Photoelectrochemical Generation of Hydrogen Using Sonic Mediated Hybrid Titania Nanotube Arrays

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Overview

Timeline

- Project start date: October, 2006
- Project end date: September, 2008
- Percent complete: 30

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: $ 1,657 K
- Funding for FY07: $ 1, 993 K

Partners

- *John Turner*, National Renewable Energy Laboratory.
- *Nilkanth Dhere*, Florida Solar Research Institute.
- *Praxair*, USA.
- *eco2 ltd.*, Denmark.

Objectives

Overall	Develop high efficiency photoelectrochemical cell using titanium dioxide nanotubular photo-anode and cathode 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 by modifying synthesis parameters. • Develop kinetics and formation mechanism of the titanium dioxide nanotubes under different synthesis conditions.
2007-2008	• Improve efficiency by mixed oxide and organic-inorganic semiconductor photoanodes. • Develop Density Functional Theory (DFT) to identify and modify the electronic properties of nanotubes. • Develop combinatorial approach to synthesize hybrid photo-anodes having multiple hetero-atoms incorporation in a single photo-anode. • Develop new TiO_2 based cathodes to increase the efficiency of the photoelectrochemical cell.

Approach

Task A. Synthesis and fabrication of nanotubular titanium dioxide arrays by electrochemical anodization method.

- Ultrasonic mediated titanium dioxide (TiO_2) nanotube arrays
- Synthesis in organic medium
- Annealing of TiO_2 nanotubes
- Characterization of nanotubes

Task B. Band-gap modification and engineering.

- Photo-anode (Doping with hetero-elements)
- Photo-cathode (Group II-VI compound semiconductors)

Task C. Application of the nanotubular materials for photo-electrochemical generation of H_2 from H_2O.

- Test hybrid photoanodes
- Test hybrid photocathodes

Task D. Materials stability of hybrid TiO_2 nanotubular photo-anodes.

- Electrochemical methods
- Scanning Kelvin Probe analysis

Task E. Scale-up and process evaluation.

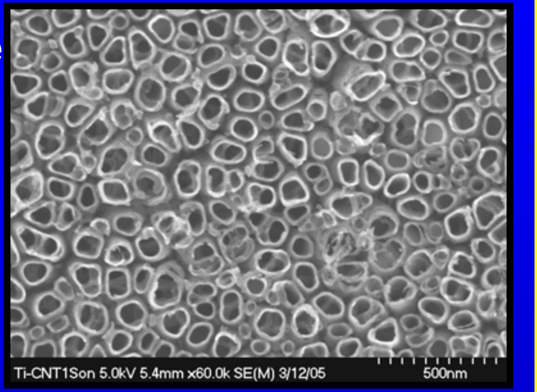
- Anodization scale-up
- Photoelectrochemical hydrogen generation in solar light

Novel methods for the formation of titania nanotubes

Conventional :

Acidified fluoride solution in the presence mechanical stirring

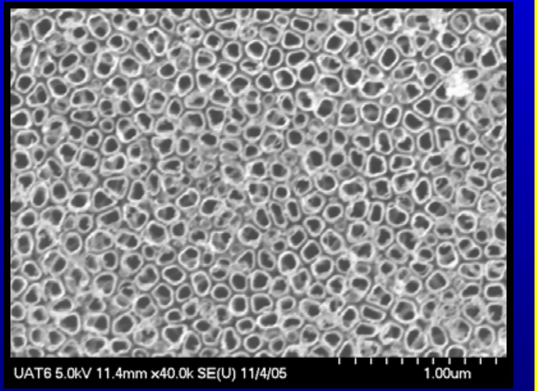
- 30 – 80 nm diameter
- 400 – 500 nm length
- Time: 45 min



Sonoelectrochemical acidic:

Acidified fluoride solution in the presence of ultrasonic waves

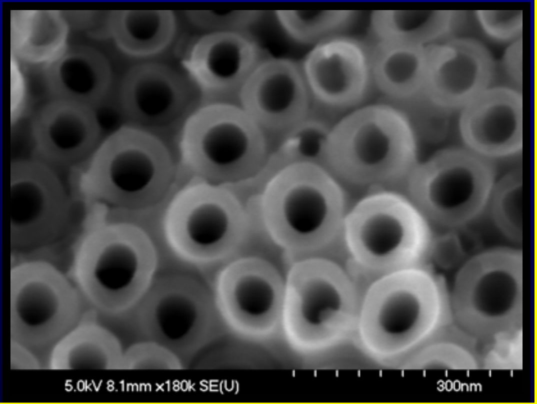
- 30-80 nm diameter
- 600-650 nm length
- Well ordered, compact, robust
- Time: 20 min

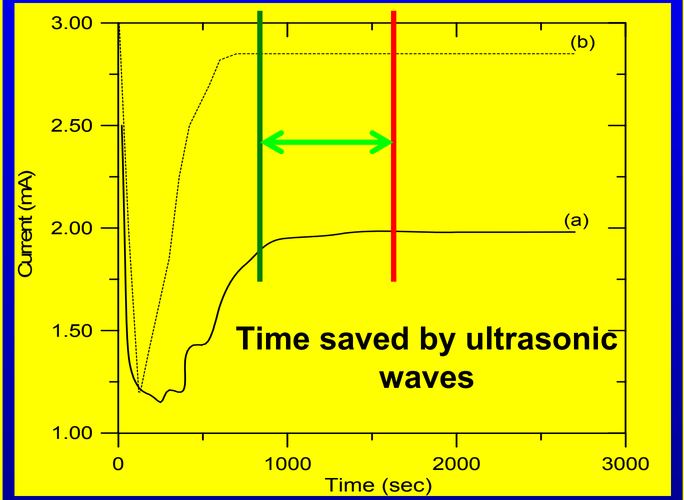


Sonoelectrochemical neutral :

Organo-fluoride solution in the presence of ultrasonic waves.

