Photoelectrochemical Generation of Hydrogen from Water Using Visible Light Sensitive Semiconductor Nanotube Arrays

Mano Misra
Principal Investigator
Chemical and Materials Engineering
University of Nevada, Reno
Reno, Nevada, 89557
Phone: 775-784-1603
Email: misra@unr.edu

May 18-22, 2009

Project ID # PDP_09_Misra

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

Overview

Timeline

- Project start date: October, 2006
- Project end date: September, 2009
- Percent complete: 80

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 nanotubular 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

2009-2010

- Develop semiconductors which absorb in the visible region of the solar spectrum

Approach

Task A. Synthesis and fabrication of metal oxide and oxynitride nanotube arrays

Ultrasonic mediated metal (Fe and Ta) oxide nanotube arrays (NTs)
Fabrication and process development of one dimensional oxynitride arrays
Characterization and fundamental understanding of the materials prepared

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

Test photoanodes

Reducing e-h recombination using plasma sputtering and high energy irradiation
Increasing charge transport properties

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

Electrochemical methods
Spectroscopic analysis

Task D. Scale-up and process evaluation.

Scale-up of photoanodes
Photoelectrochemical hydrogen generation under real solar irradiation

A. Synthesis of Tantalum Oxynitride (TaON) Nanotubes

Background

Predicted band gap: 2.0-2.4 eV

Good charge transport properties

Ideal material for PEC applications

Conduction and Valence Band Positions of Ta_2O_5, TaON, and Ta_3N_5 by UPS and Electrochemical Methods

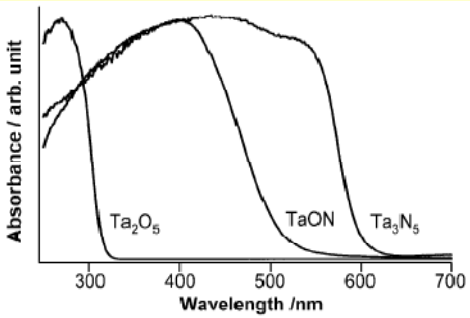
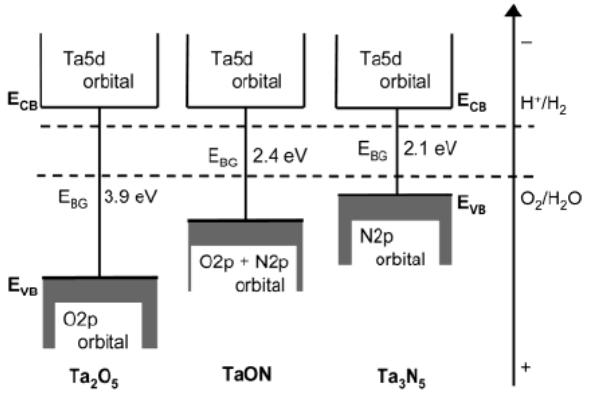


Figure 5. U− vis diffuse reflectance spectra of Ta_2O_5, TaON, and Ta_3N_5.



Schematic band structures of Ta_2O_5, TaON, and Ta_3N_5.

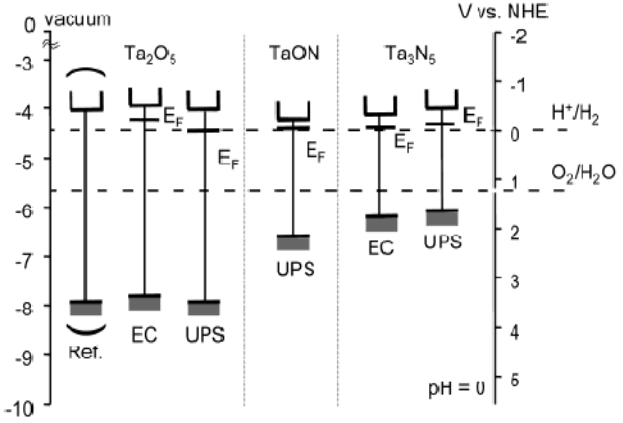
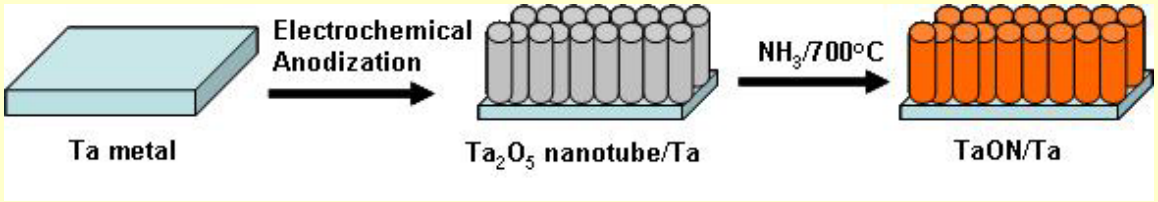


Figure 13. Band positions of Ta_2O_5, TaON, and Ta_3N_5 determined by electrochemical analysis and UPS measurements.

