Metal Oxide Semiconductor Nanotubular Arrays for Photoelectrochemical Hydrogen Generation

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DOE Hydrogen Program Review 2013

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Project ID # PD076

Overview

Timeline

- Project start date: October, 2006
- Project end date: September, 2014 (Pending DOE approval)
- 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: $ 2,970 K

Partners

- National Renewable Energy Laboratory
- University of Arkansas at Little Rock
- University of Nevada Las Vegas (pending DOE approval)

Objectives

Overall — **Develop high efficiency hybrid-semiconductor nanotubular materials for hydrogen generation by water splitting**

2006-2007
- Develop new anodization techniques to synthesize high quality and robust titanium dioxide (TiO_2) nanotubes with wide range of nanotubular architectures
- 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

2012-2013
- Enhance visible light absorption of metal oxide nanotubes
- Develop new synthesis techniques for enhanced photoelectrochemical performance

Approach

Task A. Synthesis and fabrication of photocatalysts

- Increase visible light utility of metal oxide nanotubes by
- Examine new synthesis techniques
  - Effect of surface treatment and effect of light irradiation during synthesis
- Characterization and fundamental understanding of the materials prepared

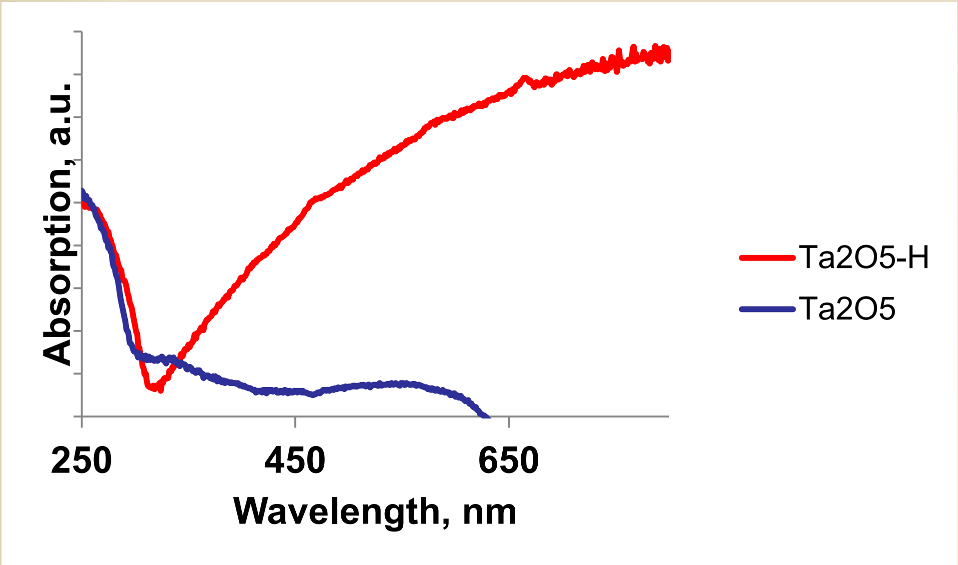
Task B. Application of the nanotubular materials for photoelectrochemical generation of H_2 from Water

- Evaluate photoelectrochemical behavior of nanotubular oxide composite photoanodes

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

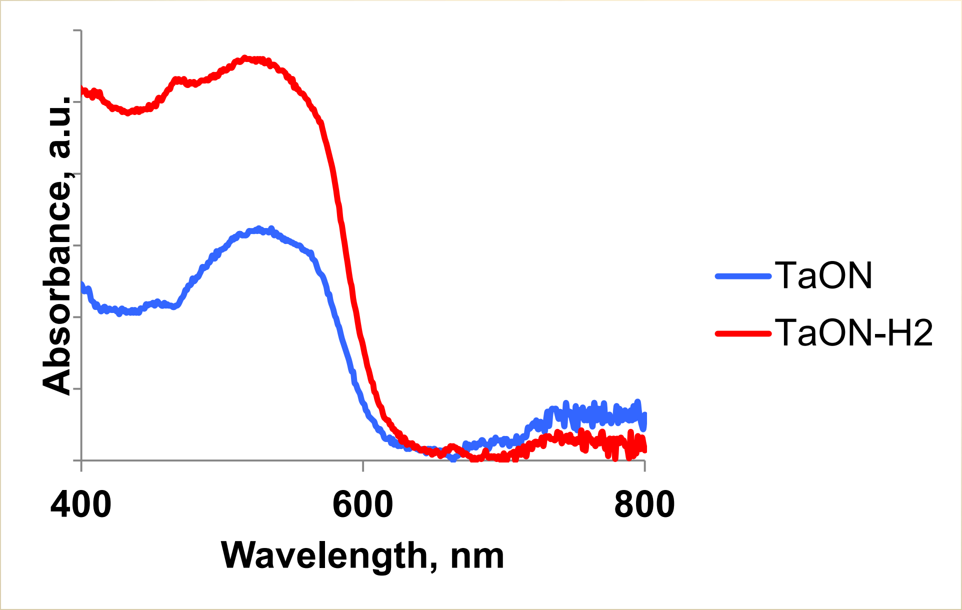
- Electrochemical methods
- Spectroscopic and Electron Microscopic analysis

