Photoelectrochemical Generation of Hydrogen from Water Using Visible Light Sensitive Ferro-Electric $BiFeO_3$ and Semiconductor Nanotubes

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DOE Hydrogen Program Review 2010

Overview

Timeline

- Project start date: October, 2006
- Project end date: September, 2010
- Percent complete: 90

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

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 nanotubular architectures
- Develop low band gap TiO_2 nanotubes
- Understand kinetics and formation mechanism of the titanium dioxide nanotubes under different synthesis conditions

2007-2008

- Develop organic-inorganic hybrid photo-anodes
- 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 photo-anodes
- 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 QD-nanotubular oxide hybrid photo-anodes based on DFT modeling

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

Low cost sol-gel based synthesis of $BiFeO_3$ ferro-electric photo catalysts

Characterization and fundamental understanding of the materials prepared

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

Evaluate photo-electrochemical behavior of nanotubular oxide photoanodes

Evaluate photo catalytic and photo electrochemical behaviors of $BiFeO_3$

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

Electrochemical methods

Spectroscopic and Electron Microscopic analyses

Task D. Scale-up and process evaluation.

Scale-up of photoanodes

Photoelectrochemical hydrogen generation under real solar irradiation

Task E. First Principle Modeling of Semiconductors for harvesting visible light

Synthesis of high-quality, low band gap, $BiFeO_3$ nanoparticles as photo catalytic materials

Major Challenge of Conventional Photo Catalysts: Low Photo Conversion Efficiency

- An internal electric field is required for effective separation of electrons and holes.
- In semiconductor photo catalytic materials, the internal electric field exists only at the interfaces.
- Charge is transported mainly by a slow diffusion process in the bulk of the material that results in low photo conversion efficiency

UNR Approach: Ferro-electric Photo catalysts

An internal electric field exists across the bulk of the ferro-electric material because of a low-symmetry state;

This high internal electric field helps effectively separate photo induced charge carriers in the ferroelectric materials;

Generation of photo potential in the ferroelectric material is not limited by its band gap or magnitude of band bending at the interfaces;

High ferroelectric polarization of the material results in high photo induced potentials.

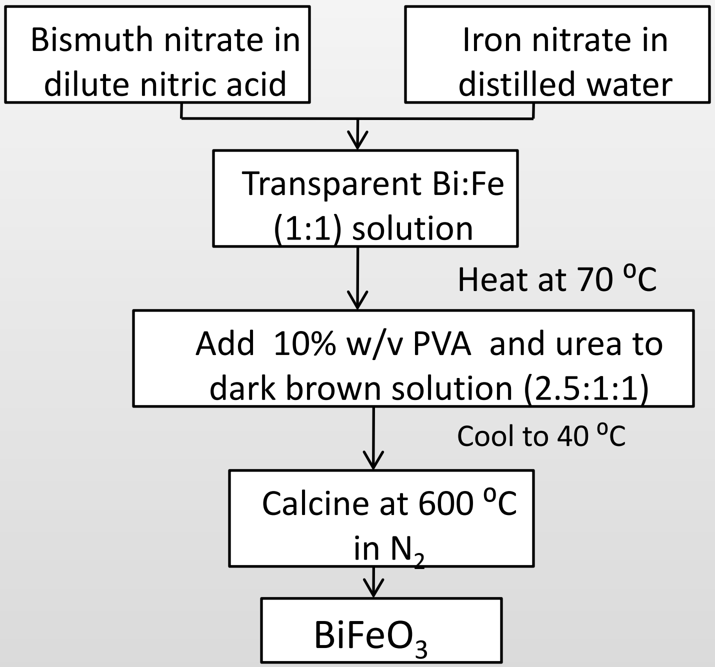
Barriers

Very low photo current densities due to large bandgap (>3.5 eV) and poor dc conduction