- 20-150 nm diameter
- 0.5 -15 µm length
- Smooth, compact
- Time: 0.5-12 hrs

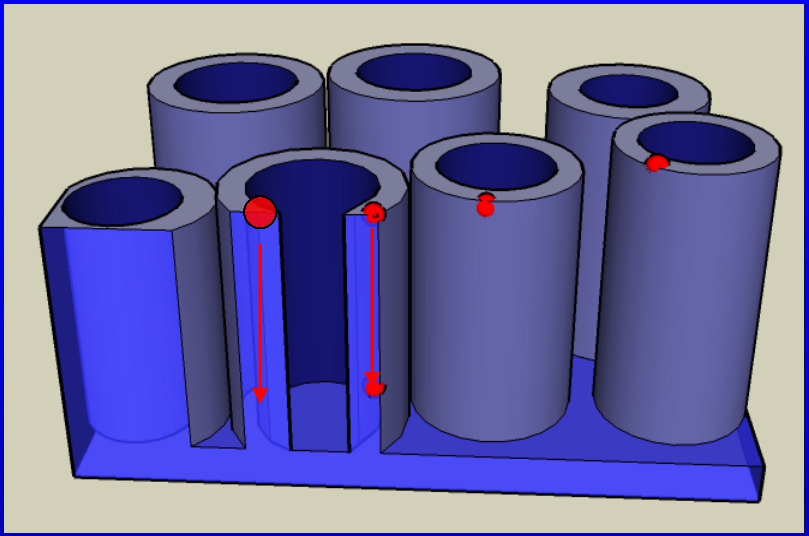




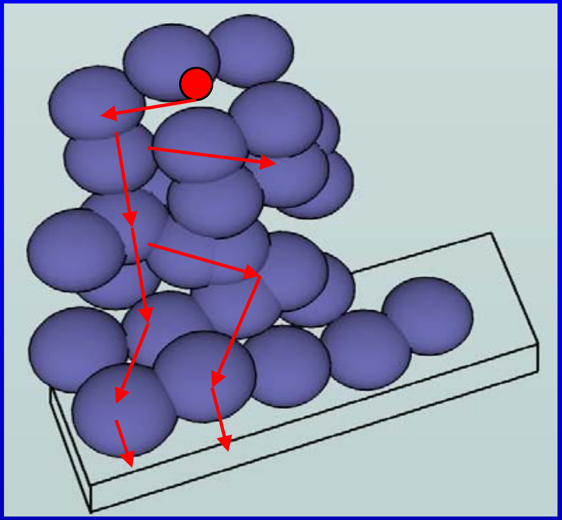
Time saved by ultrasonic waves

Current transient graph for anodization in ultrasonic and stirring conditions.

Nanotubes vs Nanoparticles



1D nanotubular TiO_2

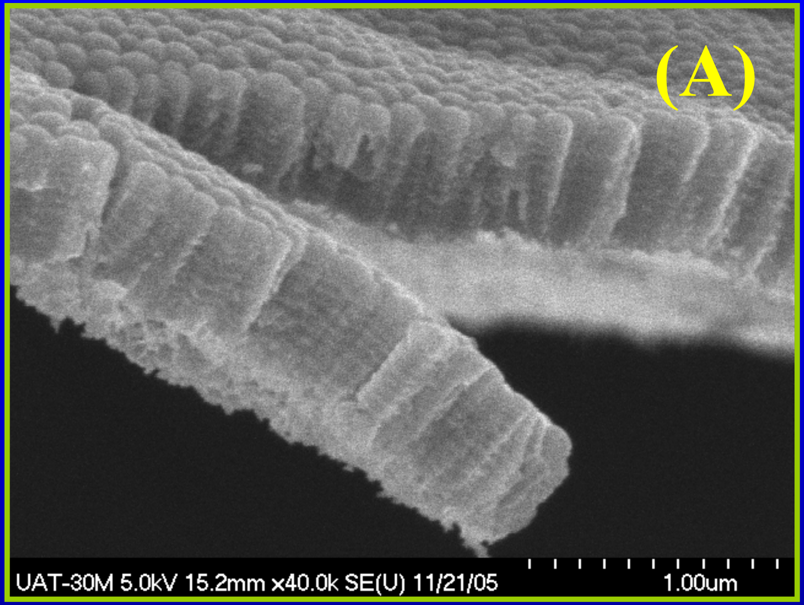


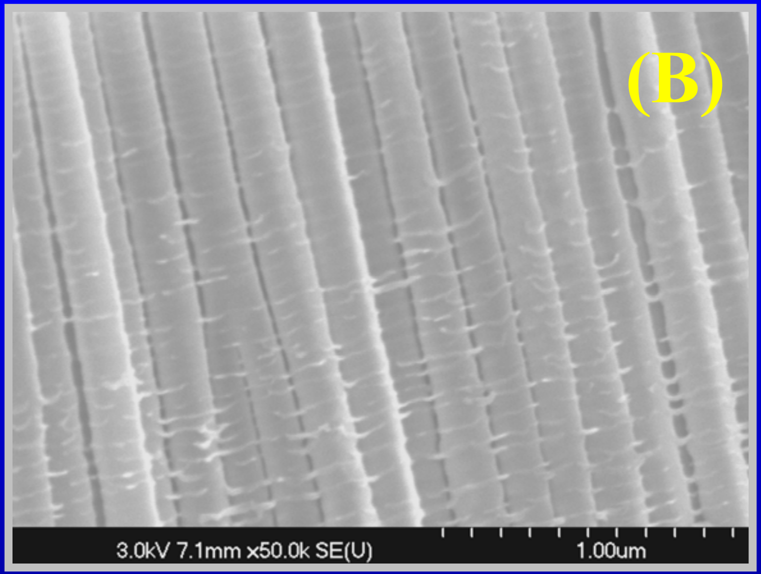
TiO_2 nanoparticles

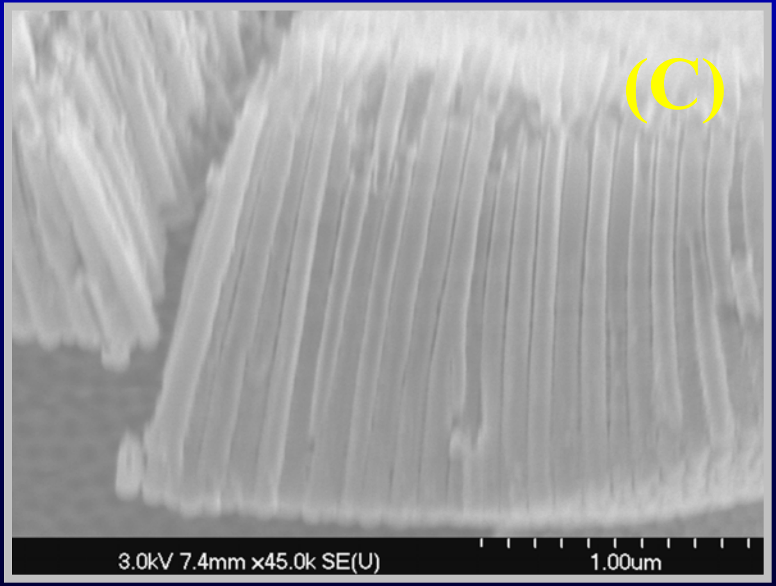
- 1 D nanotubes have improved charge transport due to quantum confinement in radial direction.
- Charge recombination losses are lower in 1 D nanotubes.

- In nanoparticles / nanocrystalline material charge transport is by sluggish hopping mechanism.
- Charge recombination losses are higher due to increased grain boundary regions in particulate nanocrystalline material.