Improved Visible Light Absorbance of TaON Nanotubes



Ta_2O_5: annealed in air at 500 ^oC 2h

Ta_2O_5-H: annealed in N_2/H_2 (95/5 mol) 500 ^oC 2h

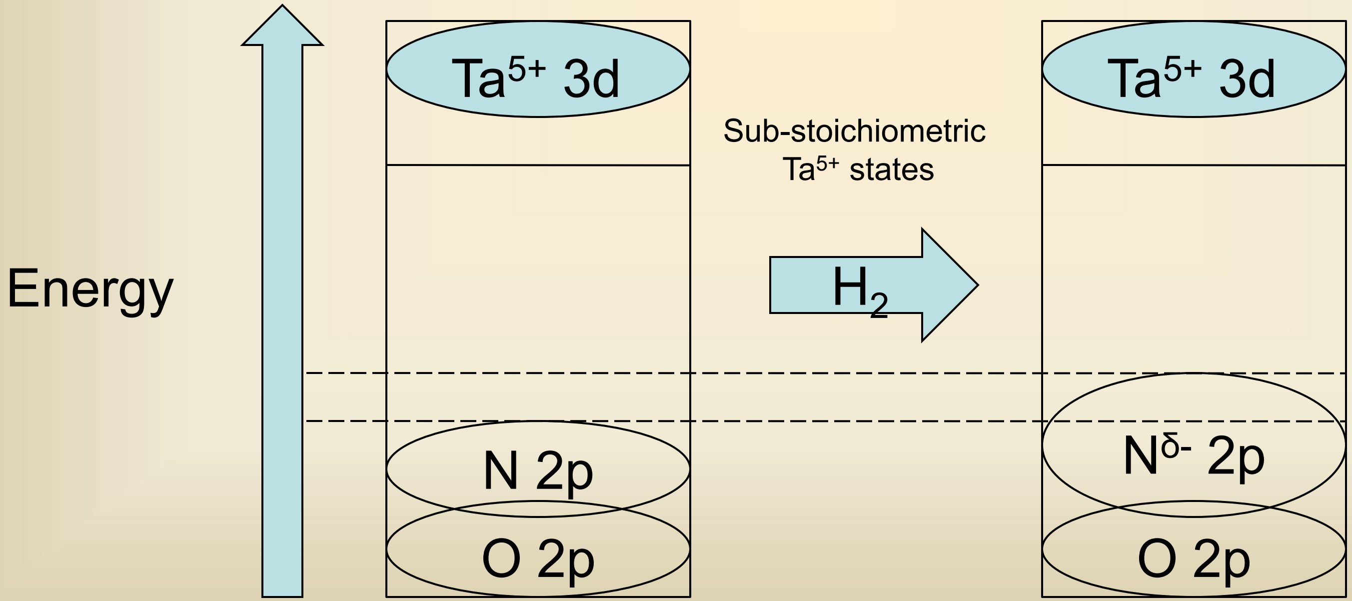


TaON: annealed in NH_3 at 700 ^oC 2h

TaON-H: Ta_2O_5-H annealed in NH_3 at 700 ^oC 2h

Improved Visible Light Absorbance of TaON Nanotubes

- Reduction in band gap of TaON-H due to N 2p states in valance band
- Improvement in visible light absorption due to synergistic interaction between sub-stoichiometric Ta and $N^{\delta-}$ 2p [2]

