynamic and potentiostatic hydrogen generation using bifacial electrodes (geometrical area=16 cm^2)

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

Stability test of titania nanotubes under PEC conditions: Evaluation of the materials for long term operation)

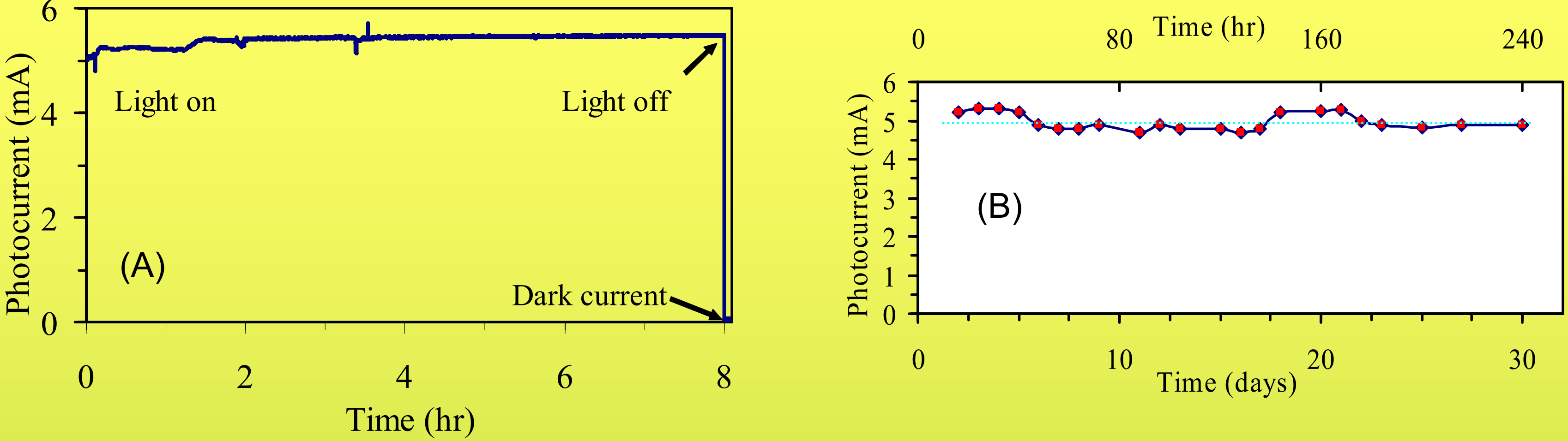


Fig. H_2 generated continuously for (a) 8 h and (b) for 30 days (8h/day). Photoanode consisting of nitrogen annealed titania nanotubes are used (geometrical area = 3.5 cm^2) in these experiments