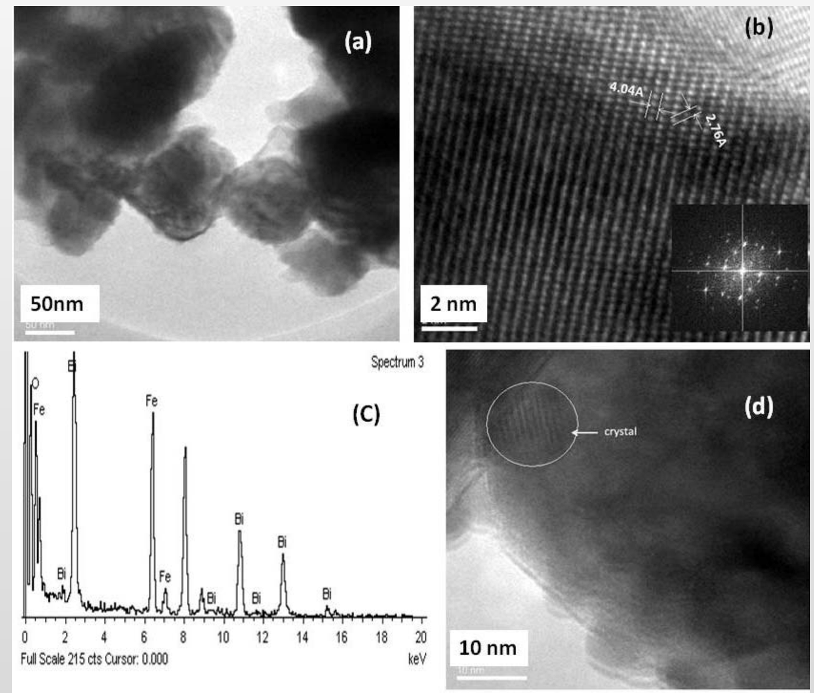
Solution

Development of band gap engineered nanoscale ferro-electric materials

Synthesis of $BiFeO_3$ Ferro-electric Photo Catalyst

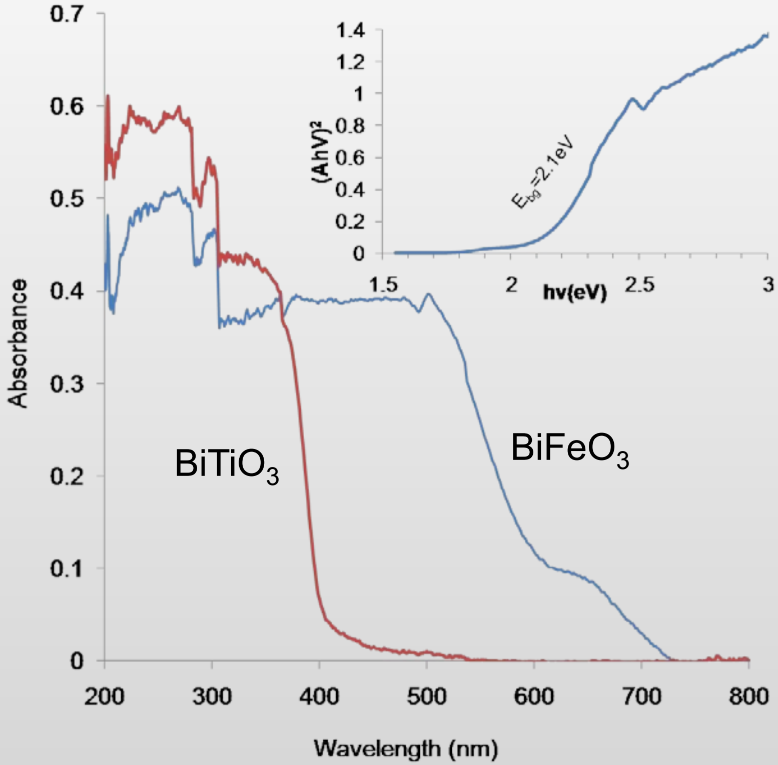


Flow diagram of sol-gel synthesis of $BiFeO_3$ nano-particles

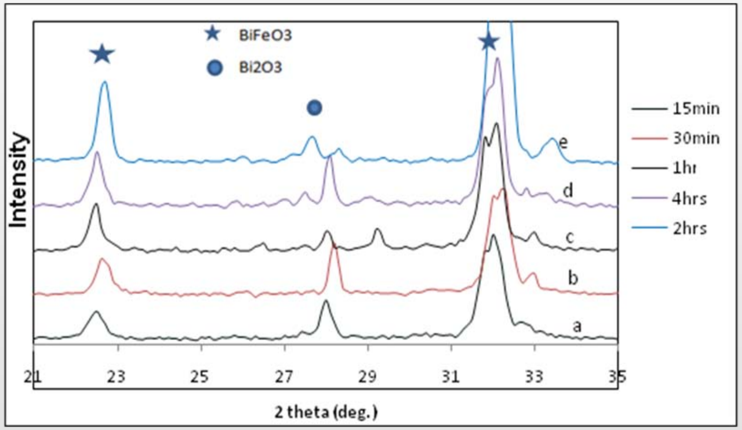


TEM images of $BiFeO_3$ calcined at 600 ^{o}C for 2 h under N_2 atmosphere