J. Phys. Chem. B **2003,** *107,* 1798−1803

Synthesis of Tantalum Oxynitride (TaON) Nanotubes



Ta_2O_5 NTs

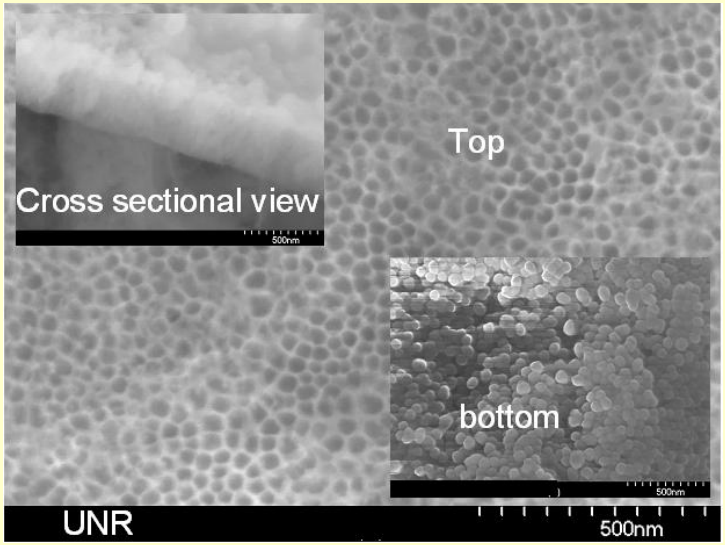


Fig. SEM images of Ta_2O_5 nanotube arrays on Ta foil. The insets show the cross sectional image of Ta_2O_5 NT arrays of 525 nm and bottom of the nanotubes

Anodizing solution:
Ethylene glycol + water + NH_4F

Formation mechanism:

$2Ta + 5H_2O \rightarrow Ta_2O_5(anodic) + 5H_2(cathodic)\uparrow$ (1)

$Ta_2O_5 + 12F^- + 10H^+ \rightarrow 2[TaF_6]^- + 5H_2O$ (2)

Characteristics:

- **525nm long in just 2 minutes**
- **50 ± 5 nm internal tube diameter**

Synthesis of Tantalum Oxynitride (TaON) Nanotubes

TaON NTs

Ta_2O_5 NTs $\xrightarrow{700\ ^oC,\ NH_3}$ TaON NTs

One step:

- **Conversion to TaON**
- **Annealing**

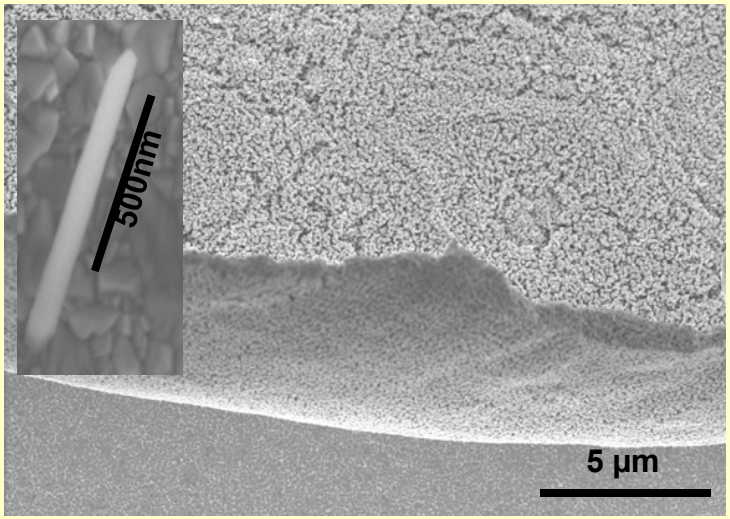


Fig. SEM image of TaON nanotube arrays on Ta foil. The morphology is same as Ta_2O_5 NTs