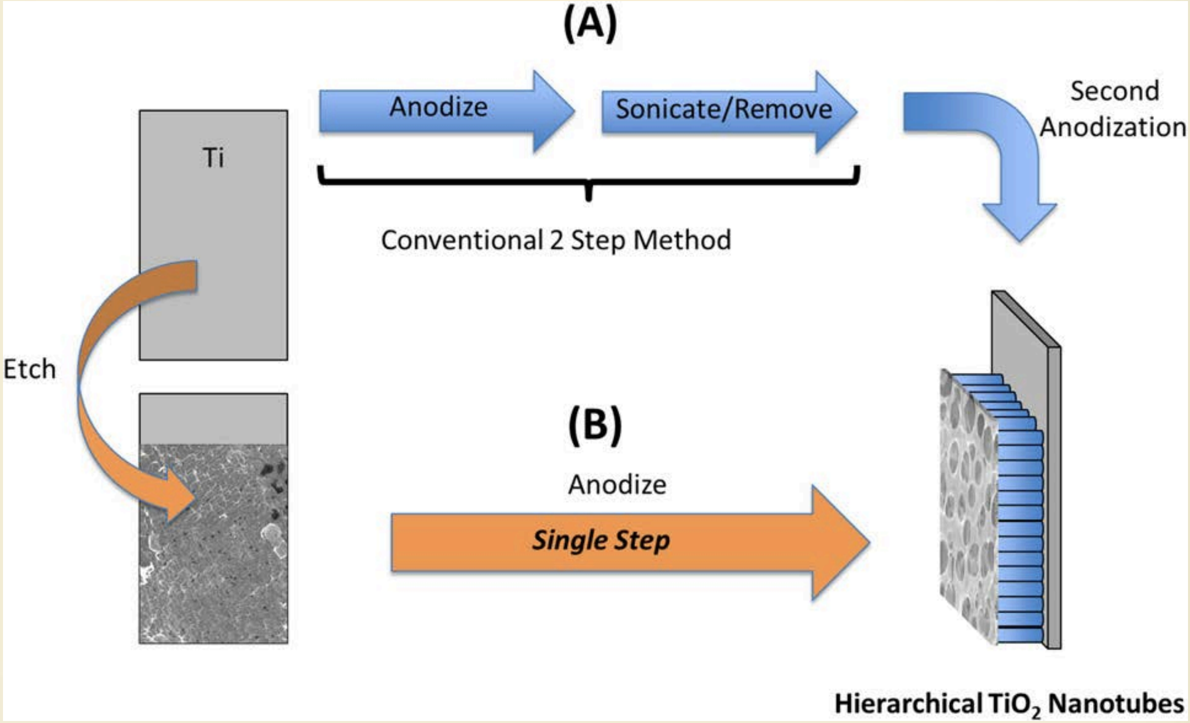


[2] *J Am Chem Soc*, 2012, *134*, 3659

New Approach to Synthesize Hierarchical TiO_2 Nanotubes (NTs)

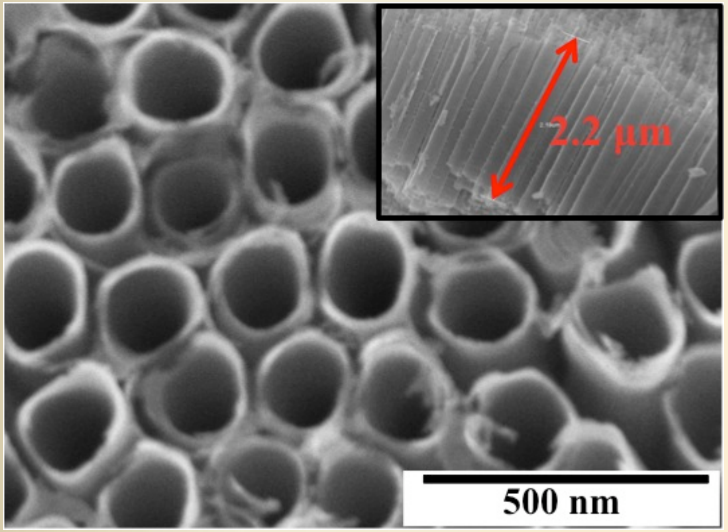
Hierarchical TiO_2 NTs demonstrate higher photoelectrochemical performance over plain TiO_2. Current synthesis of these nanostructures requires a two-step anodization process (A)

Etch solution:
HF (35 %)
HNO_3 (68-70%)
DI H_2O
1:3:50 ml, respectively

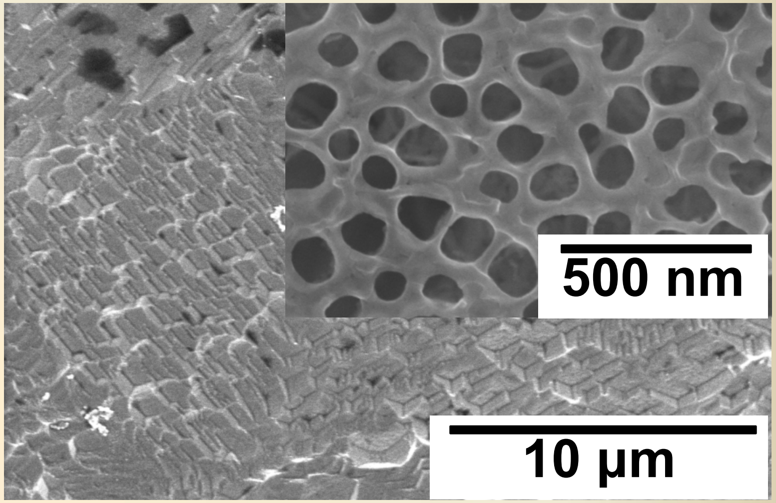


The same top-layered type nanostructure can be obtain by a single anodization process (B) utilizing a surface etching treatment prior to anodization