Characterization of $BiFeO_3$ Ferro-electric Photo Catalyst



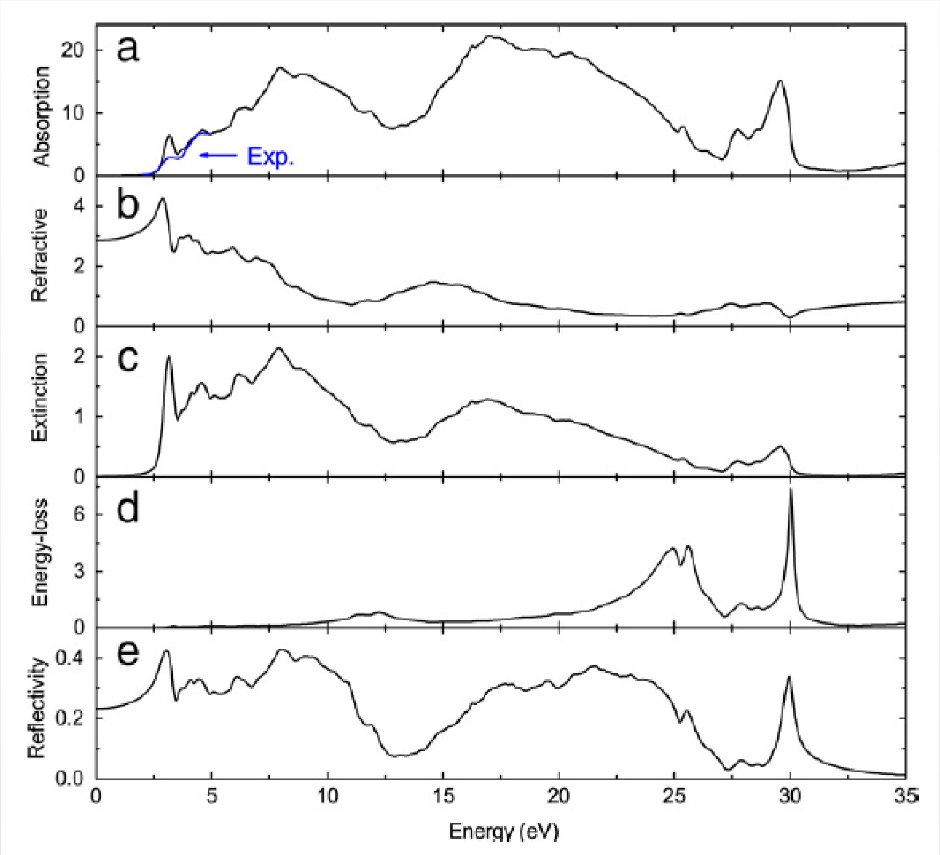
UV-Vis absorption spectrums of $BiFeO_3$ and $BaTiO_3$; The inset shows the $BiFeO_3$ plot of $(\alpha h\nu)^2$ as a function of photon energy



XRD patterns of $BiFeO_3$ annealed under N_2 at 600 ^oC for (a) 15 min, (b) 30 min, (c) 1 h, (d) 4 h and (e) 2 h