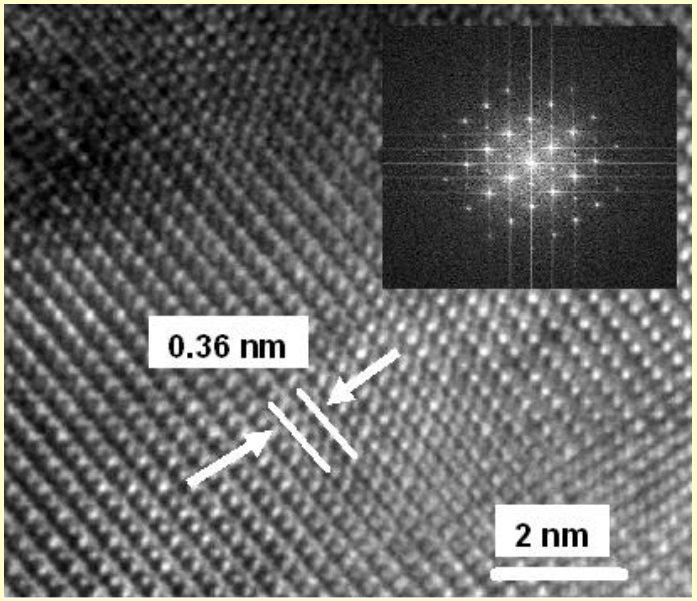


Fig. TEM image of TaON nanotube arrays

NT arrays are stable after nitridation

NTs are highly crystalline

Synthesis of Tantalum Oxynitride (TaON) Nanotubes

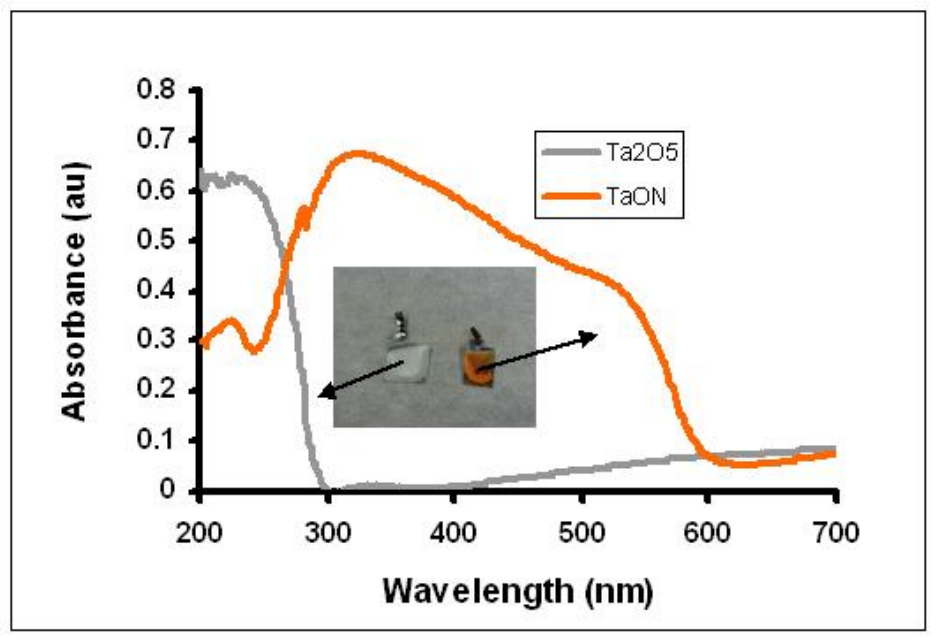


Fig. DRUV-Vis spectra of Ta_2O_5 and TaON NTs

Band gap: 2.07 eV

- **Absorption band-edge of TaON is at *ca.* 600 nm, being shifted by about 300 nm from that of Ta_2O_5**
- **Band gap: 2.07 eV**
  Ideal band gap the photosplitting of water
- **Band edge (literature, sol-gel process): 500 nm**
- **Red shift of 100 nm (from 500nm to 600 nm) : May be due to a) presence of carbon in the as-anodized Ta_2O_5 nanotubular sample. b) The sample is nanotubular. However, this strange behavior is not clear yet and further investigations are necessary**

Photoelectrolysis Using TaON NTs and Pt cathode

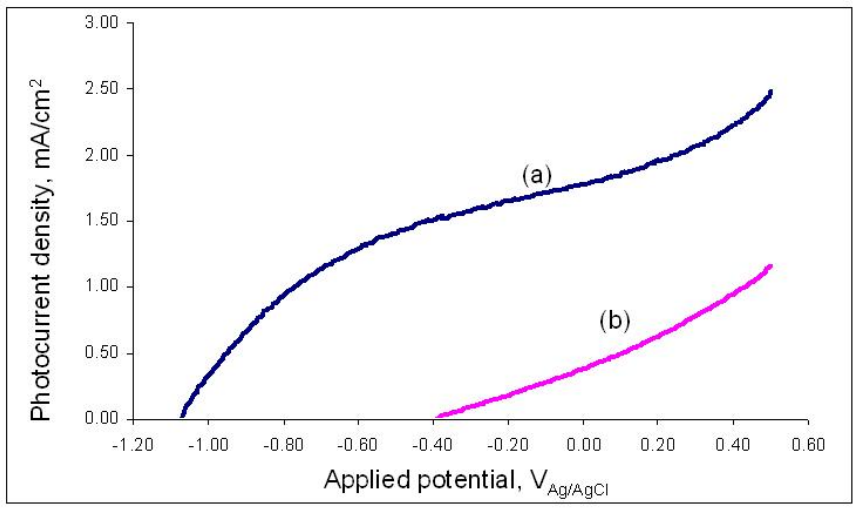


Fig. Potentiodynamic plot of TaON NTs under global AM 1.5 solar light (a) and visible light (≥ 420 nm) illumination. Nanotubes of 50 nm internal diameter and 525 nm long are used. Sample are: 1 cm^2