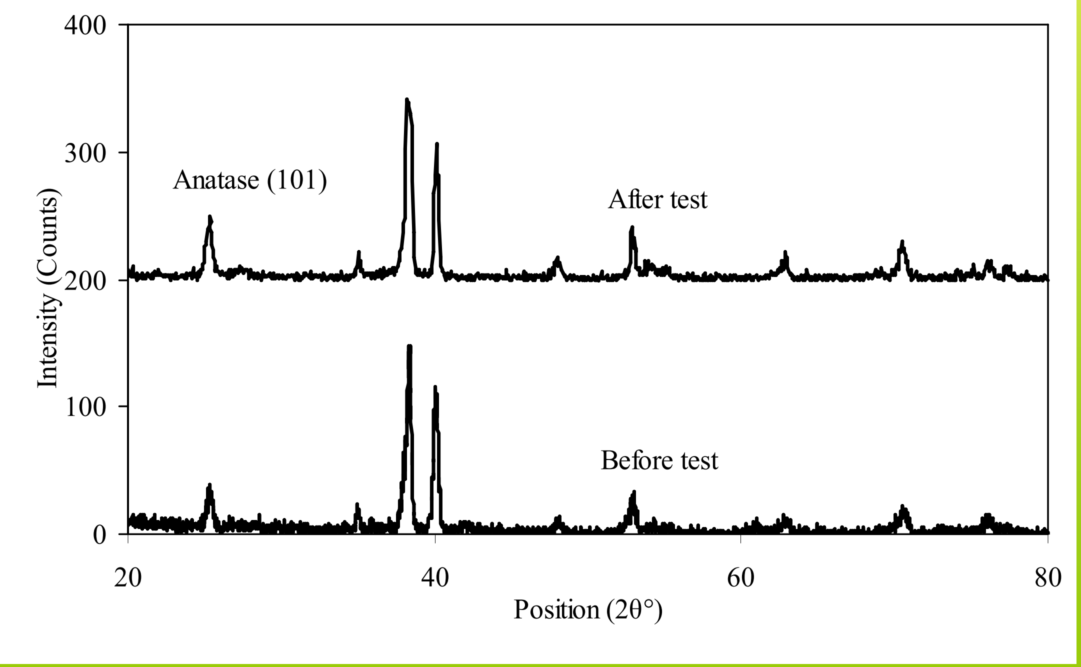


Fig. XRD of the photoanode before and after the long term test. It shows the photoanode is stable after one month operation. This is also confirmed by DRUV-Vis and SEM measurements

Organic-inorganic hybrid photoanode: Surface functionalization of titania nanotubes with 2,6-dihydroxyanthraquinone (DHA)

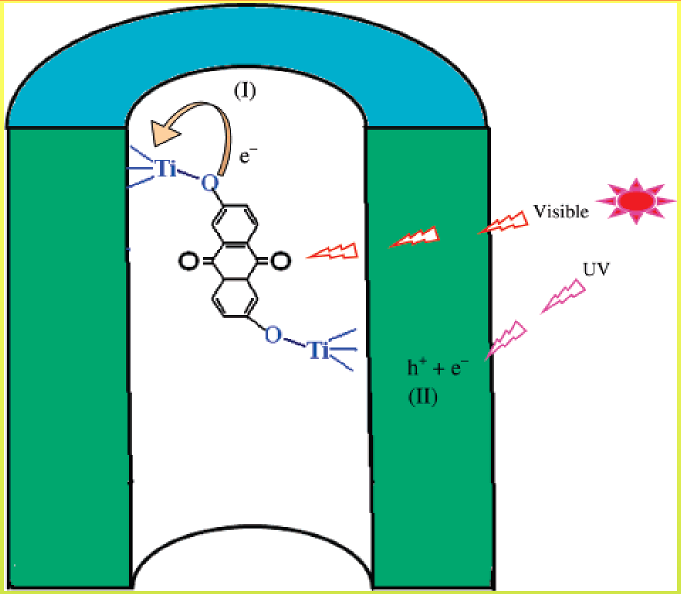
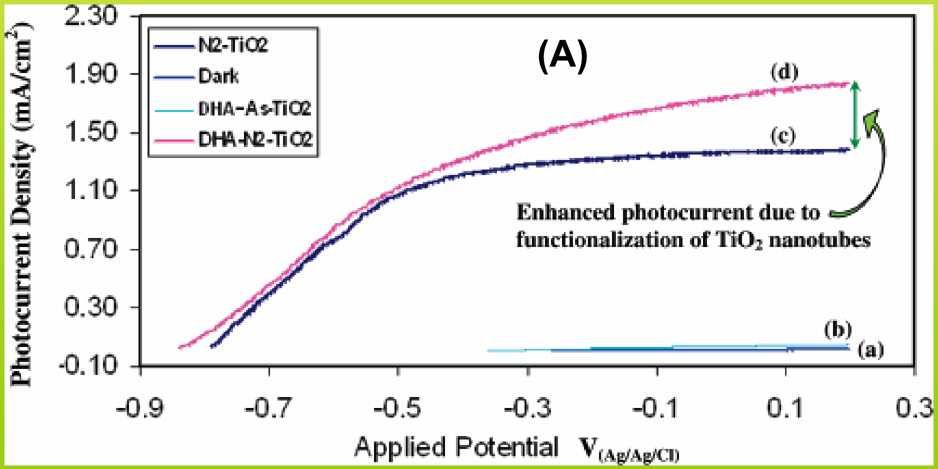


Fig. The hybrid photoanode absorbs visible photons efficiently than titania nanotubes alone