Cross sectional view of nanotubes





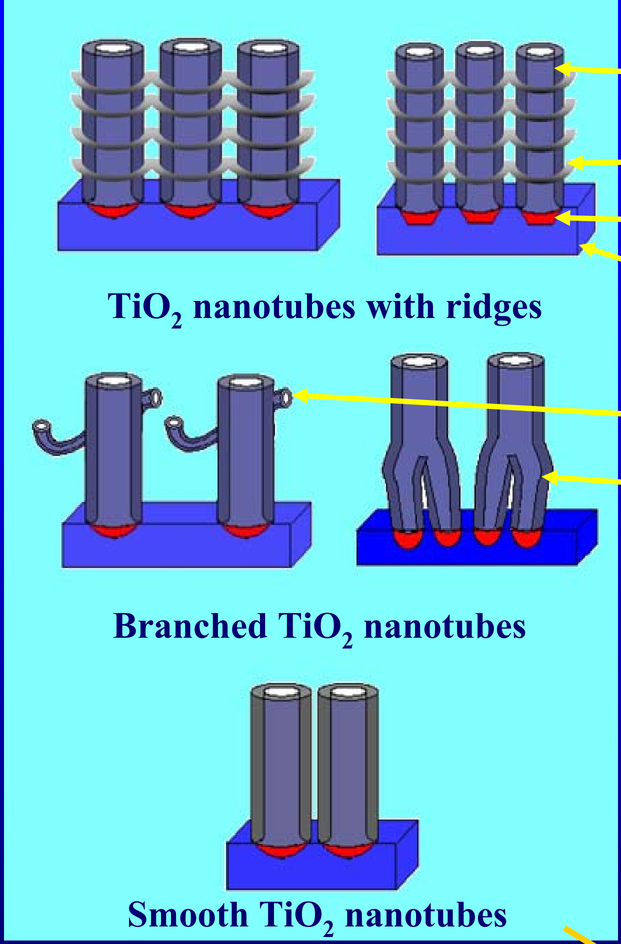


FESEM images of TiO_2 nanotubes:

(A) high ridged concentration
(B) thin ridged
(C) smooth

Preparation methods:
(A) H_3PO_4+ NaF
(B) EG + NH_4F
(C) Glycol + NH_4F

Hybrid TiO_2 nanotubes with various morphologies



TiO_2 nanotubes with ridges

Branched TiO_2 nanotubes

Smooth TiO_2 nanotubes

Tube

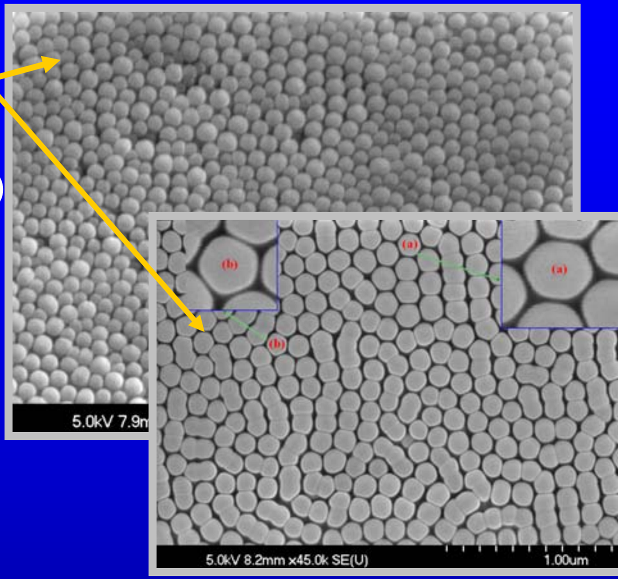
Ridges

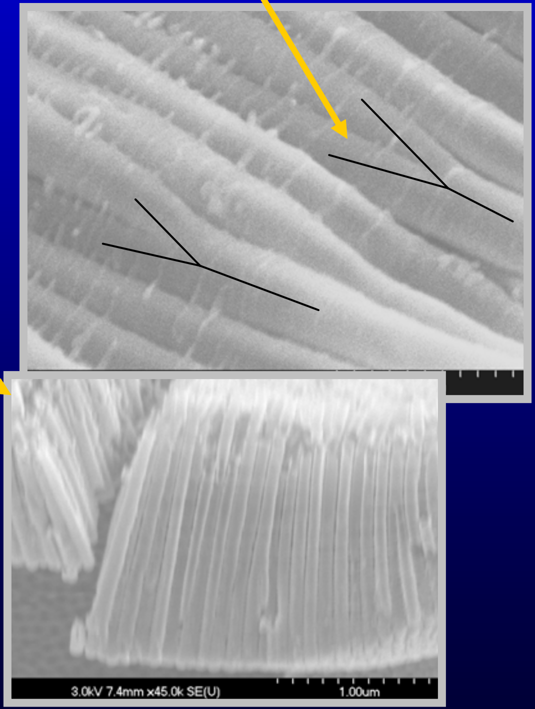
TiO_2 tube end (barrier layer)

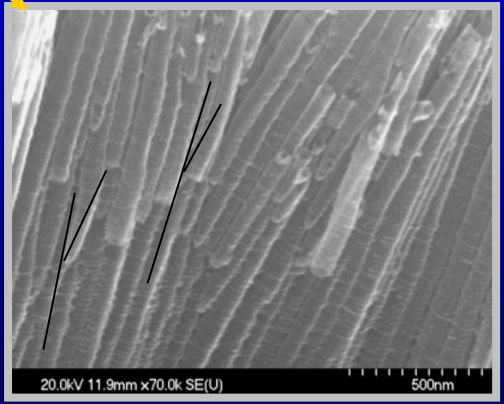
Ti

Upward branching

Downward branching





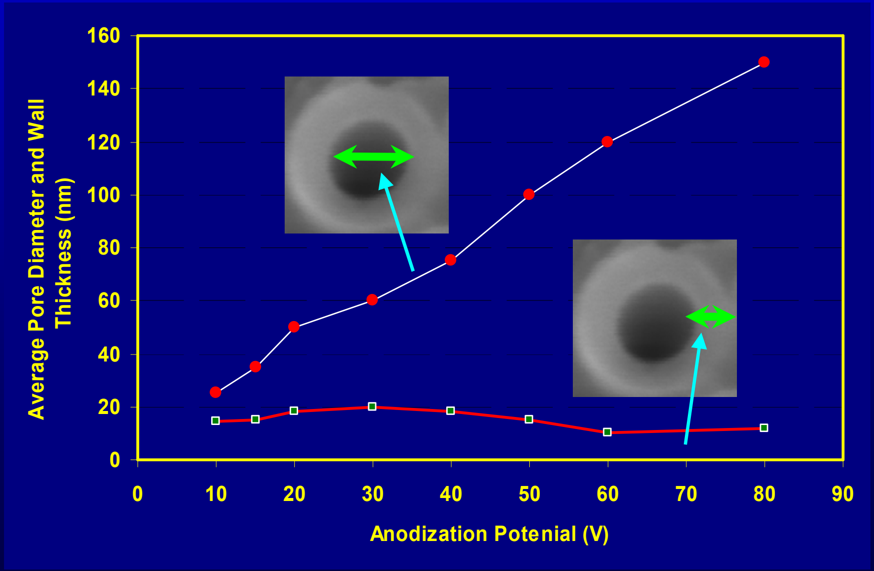


Preparation method:
Fine tuning the temperature and applied potential using ultrasonic waves.