The visible light contribution is found to be around 47 % of the total activity

Results

Table. Comparison of photocurrent density of TaON NTs with various other photocatalysts

Catalyst	Photocurrent density (mA/cm^2)[a] at 0.5 $V_{Ag/AgCl}$	Visible light contribution (%)[b]
P25/Ti	0.365	0.32
TiO_2 NTs/Ti	0.638	0.39
Fe_2O_3 NTs/Fe	1.4	50
Fe_2O_3 nanoparticle/Fe	0.004	NA
Ta_2O_5 NTs/Ta	0.25	0.28
TaON NTs/Ta	**2.6**	**47**

B. Synthesis of Iron Oxide (Fe_2O_3) Nanotubes

Theoretical band gap: 2.2 ev, Ideal material for PEC applications

Major challenges for Fe_2O_3 NTs:

- poor conductivity
- high electron-hole (e-h) recombination

Managing the challenge: Options

- Heteroatom doping
- Controlling morphology

UNR approach

Controlling morphology

Advantages: Gives a unique possibility to control the direction and path of the charge carriers through quantum confinement

Barrier: The diffusion length of the minority charge carriers in hematite is ~ 4 nm, control the quantum confinement within this range

Solution: Synthesize Fe_2O_3 NTs having wall thickness of ~ 4 nm

Synthesis of Iron Oxide (Fe_2O_3) Nanotubes

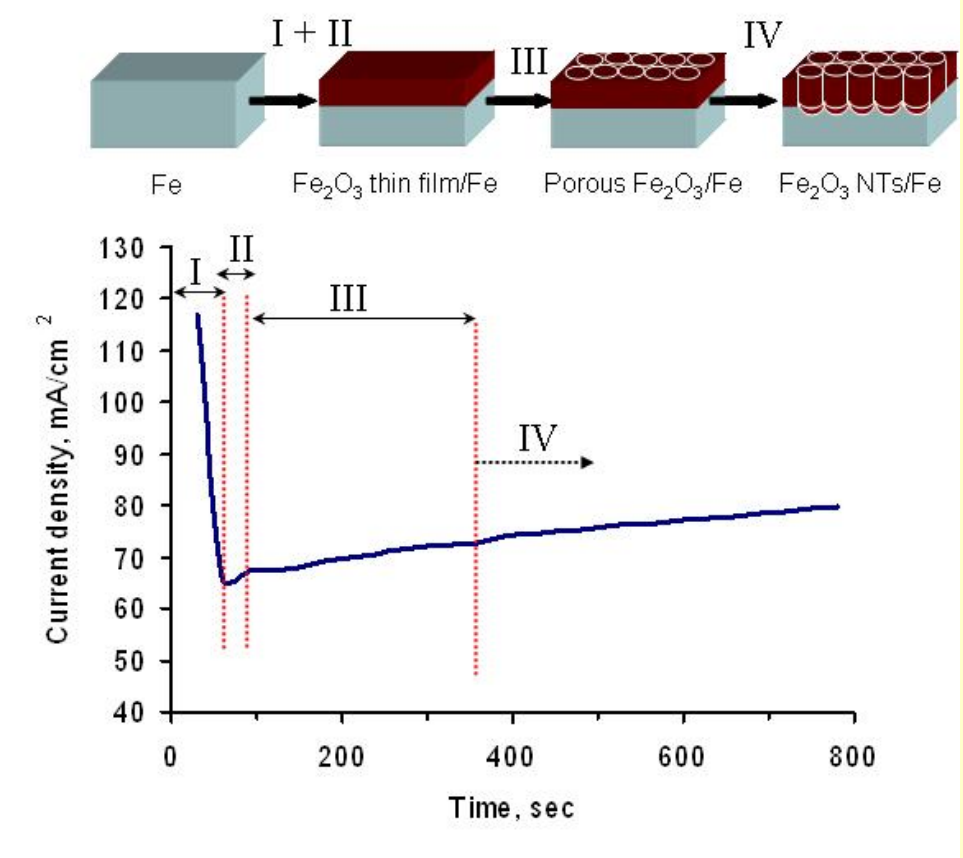


Fig. Current transient during anodization of Fe in aqueous ethylene glycol (3 v% water + 0.5 wt% NH4F) solution at 50 V. Step I: formation of compact iron oxide layers; II: nucleation of nanopores, III: formation of nanoporous structure and IV: formation of individual NTs. Even though this path goes through nanoporous structure (confirmed from SEM in various stages of anodization); for an ordered nanoporous iron oxide structure a lower amount of water is preferred.