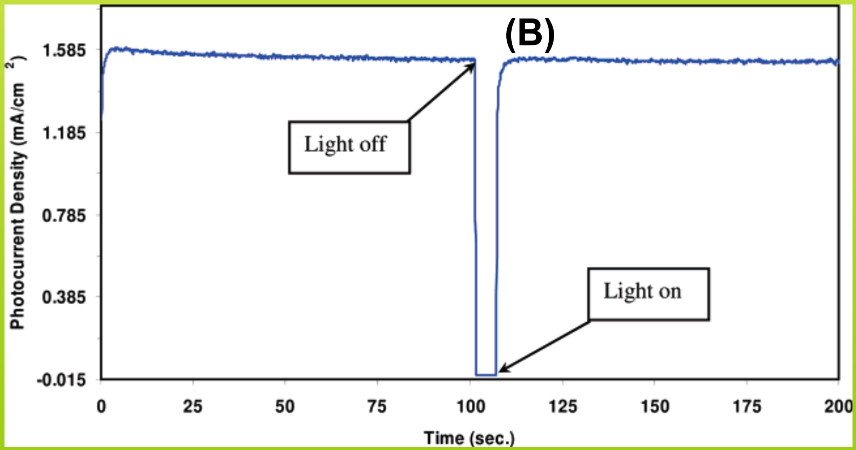


Fig. (A) The hybrid photoanode showed better photoactivity than titania nanotubes alone.
(B) Potentiostatic measurements showed that the material is stable for long operation

Fabrication of titania nanotubes with nanoparticles (Synthesis of nanoparticle/nanotube heterostructure photoanode)