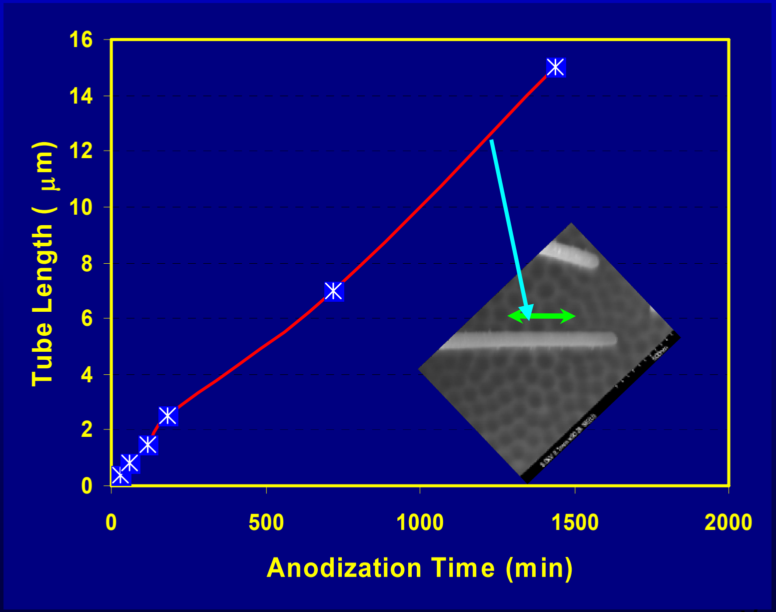
FESEM images of TiO_2 nanotubes with wide range of architecture

Synthesis of wide range of TiO_2 nanotube structure

- Pore diameter and wall thickness can be tailored by varying anodization potential.
- Pore diameter ranging from 20 nm to 150 nm can be obtained.
- Wall thickness varied between 10 to 20 nm.
- Different TiO_2 structures will be used to study charge transport and recombination phenomenon.



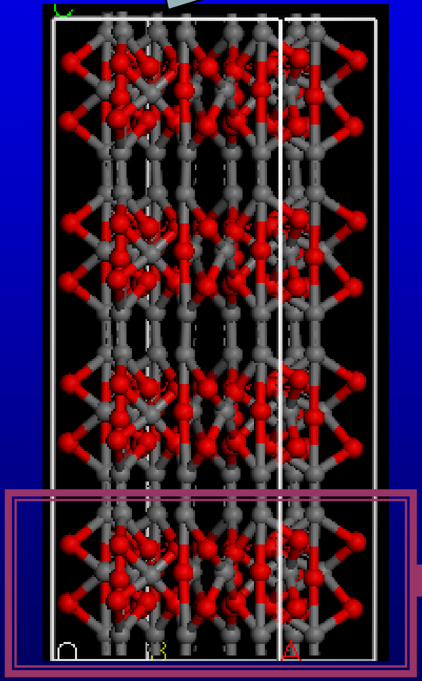
Anodization potential vs tube diameter and wall thickness



Time vs tube length

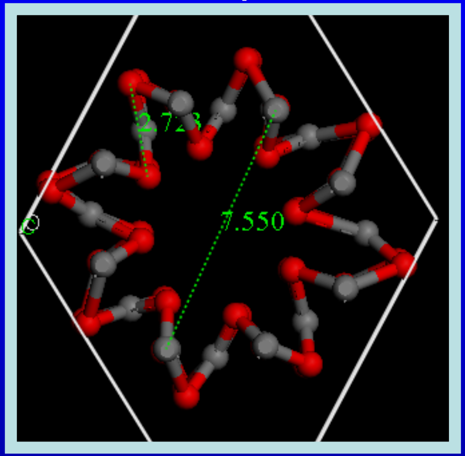
Continued…

Atomistic modeling and electronic properties of nanotubular TiO_2 network



Nano-tube structure displaying periodicity.

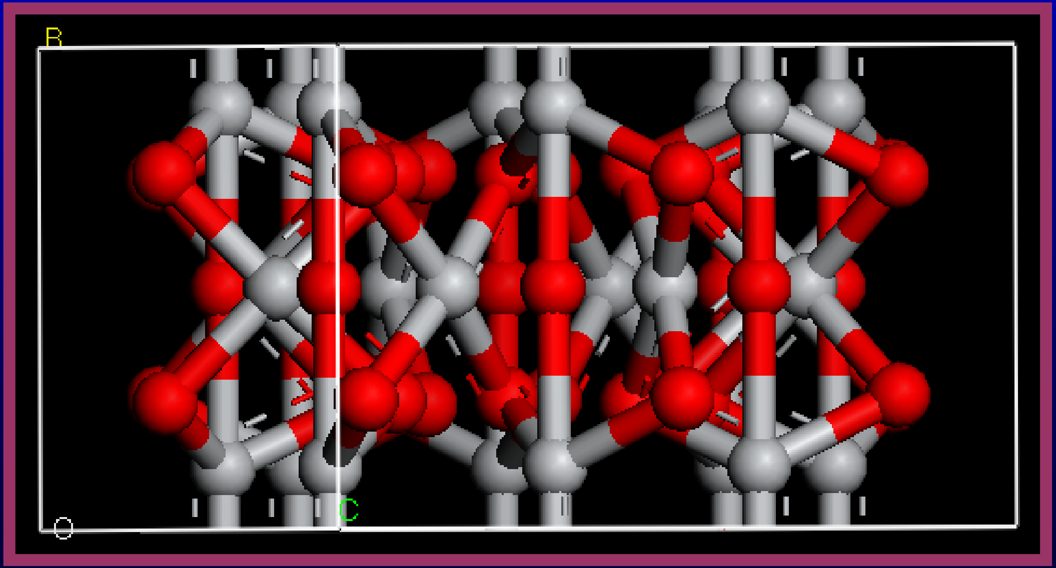
Top View



Preliminary model of the TiO_2 nanotube structure, obtained using the **Materials Studio Visualizer** software.