Anodizing condition:

Ethylene glycol (3 v% water+0.5 wt% NH_4F) solution at 50 V for 13 min

Formation mechanism:

$2Fe + 3H_2O \rightarrow Fe_2O_3(anodic) + 3H_2(cathodic)\uparrow$ (1)

$Fe_2O_3 + 12F^- + 6H^+ \rightarrow 2[FeF_6]^{3-} + 3H_2O$ (2)

Synthesis of Iron Oxide (Fe_2O_3) Nanotubes

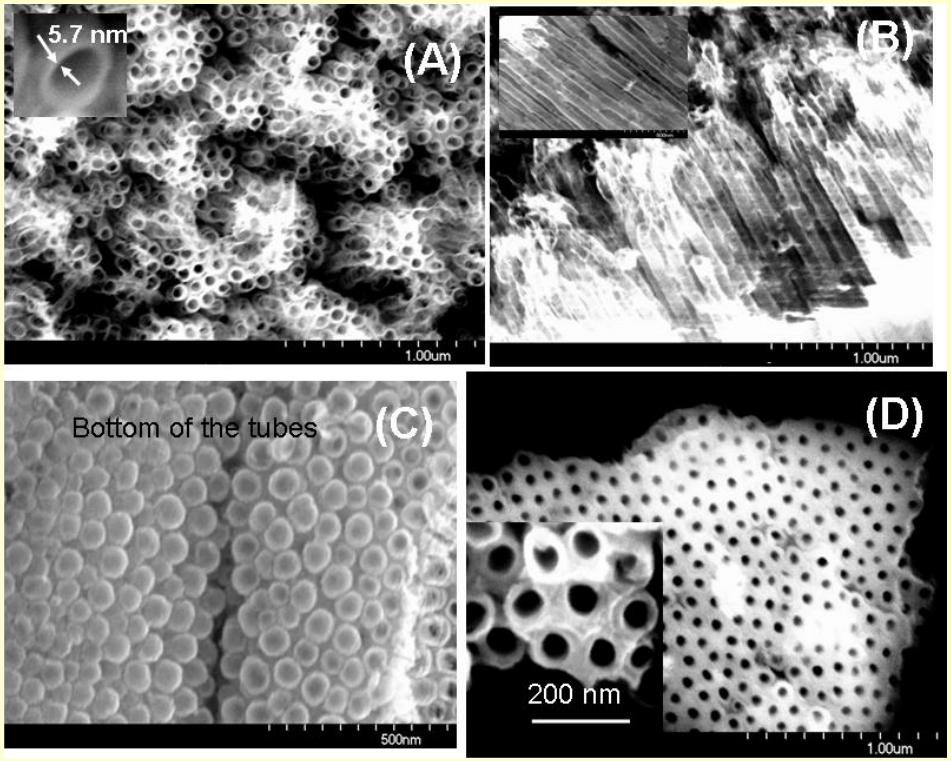
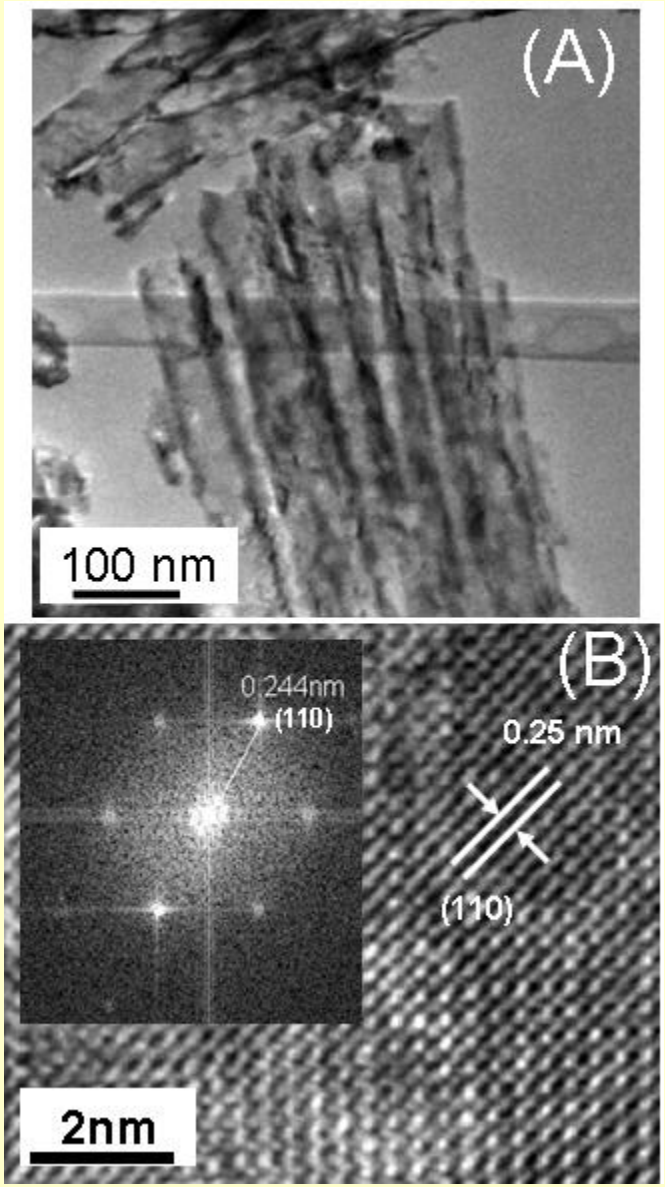