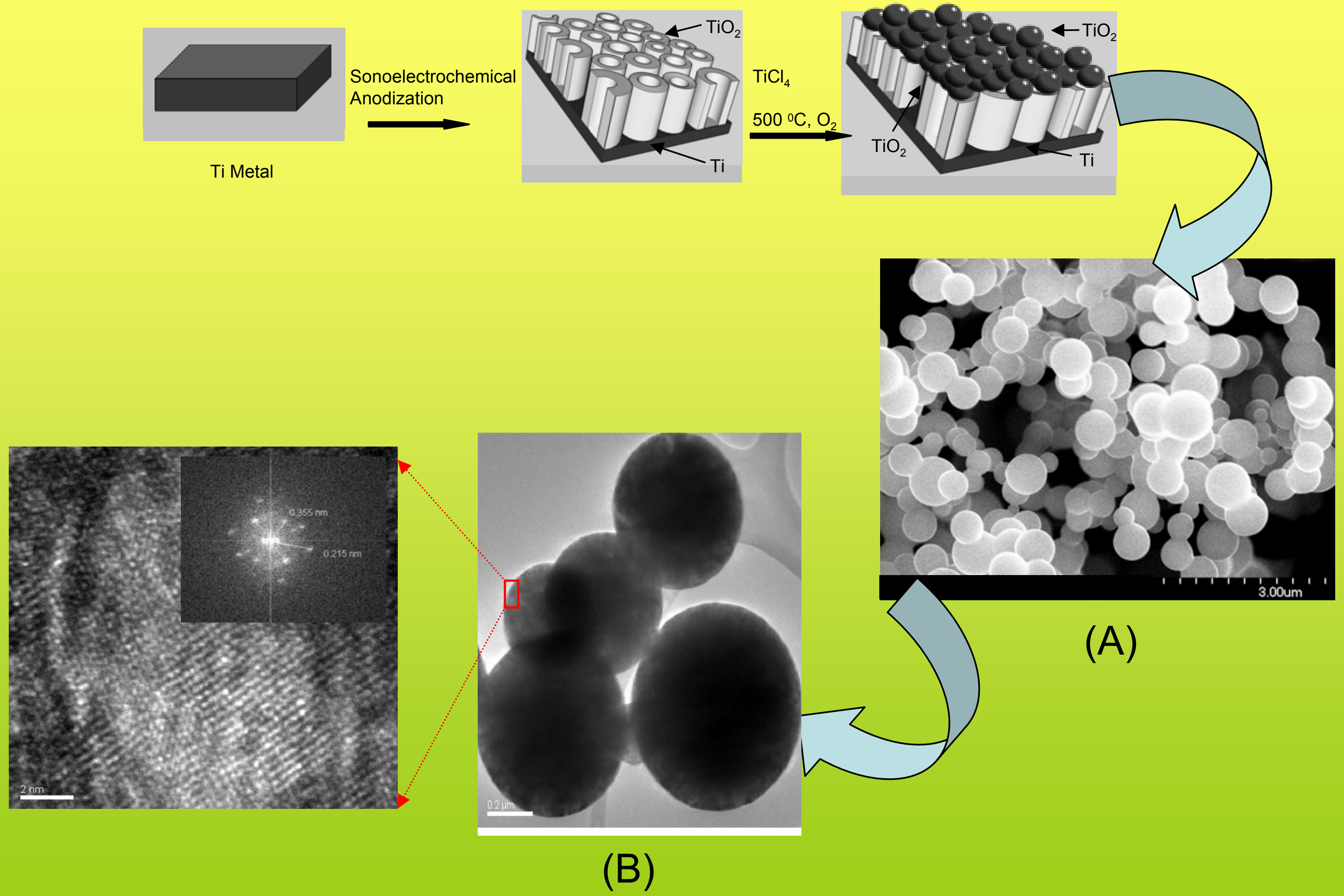


Fig. Schematic of TiO_2 nanoparticle/nanotube heterostructural photoanode preparation with (A) SEM image and (B) TEM image of the particles

Nanoparticle/nanotube heterostructure photoanode

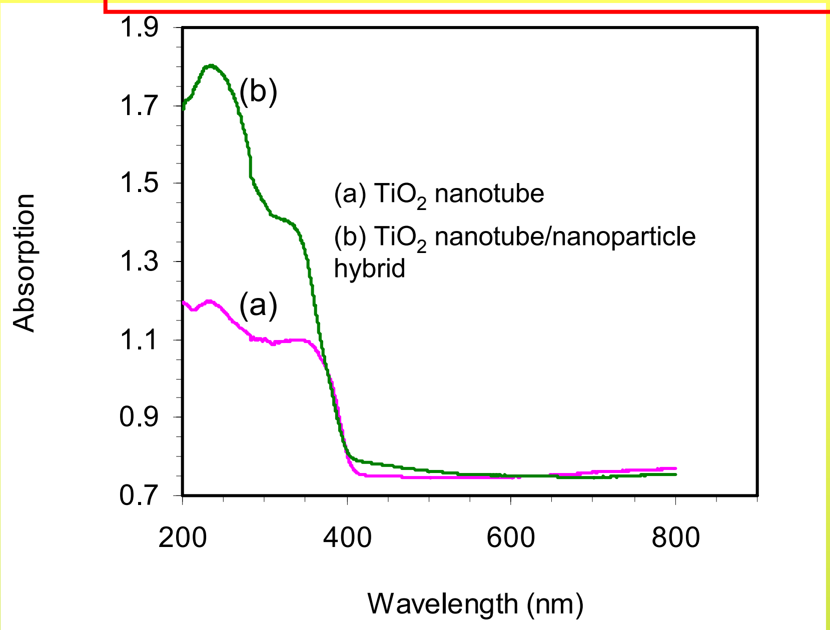


Fig. Increase in the absorption spectrum was observed in the TiO_2 nanotube/nanoparticle hybrid material