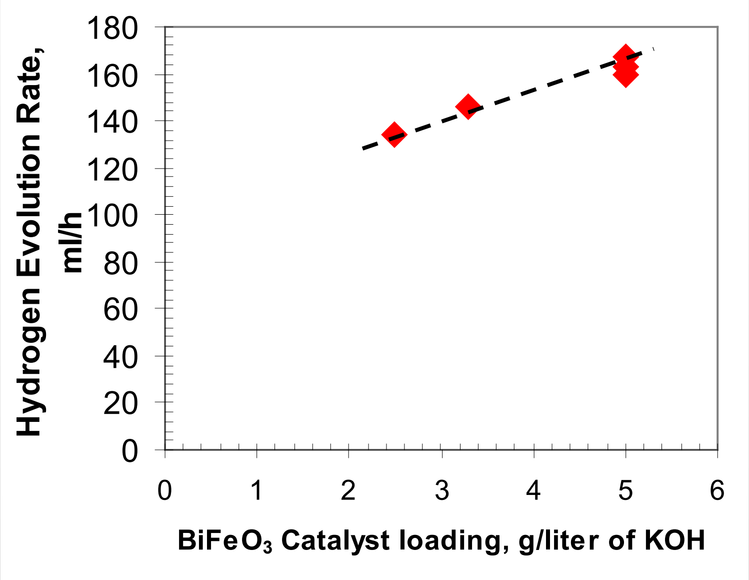
Band gap 2.1 eV

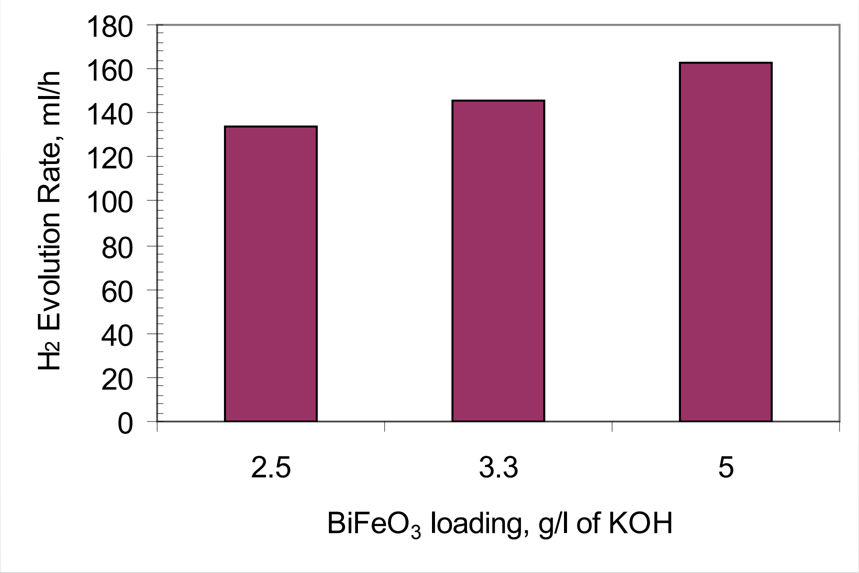
Modeling of $BiFeO_3$ Ferro-electric Photo Catalyst



SP-GGA+U is used for calculation of the band structure and optical properties of $BiFeO_3$, considering the unoccupied Fe 3d orbital state. The calculated band gap is 1.61 eV.

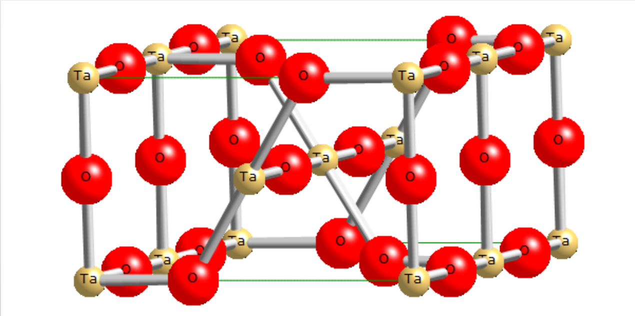
Hydrogen Generation using $BiFeO_3$ Ferro-electric Photo Catalyst in 1 M KOH under AM 1.5 Light Illumination



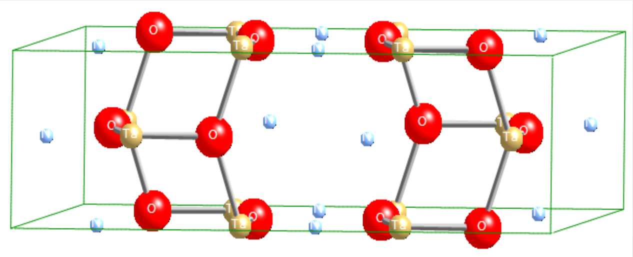


Theoretical investigation of the formation of TaON from Ta_2O_5 NTs by density functional theory

- The first principle computational calculations of Ta_2O_5 and TaON were carried out based on density functional theory (DFT) using plane wave assumption
- CASTEP program in Materials Studio® supplied by Accelrys® is the computational platform