Fig. SEM images of as-anodized Fe_2O_3 NTs on Fe foil

Characteristics:

- **Smooth and ultra-thin (5-7 nm thick)**
- **3-4 μm long in just 13 minutes**

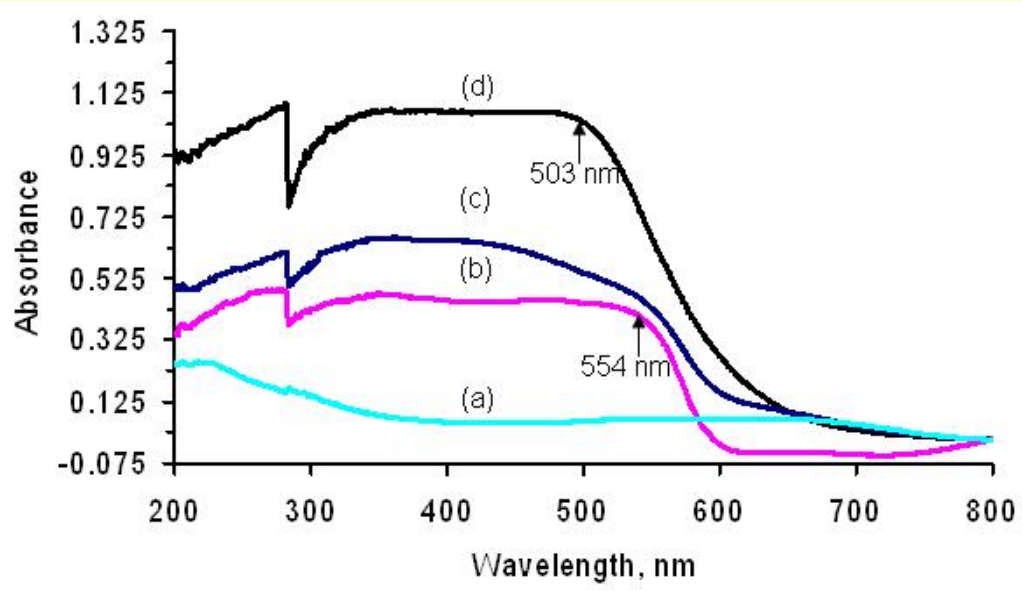
Synthesis of Iron Oxide (Fe_2O_3) Nanotubes



TEM images of hydrogen annealed iron oxide NTs showing individual transparent NTs

- **Highly crystalline NTs**
- **Lattice fringe: 0.251 nm→(110) lattice plane of hexagonal hematite structure**

Synthesis of Iron Oxide (Fe_2O_3) Nanotubes



Pre anodization: Metallic Fe foil does not absorb in the visible region

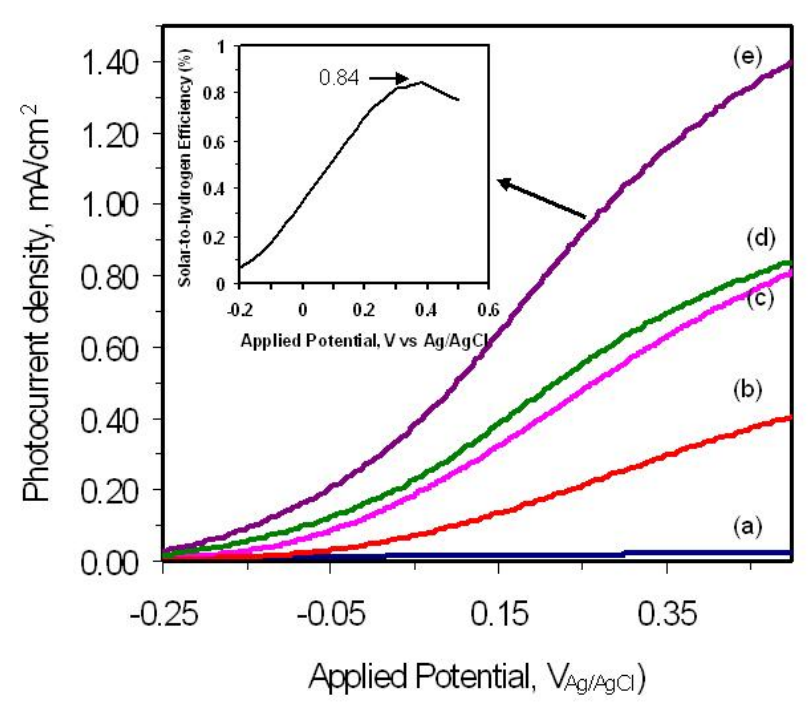
Post anodization: Fe_2O_3 reddish-brown color