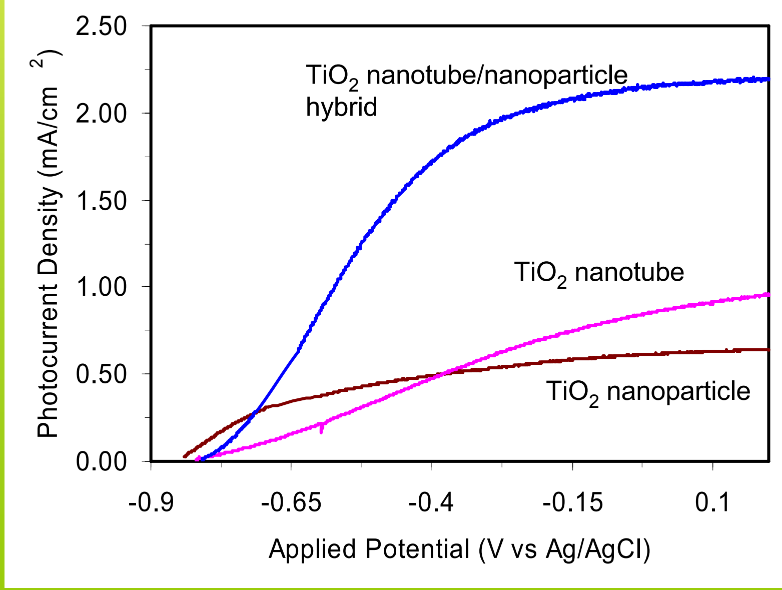


Fig. H_2 generation using the TiO_2 nanotube/nanoparticle hybrid material. A three fold enhancement in the photocurrent density was observed using the hybrid photoanode

Fabrication of titania nanotubes using low band gap semiconductors: CdS/TiO_2 core-shell photoanode

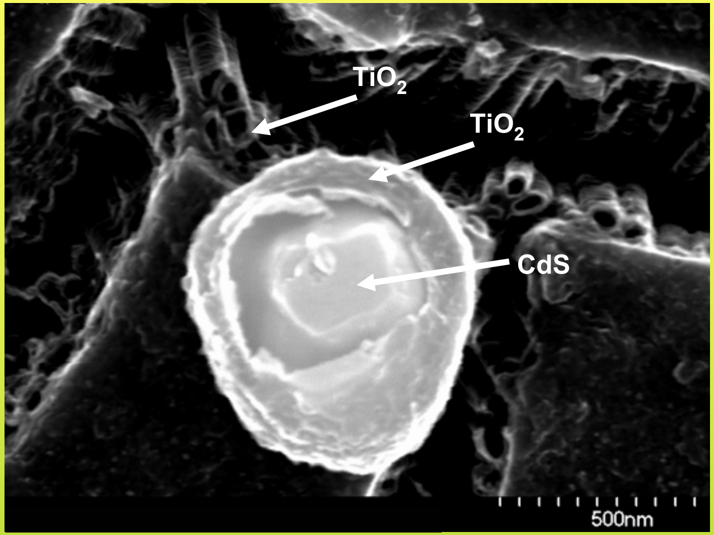


Fig. SEM image showing the CdS/TiO_2 core-shell particles on the top of the TiO_2 nanotube arrays

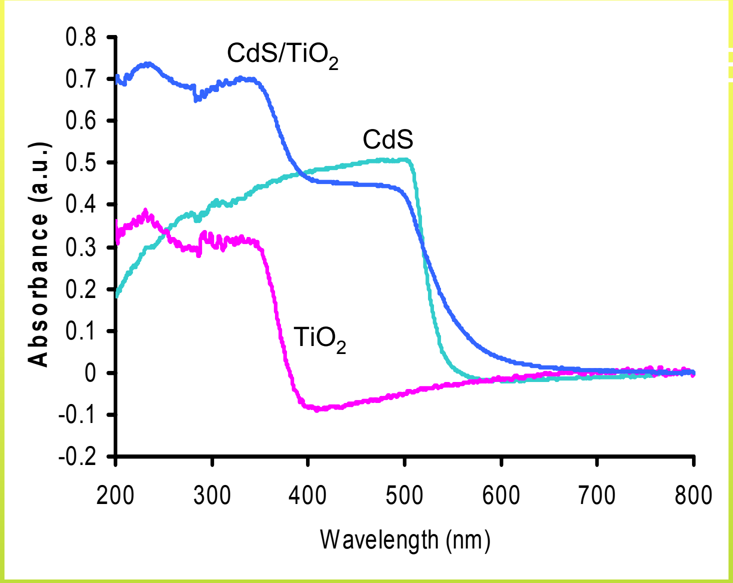


Fig. CdS/TiO_2 core shell photoanode absorb better visible light compared to TiO_2 nanotubes alone