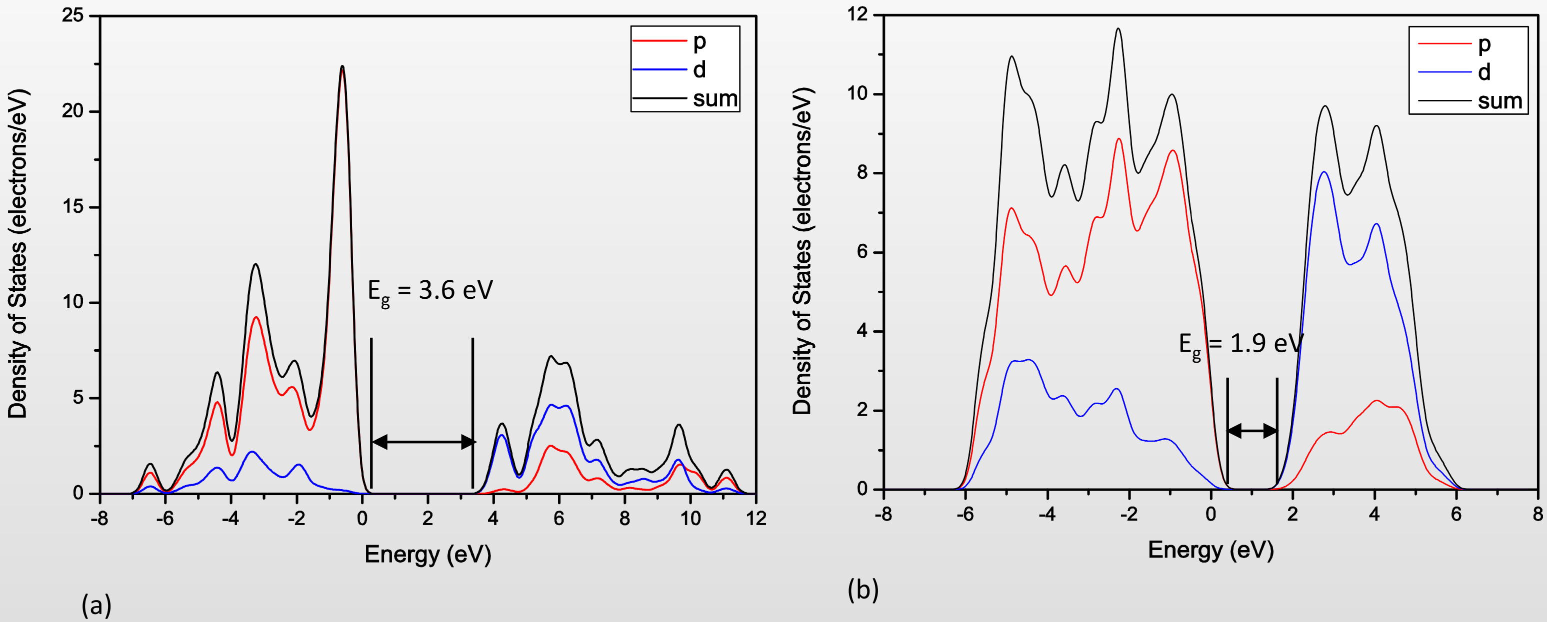
(a)



(b)

Crystal structures of (a) Ta_2O_5 and (b) γ-TaON

Theoretical investigation of the formation of TaON from Ta_2O_5 NTs by density functional theory