New Approach to Synthesize Hierarchical TiO_2 Nanotubes (NTs)

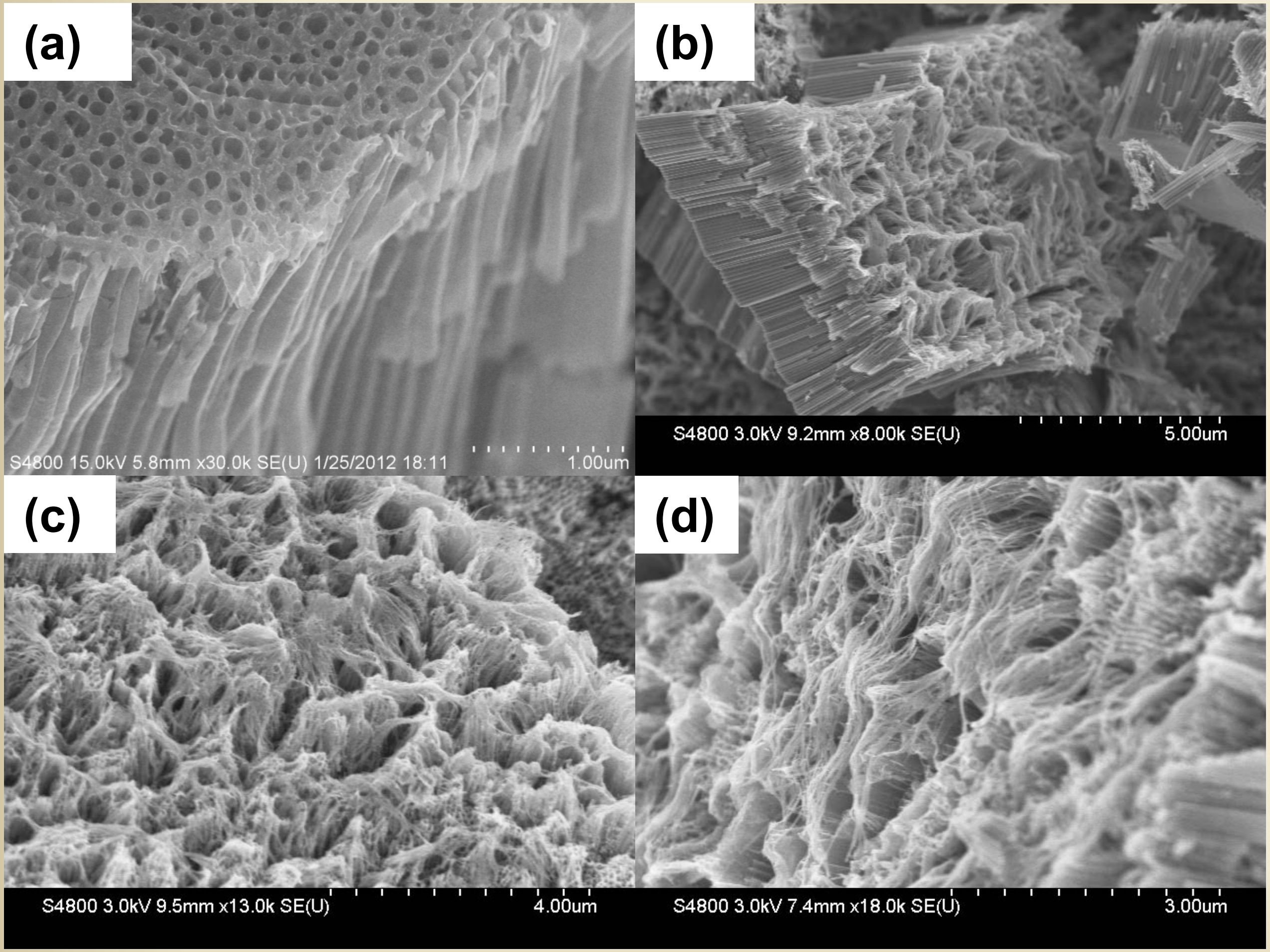


SEM TiO_2 NTs formed at 40 V for 1 h in an ethylene glycol solution (10 wt% H_2O + 0.5 wt% NH_4F without any surface treatment prior to anodization



SEM of Ti surface after etching treatment. The inset shows the surface morphology after anodization at 40 V for 1h. The etching treatment results in the formation of a thin nano-porous layer on top of the TiO_2 nanotubes