Photoelectrolysis of water using CdS/TiO_2 core/shell photoanode

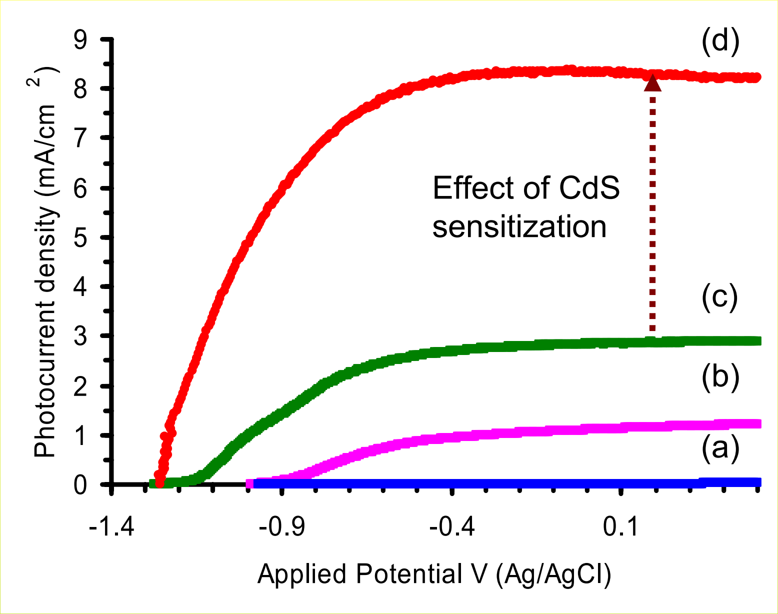


Fig. Potentiodynamic plot of (a) CdS/TiO_2 nanotubes under dark conditions, and (b) ING-TiO_2, (c) ORG-TiO_2, (d) CdS-TiO_2 (ORG) nanotubes under illumination (87 mW/cm^2). The measurements are carried out in sulfide-sulfite electrolyte

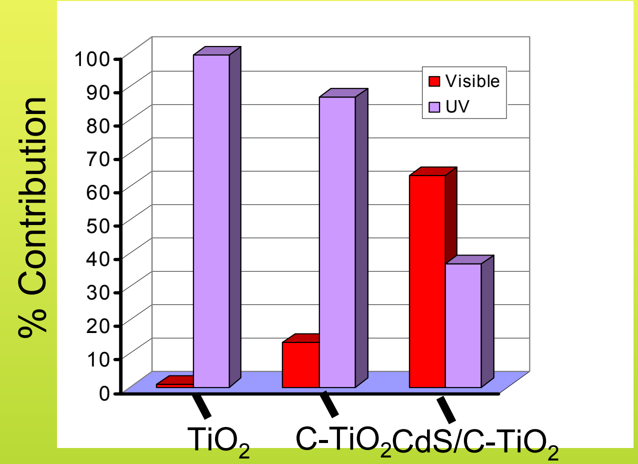


Fig. A comparison with past results. CdS/TiO_2 nanotube photoanode showed more than 60% visible light contribution. The results are calculated using AM 1.5 filter (solar spectrum) and band pass filter (λ ≥ 420 nm; visible spectrum)

Photoelectrolysis of water using CdS/TiO_2 core/shell photoanode (Contd.)

