UNIVERSITY OF ARKANSAS AT LITTLE ROCK

Photelectrochemical Hydrogen Production (Project ID: PD057)

M. K. Mazumder (PI), R. Sharma , A.S. Biris,
H. Ishihara,and M. Misra
University of Arkansas at Little Rock
University of Nevada, Reno
2010 DOE Hydrogen Program
Washington DC, June 7, 2010

Project ID PD057

Overview

Timeline

- July 2006
- August 2010
- Percent complete 80%

Barriers

- Barriers addressed
  - **(AP) Materials Efficiency**
  - **(AQ) Materials Durability**
  - **(AS) Device Configuration Designs**

Budget

- Total project funding $
  - **Hydrogen Production $297K**
  - **Contractor' share $127,181**
  - DOE Total share $ 890,998

  DOE share for Hydrogen Storage $594K; Contractor $254,362.
- Total funding received in FY08 $ 324,721(for generation and storage)

Partners

- Interactions/ collaborations

  1. University of Nevada, Reno
  2. Arkansas Nanotechnology Center, University of Arkansas at Little Rock
  3. NASA Kennedy Space Center
  4. Boston University

Objectives

Overall	**Optimize surface properties of photoanodes for efficient generation of Hydrogen**
2007-08	• **Study interfacial charge transfer process in PEC** • **Investigate the roles of surface states and nano-structures of Photoanodes (Use TiO_2 electrode as a model)** • **Develop partnership with other institutions** •**Develop outreach and educational programs**
2008-09	• **Remove surface contaminants & charge traps by He plasma treatments** • **Surface doping of TiO_2 electrode with N using plasma treatment; Create oxygen vacancies** • **Improve light absorption cross section and interfacial charge transfer rate with nanostructured anodes** • **Measure photocurrent density of nano-structured TiO_2 electrodes with simulated solar radiation**

Objectives

Overall	**Optimize nanostructures of TiO_2 Photoanodes for light absorption and corrosion resistance**
2009-2010	• **Optimize the structure of the nanotubes by varying anodization voltage** • **Use layered electrodes of $TiSi_2$ and TiO_2,** • **Optimize interfacial charge transfer,** • **Develop processes for synthesizing layered patterned nanotubular electrodes of $TiSi_2$ and TiO_2**

Rationale

- Optimize interfacial processes: photon absorption, charge separation, minimization of carrier traps.

- No single semiconductor electrode has been found to provide both high absorption and corrosion resistance

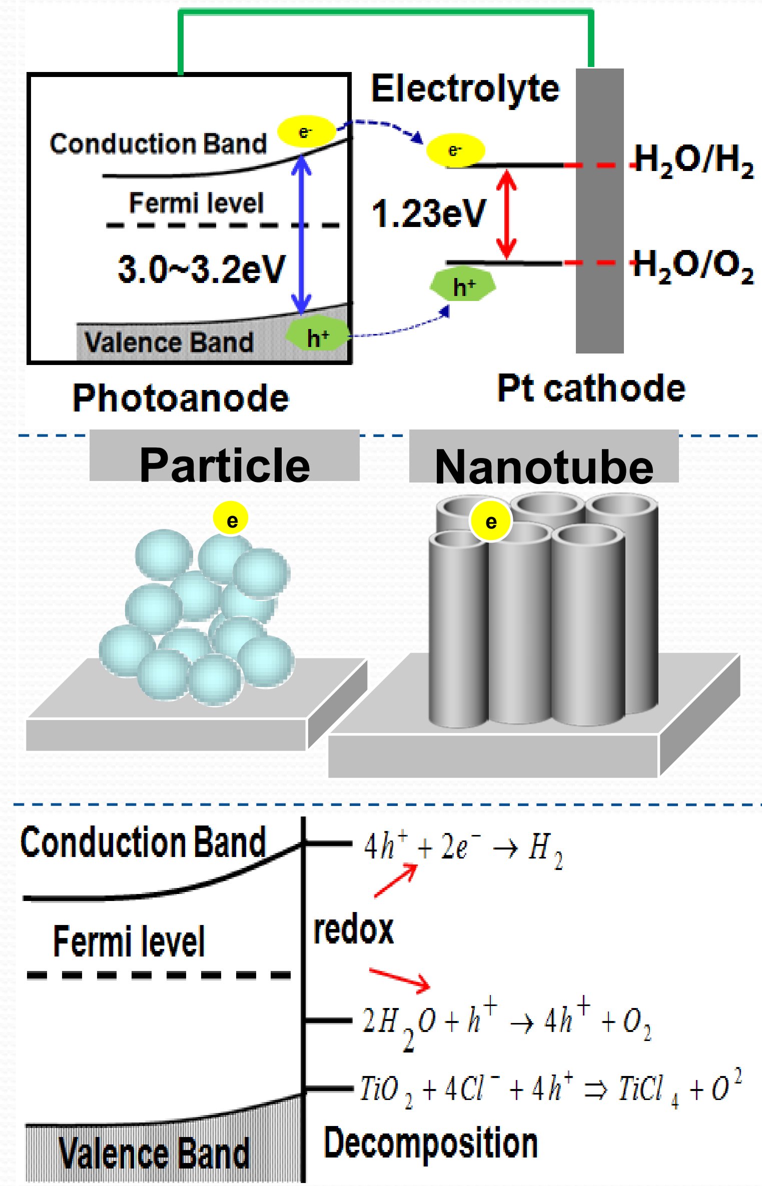
- $TiSi_2$ (bandgap ranging from 3.4 eV to 1.5 eV) can harvest the entire visible and UV spectrum of solar radiation. TiO_2 electrode layer can be used to minimize photocorrosion.