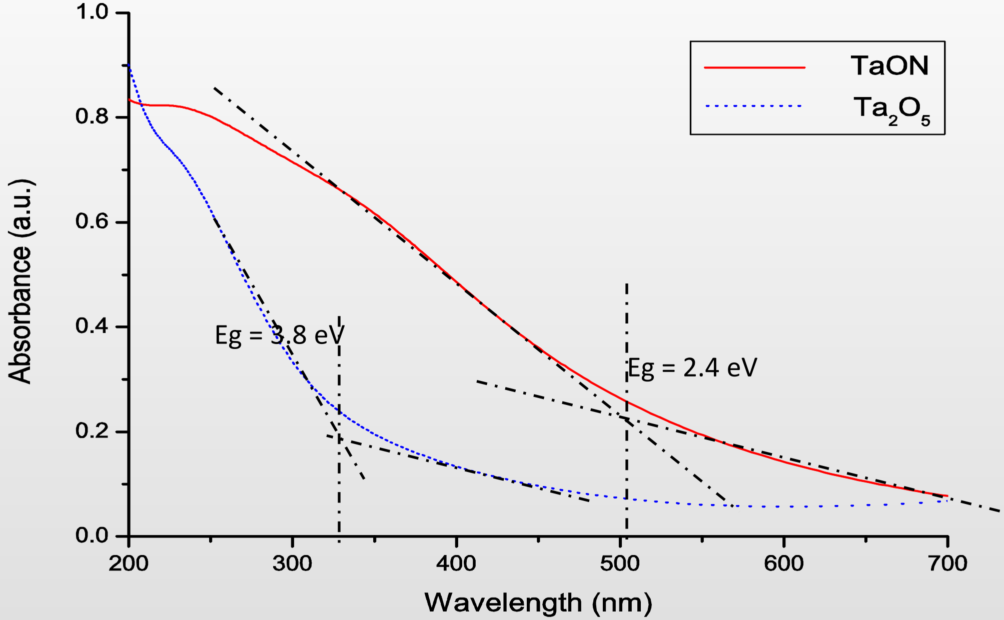


Partial density of states as a function of energy level of (a) Ta_2O_5 and (b) γ-TaON. The calculated band gaps are smaller than the experimentally determined values.

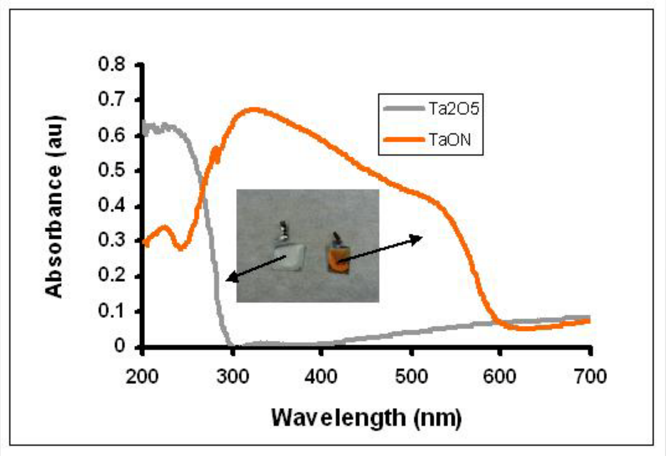
In our current simulation, the calculated band gap of Ta_2O_5 is 3.6eV, while the experimental value is 4 eV.

The calculated band gap of γ-TaON is about 1.9 eV.

Optical absorbance spectra of Ta_2O_5 and γ-TaON



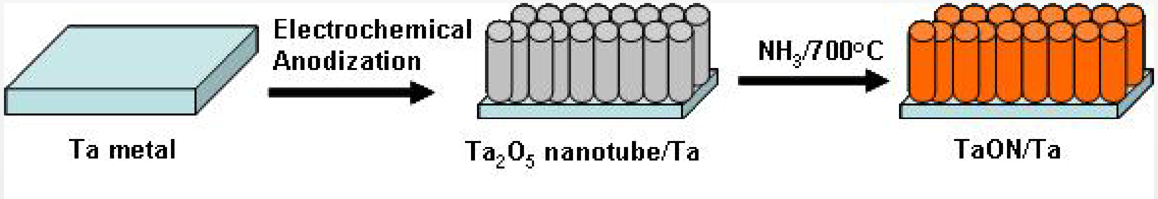
Calculated UV-Vis optical absorbance spectra of Ta_2O_5 and TaON and extrapolated band-gap values.



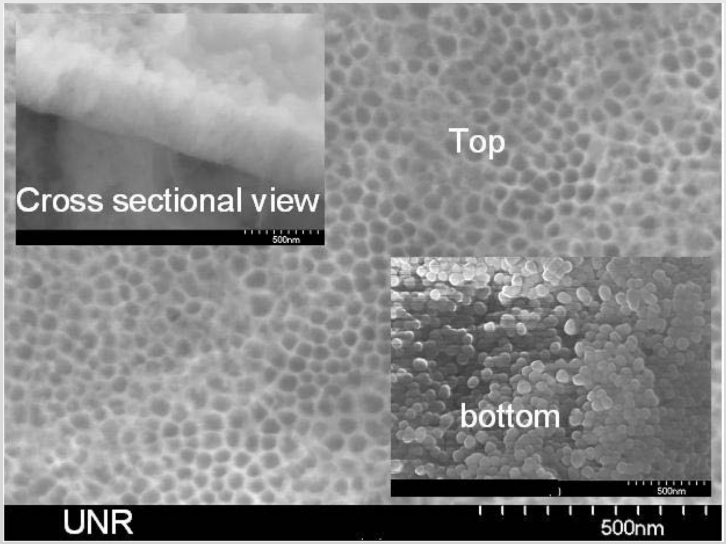
Experimental UV-Vis optical absorbance spectra of Ta_2O_5 and TaON.