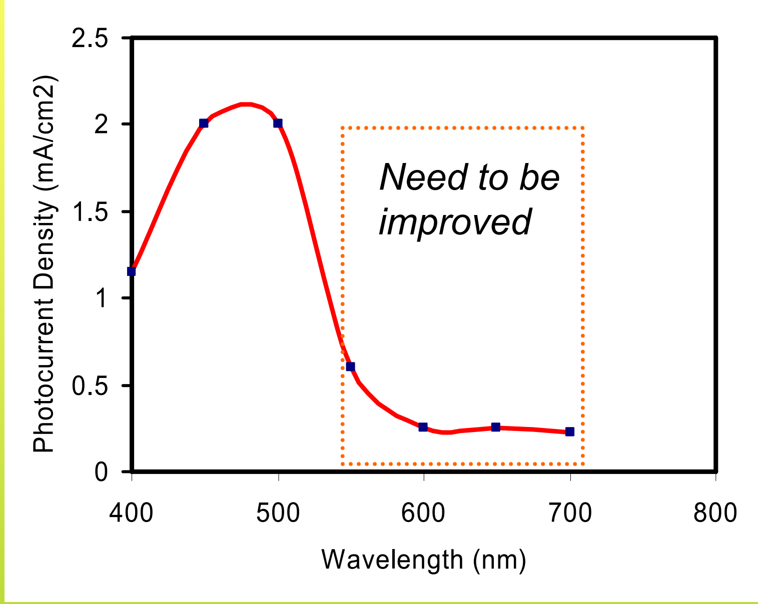


Fig. Contribution of various wavelength regions to the photoactivity of CdS/TiO_2 (ORG) nanotube composite material. It shows that most of the activity is contributed from the solar spectrum of wavelengths in the range of 400-550 nm. Interference filters with CWL of ±15 nm and FWHM of 50 nm are used for the potentiodynamic measurements

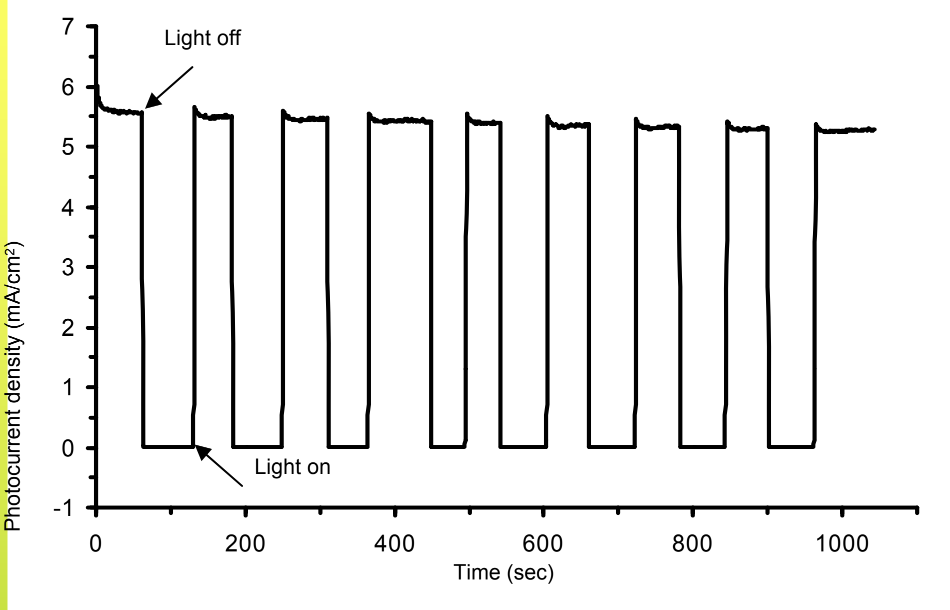


Fig. Potentiostatic (I-t) graph obtained using CdS/TiO_2 (ORG) nanotubes as photoanode in sulfide-sulfite electrolyte at –0.8 V $_{Ag/AgCl}$ (under the illumination of 87 mW/cm^2 solar light). The photocurrent becomes zero when the light is off and the original current comes back as soon as the light is illuminated

Photoelectrolysis of water using CdS/TiO_2 core/shell photoanode: Tentative mechanism