Absorption: upto 550 nm with the onset being around 629 nm

Band gap = 1.97 eV

Fig. DRUV-Vis spectra of: (a) as-received Fe foil, (b) bulk iron oxide,
(c) iron oxide nanoparticles coated on Fe foil and
(d) hematite nanotubular arrays on Fe foil prepared by anodization process (50 V for 13 min).
The absorption in the UV region corresponds to the direct charge transfer transitions from O2- *2p* to Fe3+ *3d* charge.
On the other hand, the absorption in the visible region is due to the Fe3+ 3d→3d spin forbidden transition excitation (indirect transition).

Photoelectrolysis Using Fe_2O_3 NTs and Pt Cathode



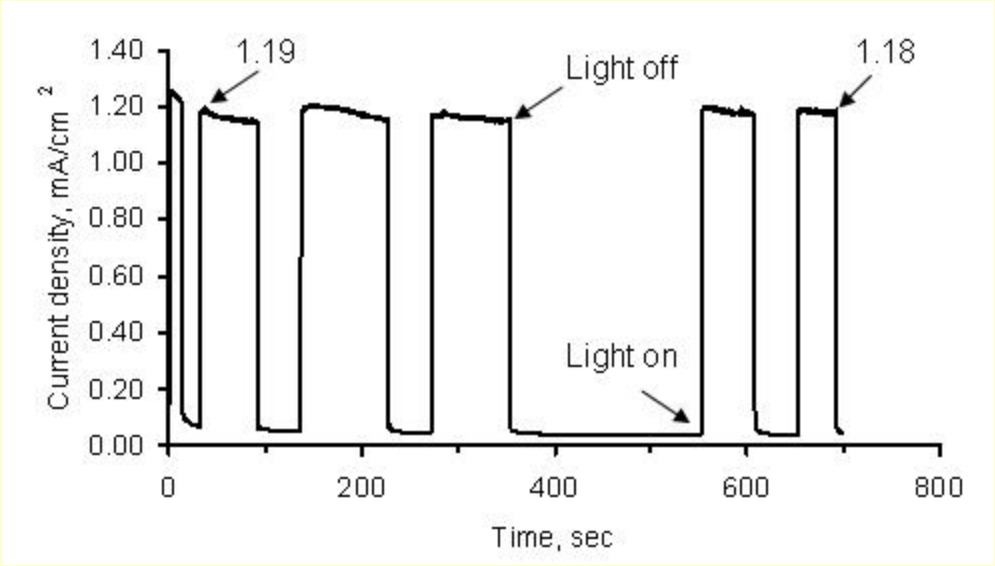


Fig. Potentiodynamic (I–V) behavior of iron oxide NTs conditions: (a) as-anodized under AM 1.5 illumination (87 mW/cm2) (c) oxygen annealed under AM 1.5 illumination (e) hydrogen annealed under AM 1.5 illumination, (b) oxygen annealed under visible light illumination and (e) hydrogen annealed under visible light illumination. Inset shows the efficiency of the NT arrays.

Fig. Photoresponse of hydrogen annealed iron oxide nanotube arrays under the illumination of global AM 1.5 light source (87 mW/cm2) at 0.4VAg/AgCl. The photocurrent became almost zero when the light is switched off (illumination stopped) and the original photocurrent again came back after illumination.