🔴 → **Oxygen atom**

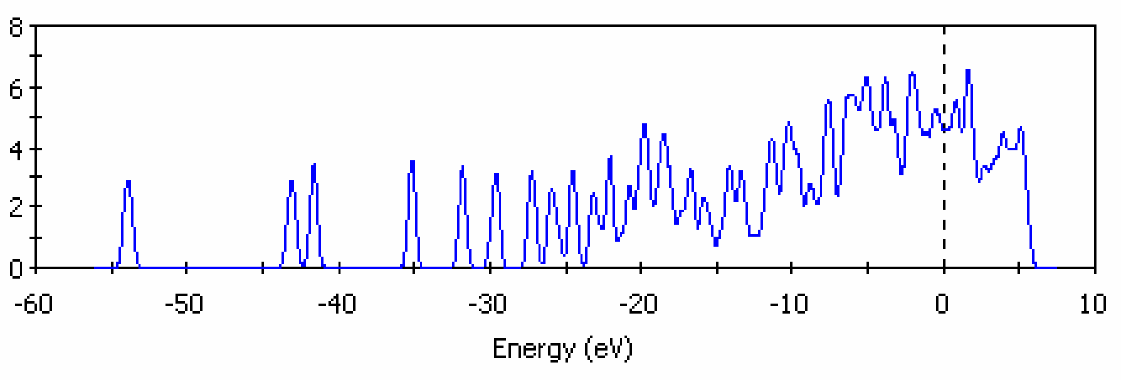
⚪ → **Titanium atom**



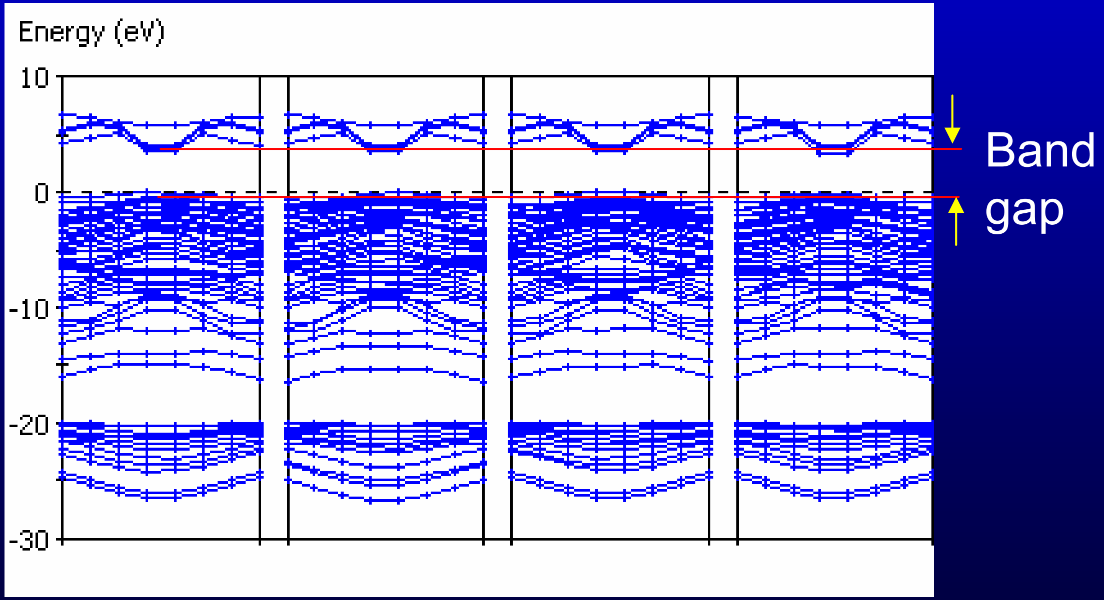
Lateral view of the (8,0) TiO_2

Preliminary results of DFT calculations for TiO_2 nanotubes

(a)



(b)



(a) Density of states (DOS) of the optimized TiO_2 structure. The dashed line shows the Fermi level.

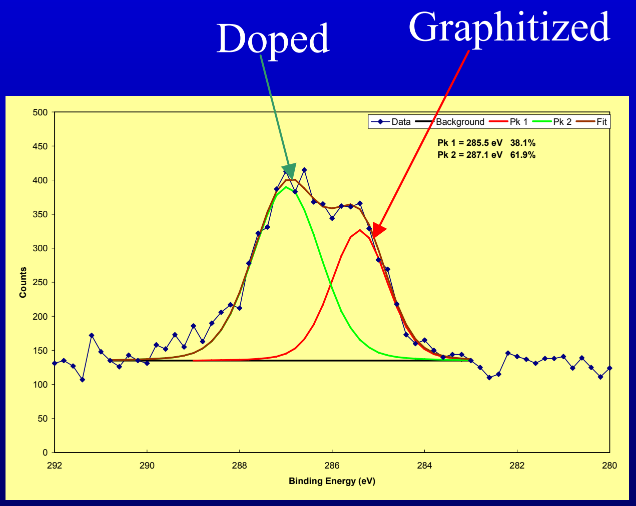
(b) Band structure of the TiO_2 nanotubes at selected crystal planes. The Fermi energy in the band-structure plot is shown to correspond to that in the DOS plot.

Fabrication by C-doping

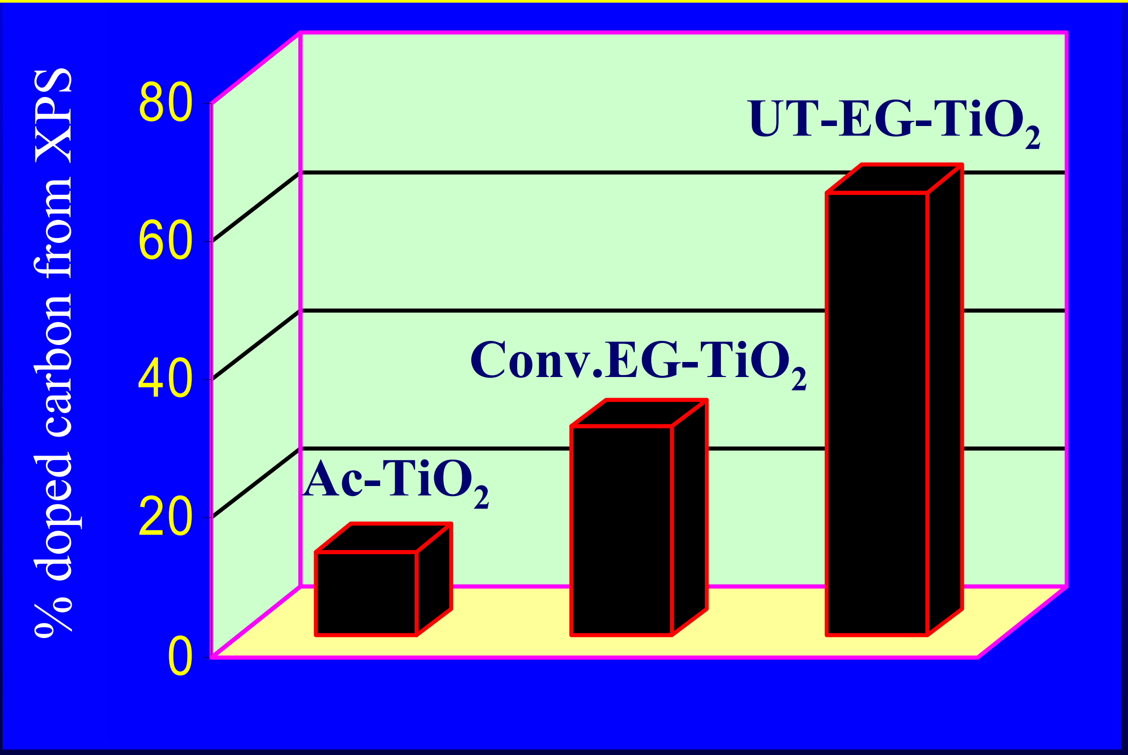
TiO_2 synthesis in organic medium found to be beneficial for carbon doping:

A. Single step carbon doping after heat treatment.

B. Most of the carbon present, is in the form of doped carbon.

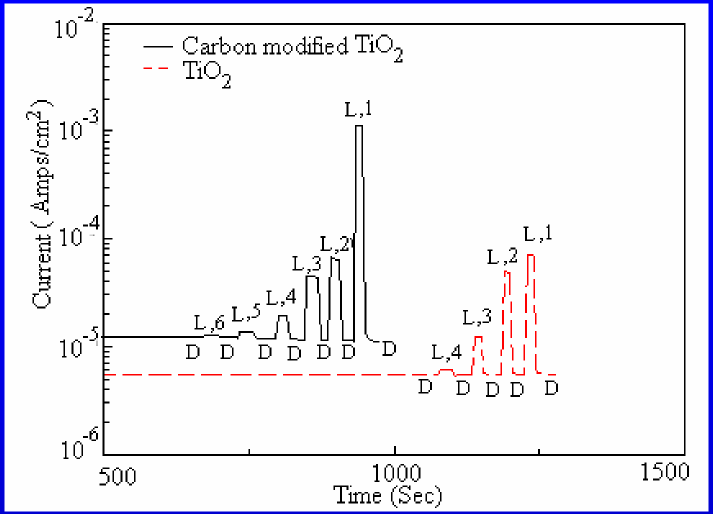


XPS C 1s spectra

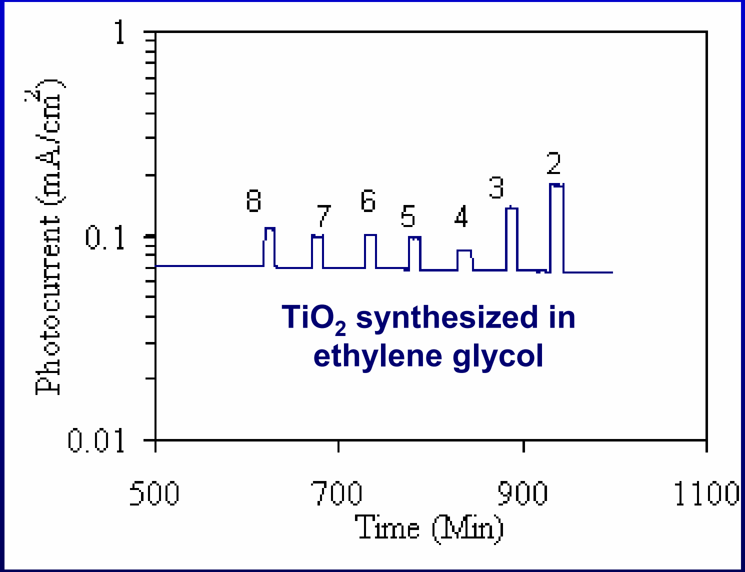


Effect of carbon source and doping method on the concentration of the doped carbon in TiO_2 matrix.

IPCE and band gap measurements



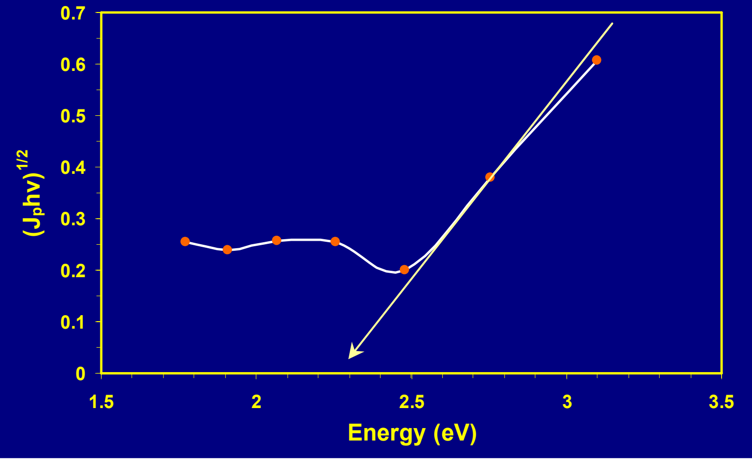
Sl. No.	Wavelength (nm)	Power mW/cm^2	Photocurrent, J_{ph} (mA/cm^2)	IPCE
1	330, ±100 nm	13.92	1.6	48.80
2	400, ±15nm	2.51	0.11	15.08
3	450, ±15nm	3.71	0.07	5.90
4	500 , ±15nm	4.41	0.016	1.02
5	550 , ±15nm	5.05	0.029	1.45
6	600 , ±15nm	4.93	0.032	1.50
7	650 , ±15nm	4.47	0.030	1.45
8	700 , ±15nm	4.79	0.036	1.52



Current transient plots

$(J_{ph}h\nu)^n$
n = 0.5 for indirect band gap,
n = 2 for direct band gap

J_{ph} = Photocurrent,
$h\nu$ = Photon energy = hc/λ



Tauc plots showing the indirect band gap of carbon doped TiO_2 nanotubes.

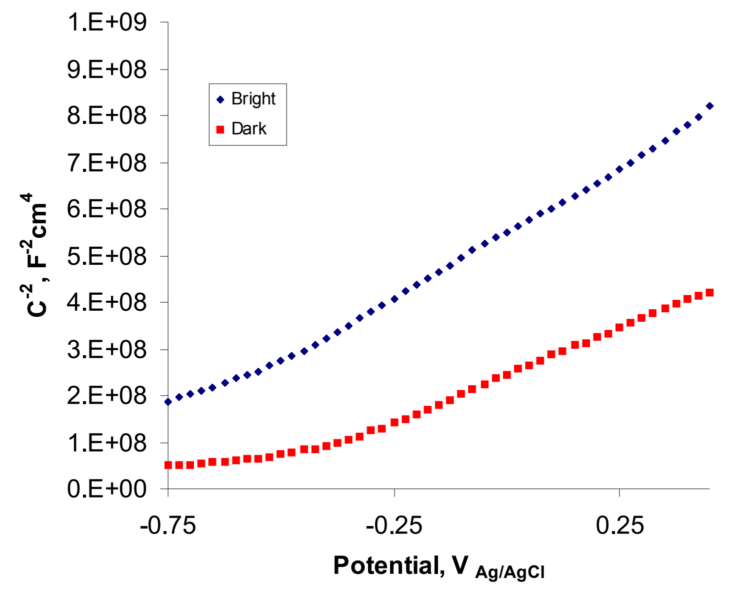
Determination of charge carrier density and flat band potential of nanotubular TiO_2

Charge carrier density = $N_D = 2/(E*\varepsilon*\varepsilon0*m)$;

where, E = elementary electron charge, ε = dielectric constant,

ε_0= permittivity in vacuum, m = slope of the V vs $1/C^2$ plot.