The calculated optical absorbance spectra follow a similar trend of the experimentally determined optical absorbance of anodic Ta_2O_5 and transformed TaON nanotubes.

Synthesis of Tantalum Oxynitride (TaON) Nanotubes



Ta_2O_5 NTs



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)↑ (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 —(700 ^oC, NH_3)→ TaON NTs

One step:
- **Conversion to TaON**
- **Annealing**

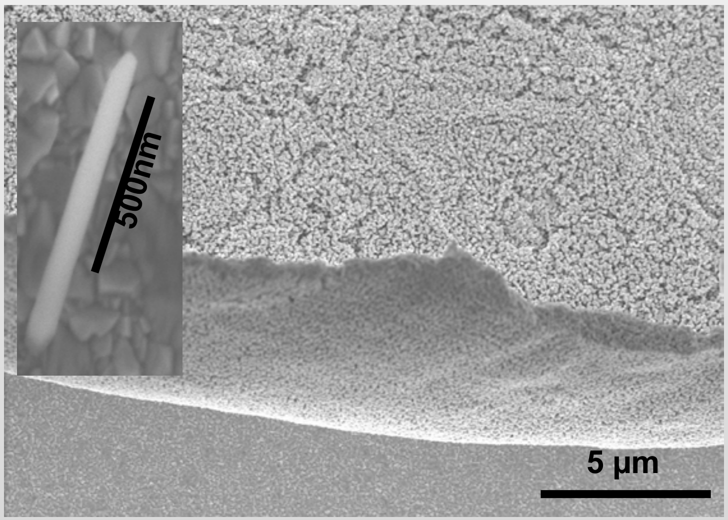


Fig. SEM image of TaON nanotube arrays on Ta foil. The morphology is same as Ta_2O_5 NTs