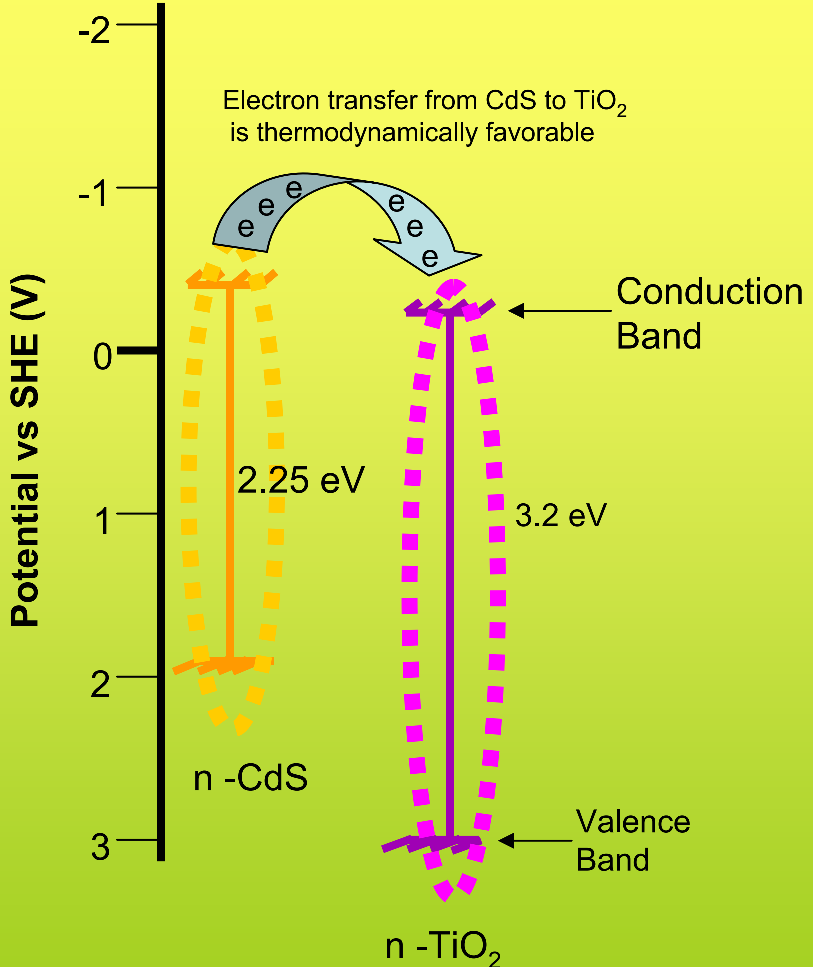
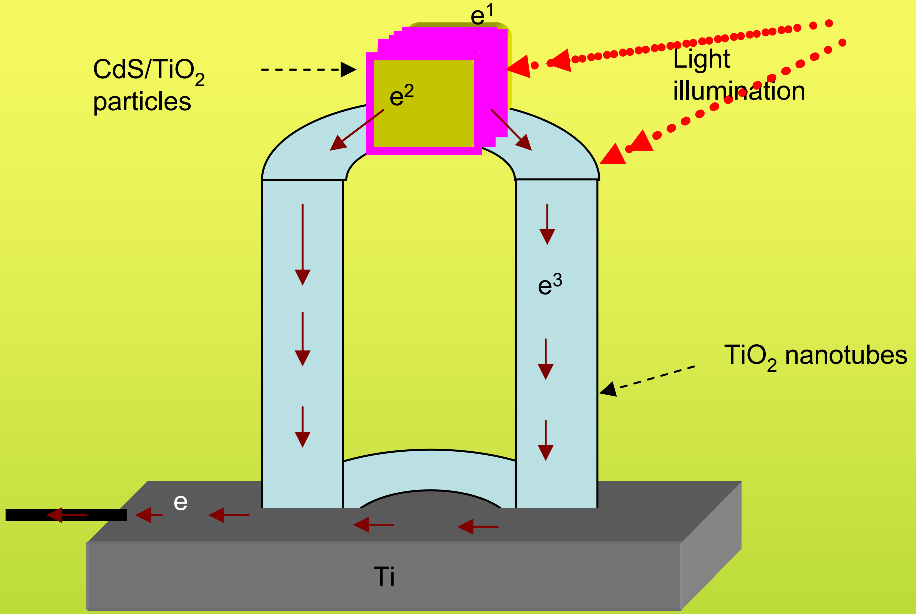


Fig. A schematic showing the thermodynamic favorable energy bands for CdS and TiO_2.
The photogenerated electrons transfer from the CdS CB to the TiO_2 and the holes transfer from the CB of the CdS To the solution.



e1 = photoelectrons generated from the thin film coated on the CdS particles
e2 = photoelectrons generated from the CdS particles
e3 = photoelectrons generated from the TiO_2 nanotubes
e (e1 + e2 + e3) = overall photoelectrons generated from the system

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 TiO_2 with Ni.
- Investigation of the photoanode and cathode by microstructural and electrochemical techniques.
- Kinetics studies of the titania nanotubes formation by the H_2O_2 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 TiO_2 composite arrays as photoanode and nanoparticles decorated cathodes for improved photo conversion process.
- *Technical accomplishments and process*: Developed a hybrid composite photoanode comprising of TiO_2 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.