Mott – Shottky plot of carbon modified hybrid TiO_2 nanotubes

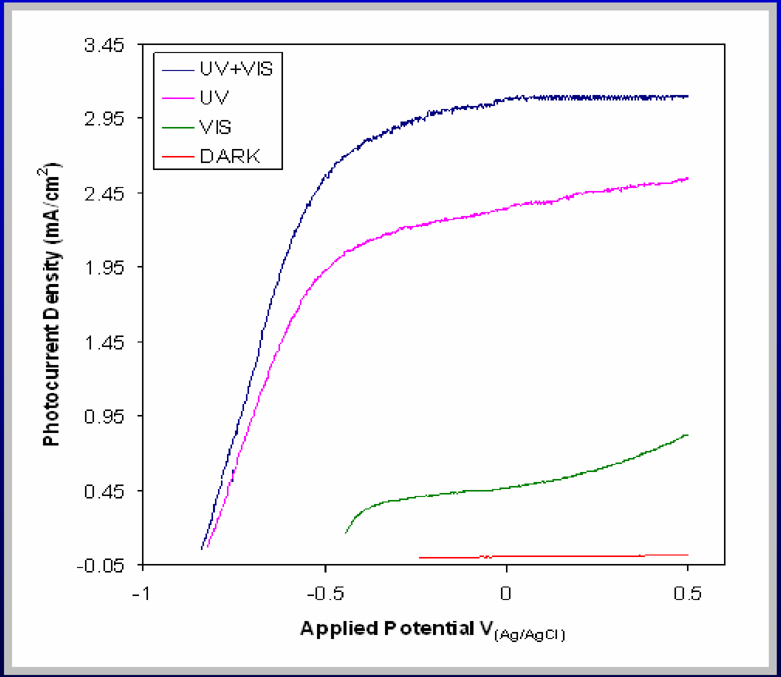


Specimen	Charge carrier density cm^{-3}	Flat band potential (bright), $V_{Ag/AgCl}$
As-anodized	1.1×10^{17}	– 1.2
N_2 annealed	2×10^{19}	– 1.15
O_2 annealed	1.2×10^{15}	– 0.83
C-modified	3×10^{19}	– 1.1

Photocurrent under different light illumination

Sample description :
0.7 cm^2 photoanode (C-modified TiO_2 nanotubes , 1 μm nanotube length,
50 – 55 nm diameter)

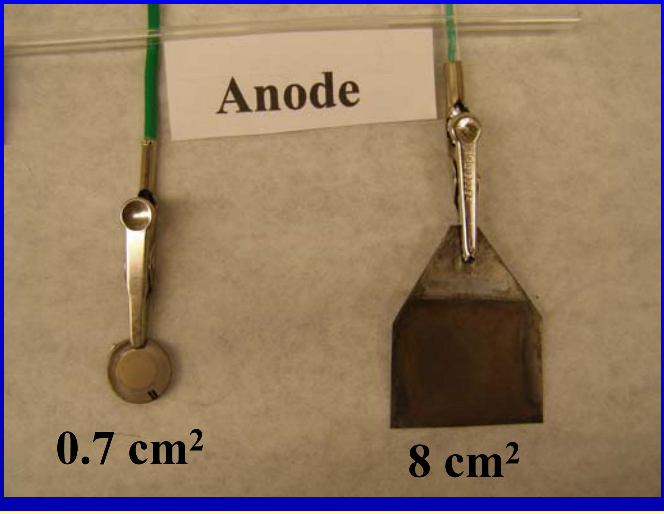
Illuminations	Power mWatt/cm^2	Photocurrent (max)(mA/cm^2)
Dark	–	0.01
Vis 520, ±46 nm	5.27	0.8
UV 330, ±70 nm	13.9	2.5
UV + Vis	87.0	3.3

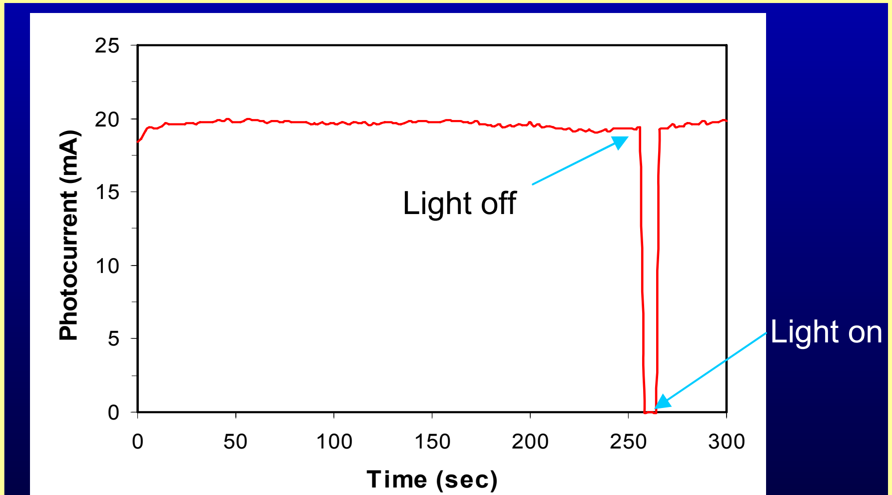


Potentiodynamic plot of carbon modified TiO_2 photoanode under various illuminations.

Preliminary scale-up of photoanode

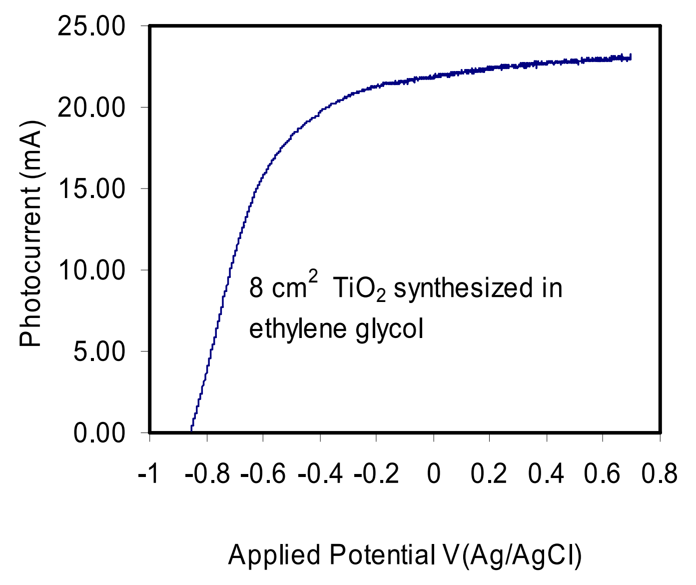
Anodization of 8 cm^2 titanium sheet produces uniform TiO_2 nanotubes.