Approach

- Remove surface contaminants and surface states that act as charge carrier traps
- Apply Plasma surface modification for surface cleaning as well as for surface doping of n-type dopants (N)
- Test surface modified nanostructured $TiSi_2$ and TiO_2 anodes for photoelectrochemical generation of hydrogen

TiO_2 photoanode nanotube

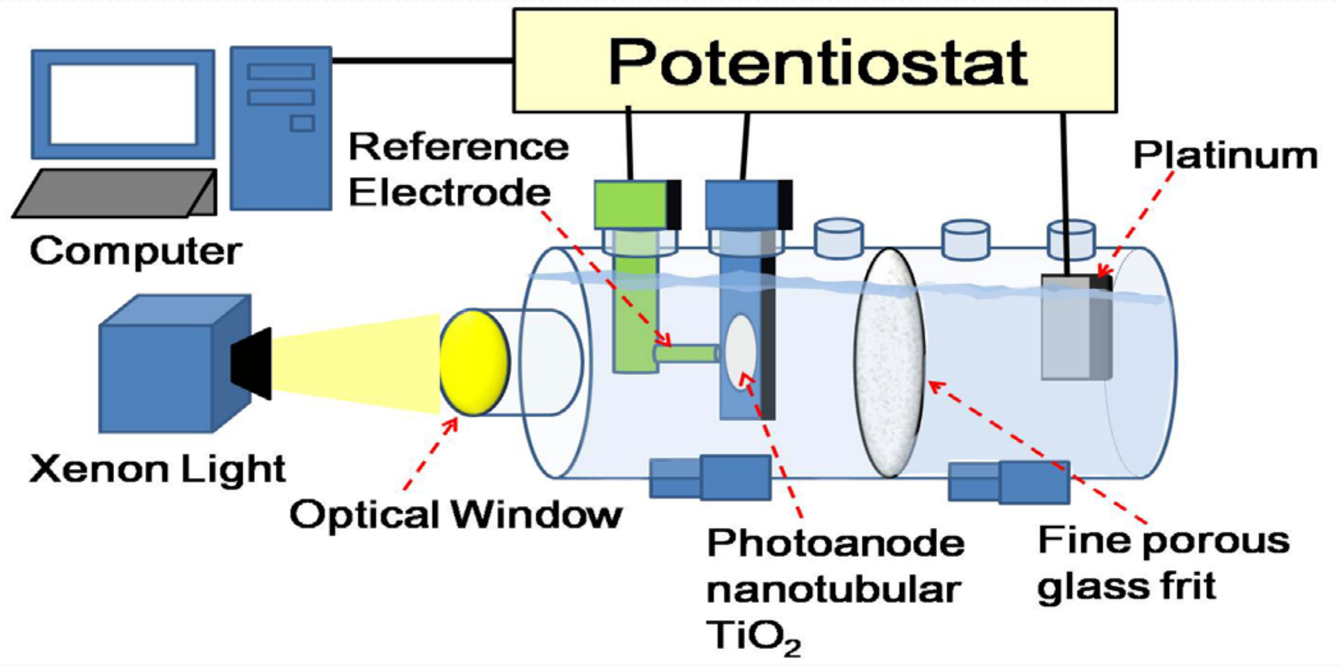
- Energy band gap required more than 1.23ev
  - TiO_2 energy band gap is 3.0~3.2eV (7% of the solar spectrum)
- TiO_2 nanotube array (electron mobility is higher compared to that of nanoparticle photoanodes)
- Durability (decomposition is slow)
- Non toxic