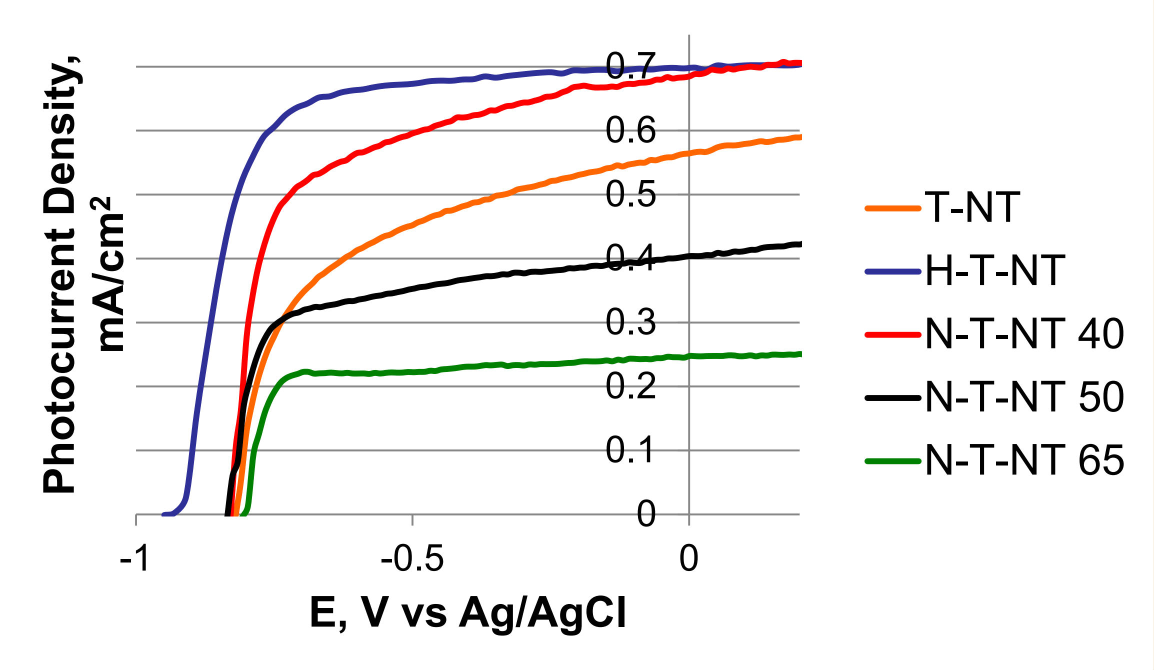
New Approach to Synthesize Hierarchical TiO_2 Nanotubes (NTs)



(a) Hierarchical TiO_2 NT (b-d) TiO_2 NTs with a nanograss top layer. This type of architecture is obtained by increasing the anodization bath temperature. Temperatures of (b)40 ^{o}C, (c) 50 ^{o}C, and (d) 65 ^{o}C were examined.

Hierarchical, Nangrass and Plain TiO_2 Nanotubes Photoelectrochemical Performance

AM 1.5 irradiation (100 mW cm^{-2}) in 1 M KOH with a Pt mesh cathode.



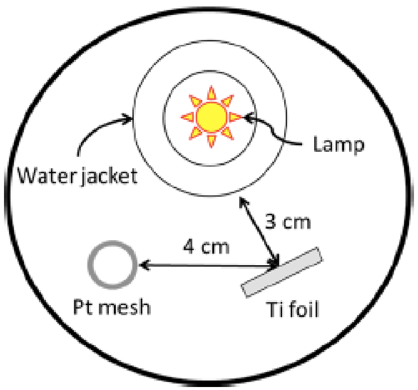
The increased performance of H-T-NT and N-T-NT 40 can be attributed to an increase in surface area for light harvesting and electrolyte interaction sites. The addition of a thin top layer can increase the workfunction over plain TiO_2 NT [3]. Too thick of a layer (eg N-T-NT 50) results in increases electron-hole recombination

[3] J Phys Chem C 113 (2009) 12759

Light-Assisted Anodized TiO_2 Nanotubes (NTs) for Enhanced Photoelectrochemical Peformance

- Photoelectrochemical etching (PEC-E) has shown to enhance the photoelectrochemical performance of rutile titania [4]
- Can potentially affect nanotube formation morphology