Potentiostatic plot for 8 cm^2 photoanode at – 0.4 $V_{Ag/AgCl}$

Potentiodynamic plot using 8 cm^2 C-modified TiO_2 photoanode

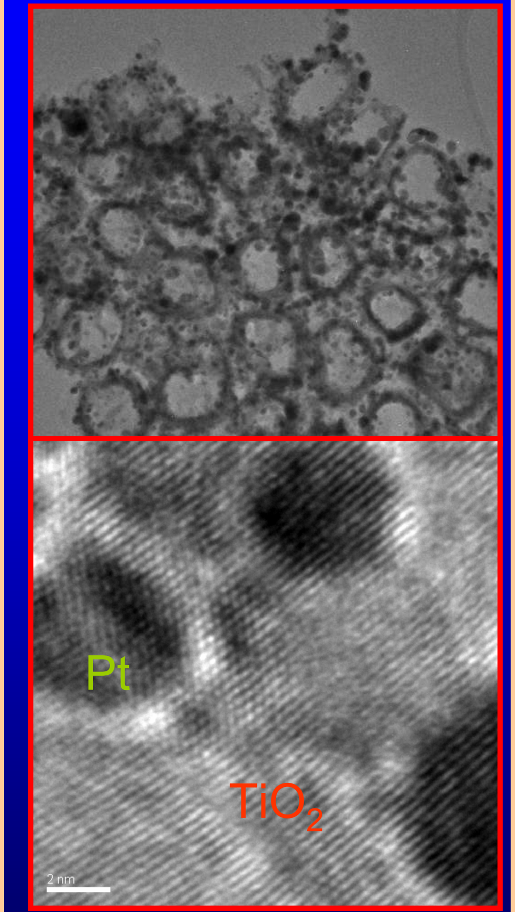


Photocurrent of 8 cm^2 electrode ≈ 24 mA

Hydrogen = 9.6 mL/hr

Design of efficient photo electrochemical cell using Pt/TiO_2 as a cathode

TEM of Pt/TiO_2



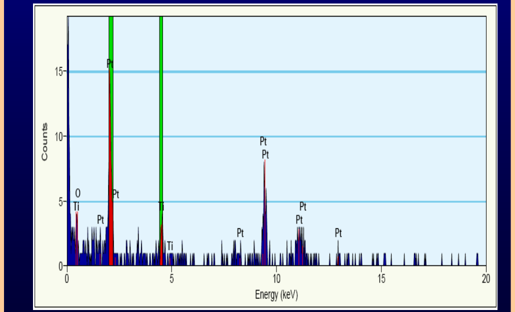
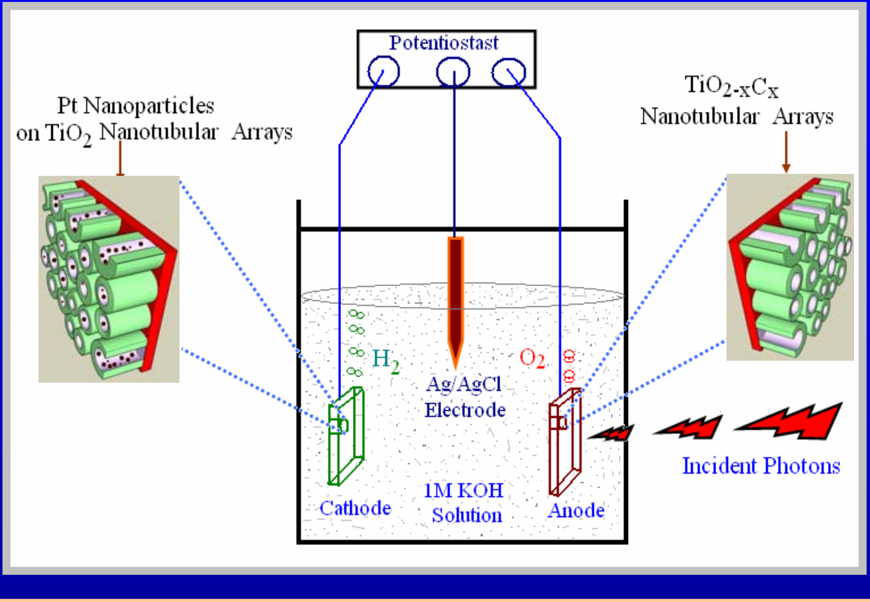
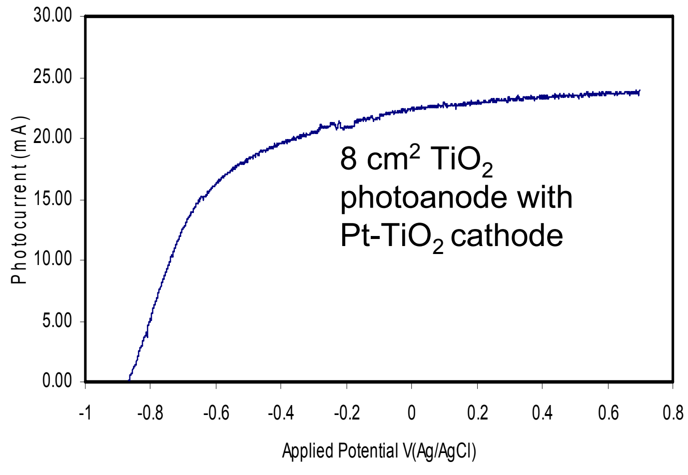


Figure 1. A schematic of the photoelectrolytic cell designed for the generation of hydrogen using light source (UV+VISIBLE). The anode is carbon doped titania nanotubular arrays prepared by sonoelectrochemical anodization technique and the cathode is platinum nanoparticles synthesized on undoped titania nanotubular arrays





- The Pt/TiO_2 cathode with 0.4 wt% Pt is found to be as efficient as a pure Pt electrode.
- This electrode is prepared by simple incipient wetness method

Future Work

- Synthesis of hybrid photoanodes:
  - Functionalization of TiO_2 nanotubes with organic compounds.
  - Synthesis of mixed oxide nanotubes (Ti-Mn / Ti-W) by various methods like sputtering-anodization, pulsed electrodeposition-oxidation, electrochemical deposition-anodization and co-precipitation on TiO_2 template.
- Synthesis of hybrid cathodes:
  - Pt surface with atomic layers of Pd-Ru-Rh-Re, Ru-Re, Rh-Re.
  - Preparation of inexpensive and robust cathode by fabricating TiO_2 with Ni, Pt, Cd-Te and Cd-Zn-Te.
- Investigation of the photoanode and cathode by microstructural and electrochemical characterizations.
- Kinetics studies of the titania nanotubes formation by the H_2O_2 titration and ICP analysis.
- Architect the shape of the nanotubes and photoanode to harvest sunlight more efficiently.
- Modeling of the TiO_2 nanotubes and investigation of their electronic properties by DFT.
- Stability studies by various characterization techniques and Kelvin-Probe measurements.
- Electrochemical cell with differential pH anode and cathode compartments.
- Scale-up set up for actual solar light harvesting.

Summary

- *Relevance*: Develop a stable and highly efficient photoelectrochemical cell for solar hydrogen generation by water splitting.
- *Approach*: Synthesize hybrid nanotubular TiO_2 composite arrays as photoanode and nanowires / nanoparticles of compound semiconductors as cathodes for improved photo conversion process.
- *Technical accomplishments and process*: Develop a single step electrochemical process for producing hybrid, low band gap TiO_2 photoanode having excellent photoelectroactivity.
- *Technology transfer/ collaboration*: Active partnership with NREL for materials characterization.
- *Proposed future research*: Develop new doping methods to reduce band gap of TiO_2 nanotubes, inorganic-organic hybrid materials for better electron transport; mixed oxide photoanodes to harvest full spectrum of sunlight, develop inexpensive cathodes using nanowires / nanoparticles of compound semiconductors; scale-up testing for actual solar light harvesting.