NT arrays are stable after nitridation

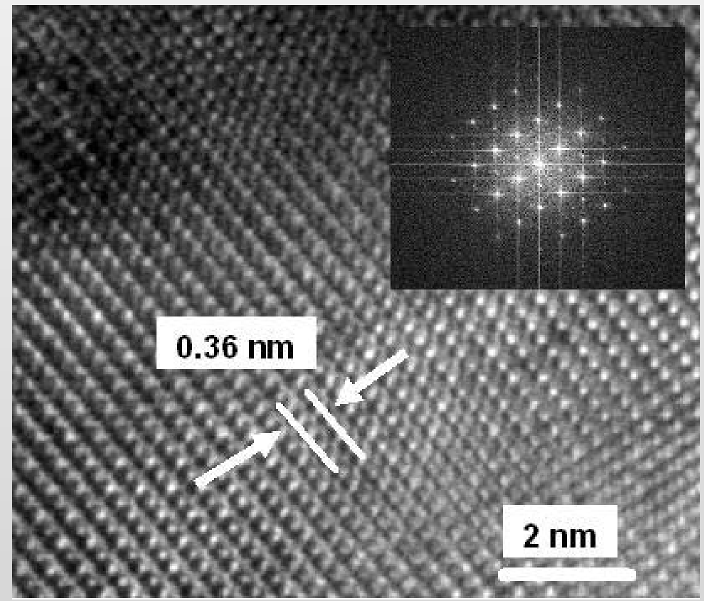


Fig. TEM image of TaON nanotube arrays

NTs are highly crystalline

Synthesis of Tantalum Oxynitride (TaON) Nanotubes

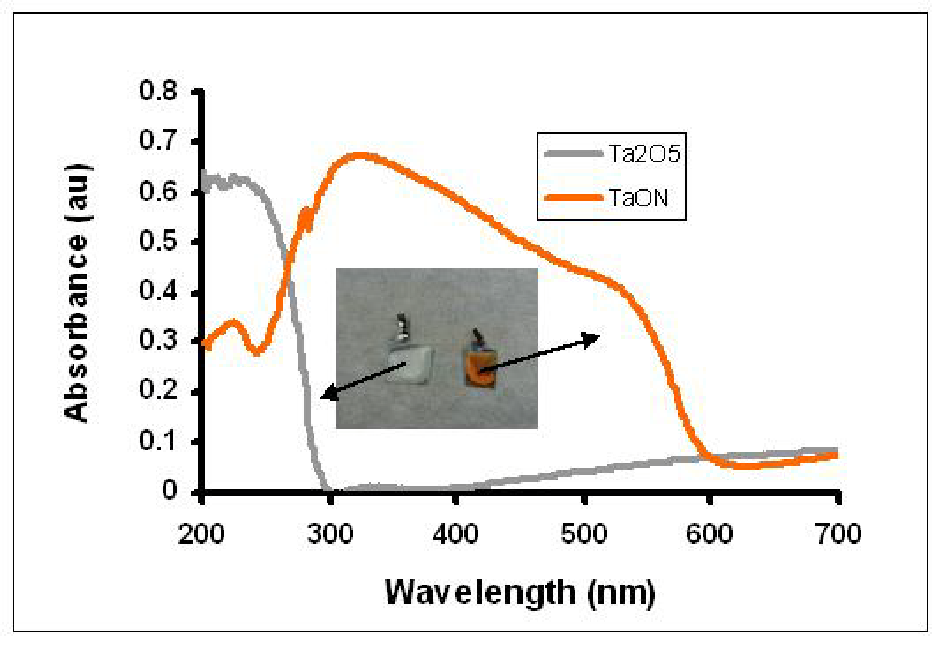


Fig. DRUV-Vis spectra of Ta_2O_5 and TaON NTs

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

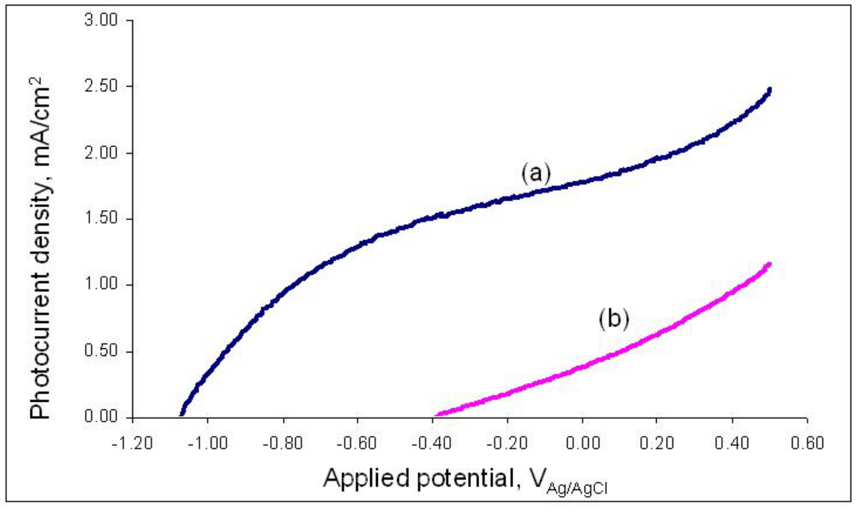


Fig. Potentiodynamic plot of TaON NTs under global AM 1.5 solar light (a) and visible light (≥ 420 nm) illumination. Nanotubes of 50 nm internal diameter and 525 nm long are used. Sample are: 1 cm^2

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**

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 and ferro-electric photo catalysts for improved photo conversion process
- **Technical accomplishments and process:** Developed ultra-thin TaON nanotube arrays with band gap around 2 eV with 40-50% visible light activity and a low-cost process for synthesis of nanostructured $BiFeO_3$ ferro-electric photo catalyst.
- **Technology transfer/collaboration:** Active partnership with NREL and University of Arkansas at Little Rock.
- **Proposed future research:** (a) Synthesize QD-sensitized photoanodes that can harvest full spectrum of sunlight based on first-principle calculations, (b) theoretical and experimental investigations on the ferro-electric photo catalytic materials, (c) scale-up the PEC system, and (d) on-field testing under real solar irradiation.

Future Work

- ❖Synthesis of visible light sensitive QD sensitized photoanodes based on the DFT calculations
- ❖Optimize synthesis process of TaON NTs and ferro-electric photocatalysts
- ❖Increase charge transport properties of $BiFeO_3$
- ❖Kinetics studies of nanotubes formation by titration using spectrophotometric analysis
- ❖Incident photon to current conversion efficiency (IPCE) measurements
- ❖Scale-up the system
- ❖Design PEC system for on-field testing under real solar irradiation.
- ❖Fundamental understanding of TaON formation from Ta_2O_5 structure, and structural, electronic, and optical properties of various TaON polymorphs
- ❖To understand the ordering of oxygen vacancies and their role on charge transport properties and recombination losses in oxide and oxynitride semiconductors