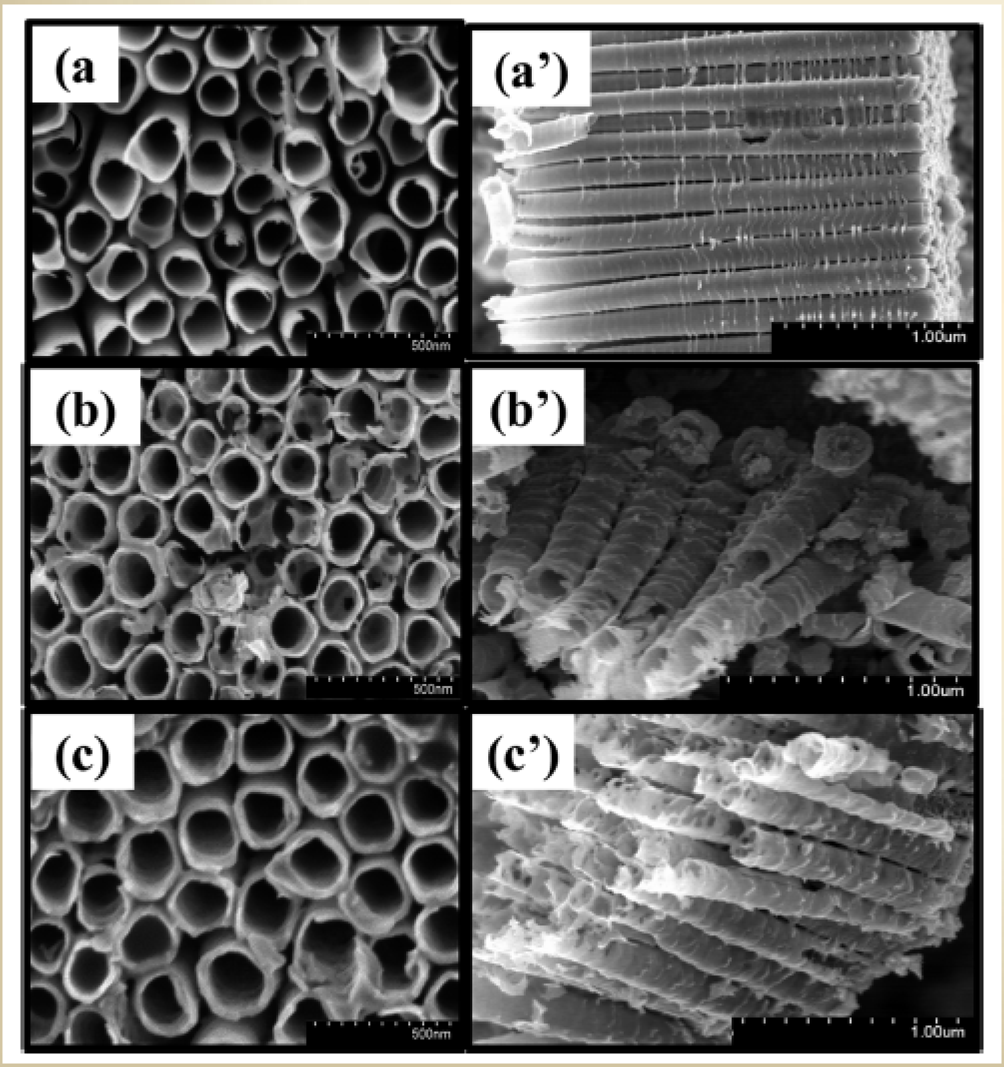
Scheme 1. Depiction of the Top View of the Experimental Setup Used for Anodization in the Presences of UV–Vis Irradiation[a]



[4] J. Electroanal. Chem. 1995, 396, 35

Light-Assisted Anodized TiO_2 Nanotubes (NTs) for Enhanced Photoelectrochemical Peformance

Top View   Side View



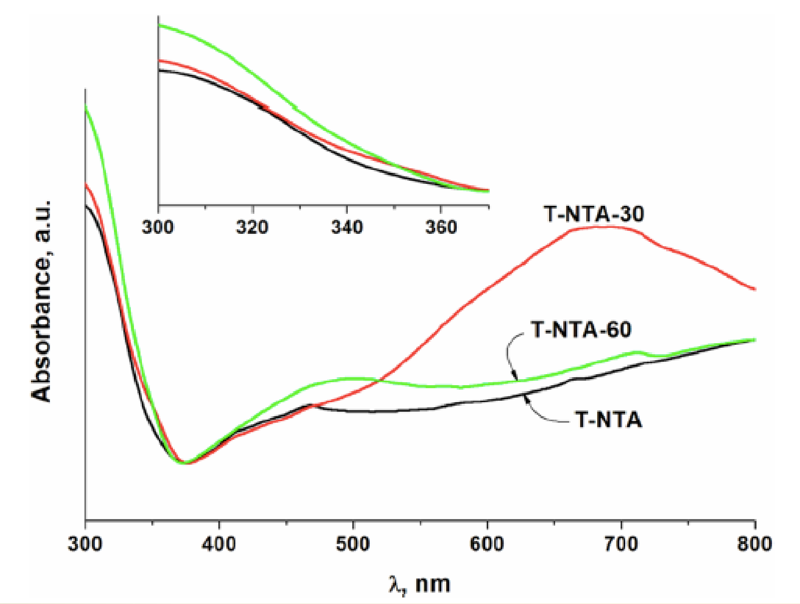
Plain TiO_2 NTs (T-NTA)
60 V, 1h
Ethylene glycol electrolyte
(10 wt% H_2O + 0.5 wt% NH_4F)
annealed in N_2/H_2 (95/5 mol) at
500 ^oC for 2h.