Photoelectrolysis Using Fe_2O_3 NTs and Pt Cathode

Mechanism

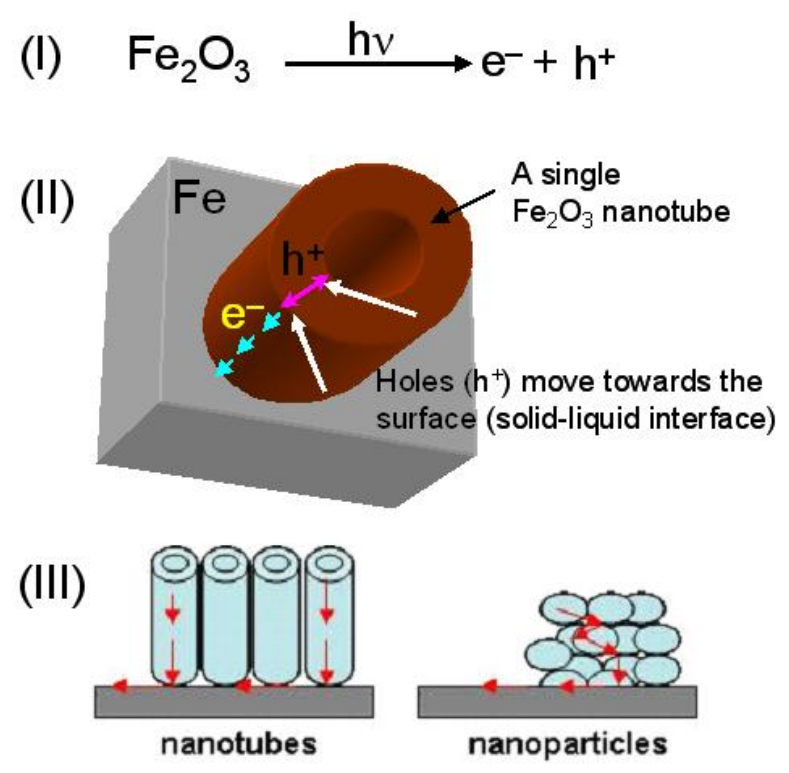


Fig. H_2 generation mechanism using Fe_2O_3 NTs

Advantages of such an architecture:

Path covered by the hole to reach the surface is the most important factor on the photoresponse of any iron oxide based catalysts.

In this work:

- Ultra-thin walls of the NTs, holes can reach at the surfacefaster than other iron oxide architectures, which reduce the e-h recombination loss
- The 1D nature of the NTs also help for a faster electron transfer properties of the electrodes

Photoelectrolysis Using Fe_2O_3 NTs and Pt Cathode

Results

Table. Comparison of photocurrent density of various Fe_2O_3 nano-catalysts

Catalyst	Photocurrent density ($\mu A/cm^2$) at 0.5 $V_{Ag/AgCl}$
1-D NTs	**810[a] (1410)[b]**
Nanoporous	263
Scattered NTs	145
Nanoparticles	4

[a] **a mixture of hematite and magnetite NTs**
[b]**pure hematite NTs**

Table. Electrochemical Measurements of Fe_2O_3 NTs and NPs under dark and illuminated conditions

Catalysts	Conditions	N_D[a]	U_B[b] ($V_{Ag/AgCl}$)
Fe_2O_3 NT/Fe	Dark	7.05×10^{21}	-0.50
	Bright	9.21×10^{23}	-0.60
Fe_2O_3 NPs/Fe	Dark	5.15×10^{21}	-0.75
	Bright	5.62×10^{21}	-0.70

[a] **Charge carrier density;** [b] **Flat band potential**

Development of UNR *easy-H_2* PEC cell to be used under solar light irradiation (on-field H_2 generation)

Fig. Preliminary results indicate that H_2 generation from on-field experiments is comparable to the experiments under simulated solar light conditions (AM 1.5)

- Two-electrode electrochemical cell, adjustable anode compartment capable of tracing the trajectory of sun, a set of alkaline batteries connected with a rheostat for application of external bias
- Maximum photocurrent density: 31 mA/cm^2, 13:30 h
- Sunlight intensity: 113 mW/cm^2
- 1 M KOH electrolyte, 10 vol% ethylene glycol under an applied bias of 0.5 V
- Hydrogen generation rate: 4.4 mL/h cm^2, solar intensity between 104 mW/cm^2 and 115 mW/cm^2 from 10:00 to 14:20 h

Future Work

- Synthesis of visible light sensitive photoanodes
- Optimize synthesis process of TaON NTs
- Increase charge transport properties of Fe_2O_3 NTs
- Kinetics studies of nanotubes formation by titration using spectrophotometric analysis
- Stability studies of photoanodes by various characterization techniques and Kelvin-Probe measurements
- Incident photon to current conversion efficiency (IPCE) measurements
- Theoretical investigation of the formation of TaON from Ta_2O_5 NTs and Fe_2O_3 by density functional theory and thereby how to increase efficiency
- 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 visible light sensitive nanotube arrays as photoanode for improved photo conversion process
- **Technical accomplishments and process:** Developed ultra-thin Fe_2O_3 nanotube arrays and TaON nanotube arrays with band gap around 2 eV with 40-50% visible light activity.
- **Technology transfer/collaboration:** Active partnership with NREL and University of Arkansas at Little Rock.
- **Proposed future research:** (a) Synthesize photoanodes that can harvest 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.