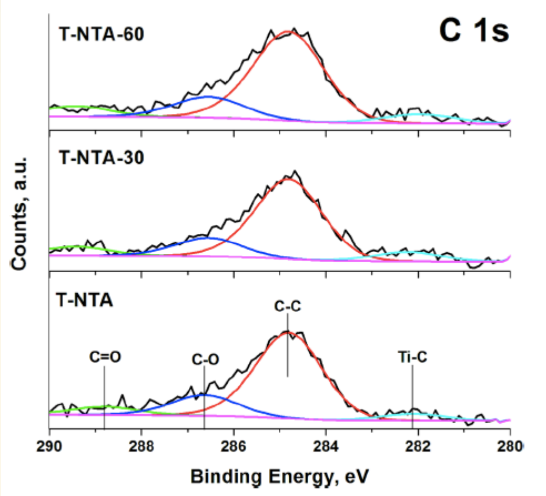
T-NTA-30
Anodized 30 min. without light
Anodized 30 min. with light

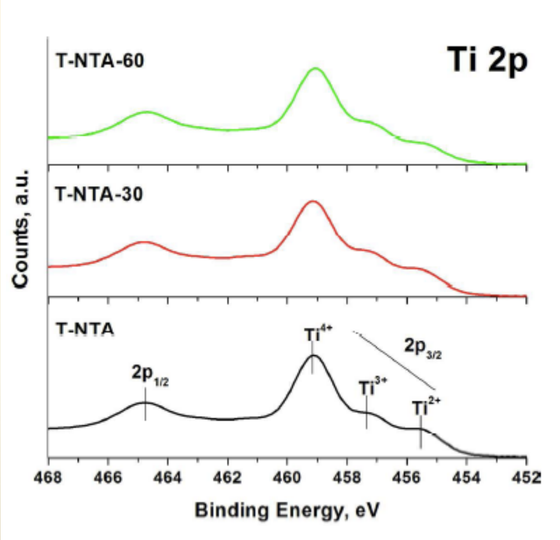
T-NTA-60
Anodized 60 min. with light

ACS Appl Mater Interfaces (2012), *4*, 5883

Light-Assisted Anodized TiO_2 Nanotubes (NTs) for Enhanced Photoelectrochemical Peformance

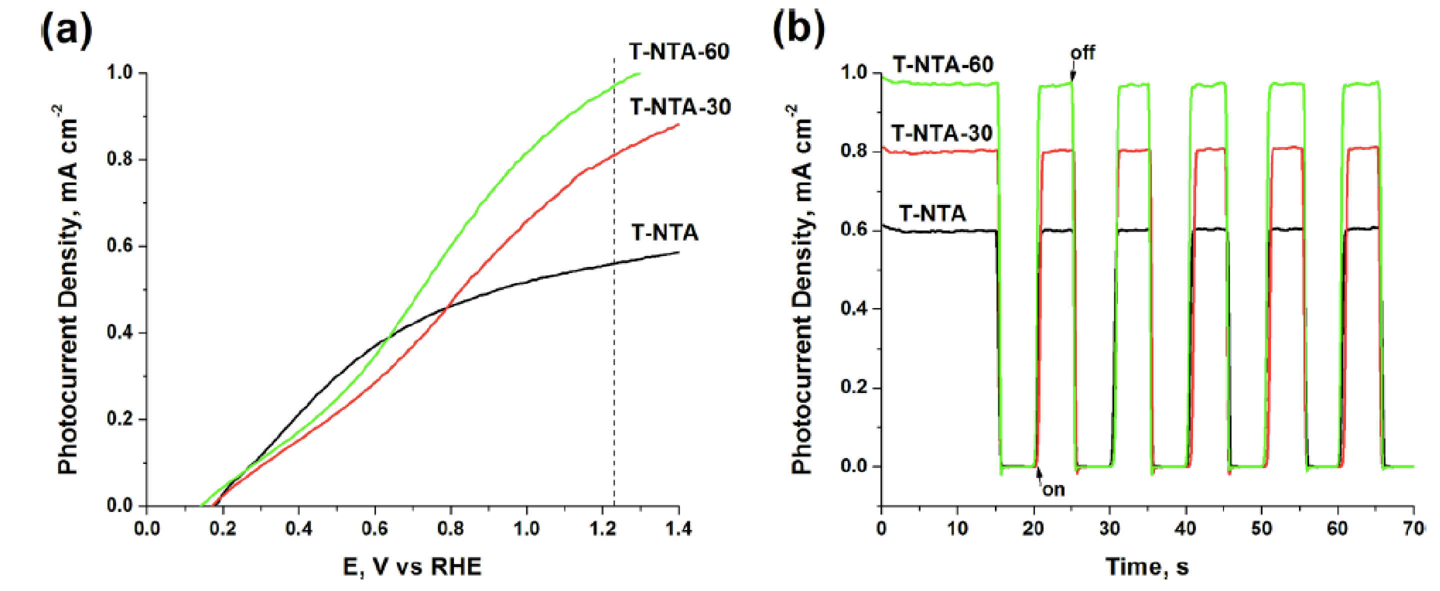






- Increase in carbon doping and sub-stoichiometric Ti^{4+} when anodized with light
- Increased visible light absorbance

Light-Assisted Anodized TiO_2 Nanotubes (NTs) for Enhanced Photoelectrochemical Peformance

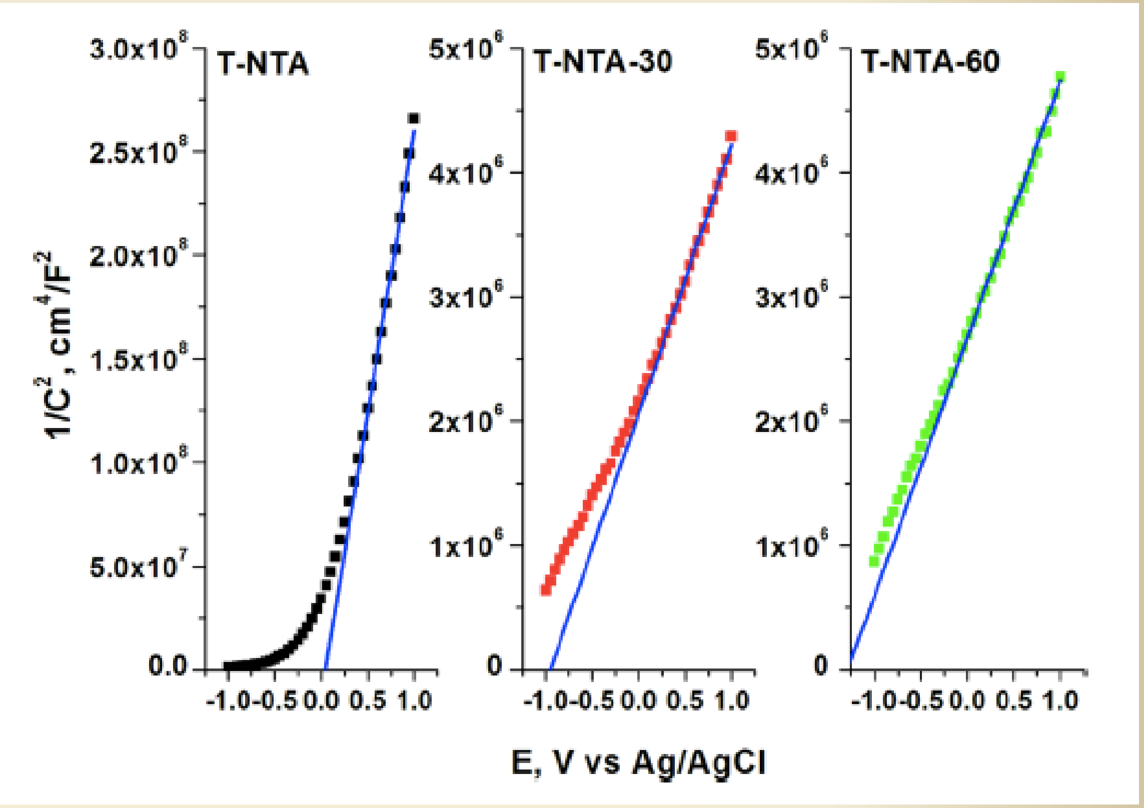


Photoelectrochemical testing: 1.5 AM irradiation (100 mW cm^{-2}) in 1 M KOH with a Pt coil cathode and Ag/AgCl (3 M) reference electrode. (A) Potentiodynamic plot and (B) Potentiostatic plot with intermittent irradiation at 1.5 V RHE (0.5 V vs Ag/AgCl)

Light-Assisted Anodized TiO_2 Nanotubes (NTs) for Enhanced Photoelectrochemical Peformance

Increase in flat-band potential as well as an increase in charge carrier density from 10^{16} to 10^{18} cm^{-3} account for enhanced photoelectrochemical performance

Greater band bending from thicker NT geometry allows for increased charge separation



Mott-Schottky Analysis: AM 1.5 irradiation at a frequency of 1 kHz with an AC imposed bias of 10 mV in 1 M KOH.

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 through combinatorial approach
- **Technical accomplishments and process:** Developed a method to extend the visible light absorbance of TaON nanotubes. Developed new synthesis techniques for higher order 1D titania nanotube architectures which demonstrate enhanced photoelectrochemical water splitting.
- **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.