Experimental procedure

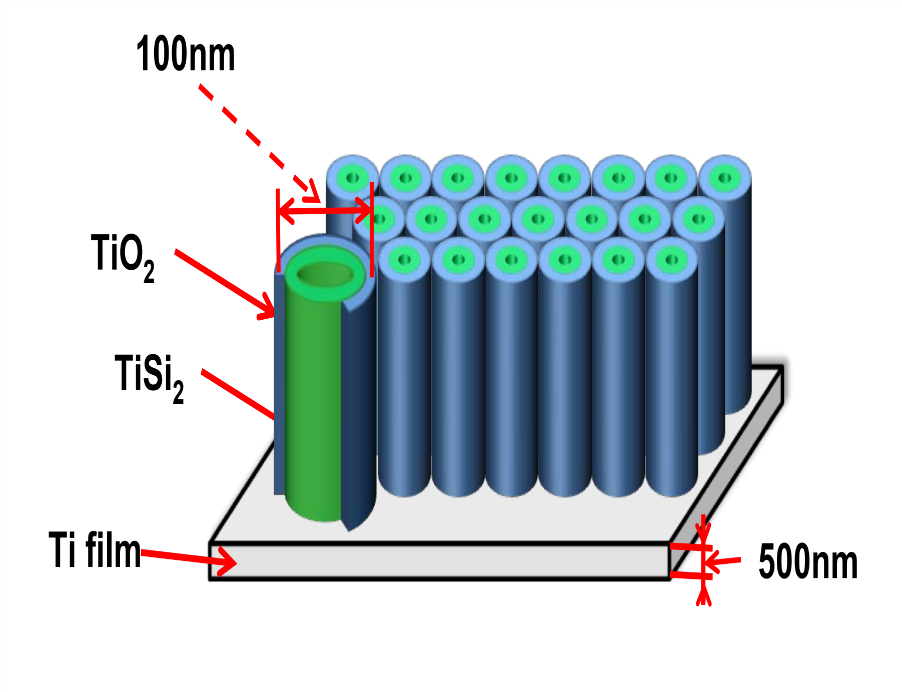
- Electrochemical synthesis of TiO_2 nanotube array by anodization of Ti film
- Plasma surface modification of TiO_2 nanorods using Nitrogen plasma
- Surface structure measurements
- Photocurrent density measurements

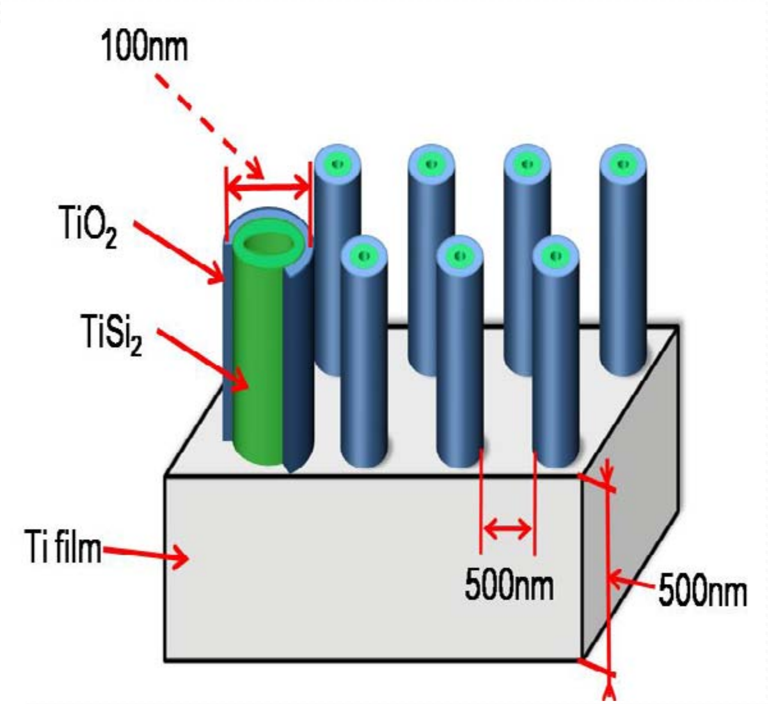
Photoelectrochemical test of photoanode



- Potentiostat/Galvanostat model 283.
- Xenon lamp (30 mW)
- 60 mm diameter quarts optical window
- A reference electrode (Ag/AgCl) was placed close to the anode
- Electrolyte; 1M KOH (pH~14) + DI water solution

Nanotubular Layered Photoelectrode

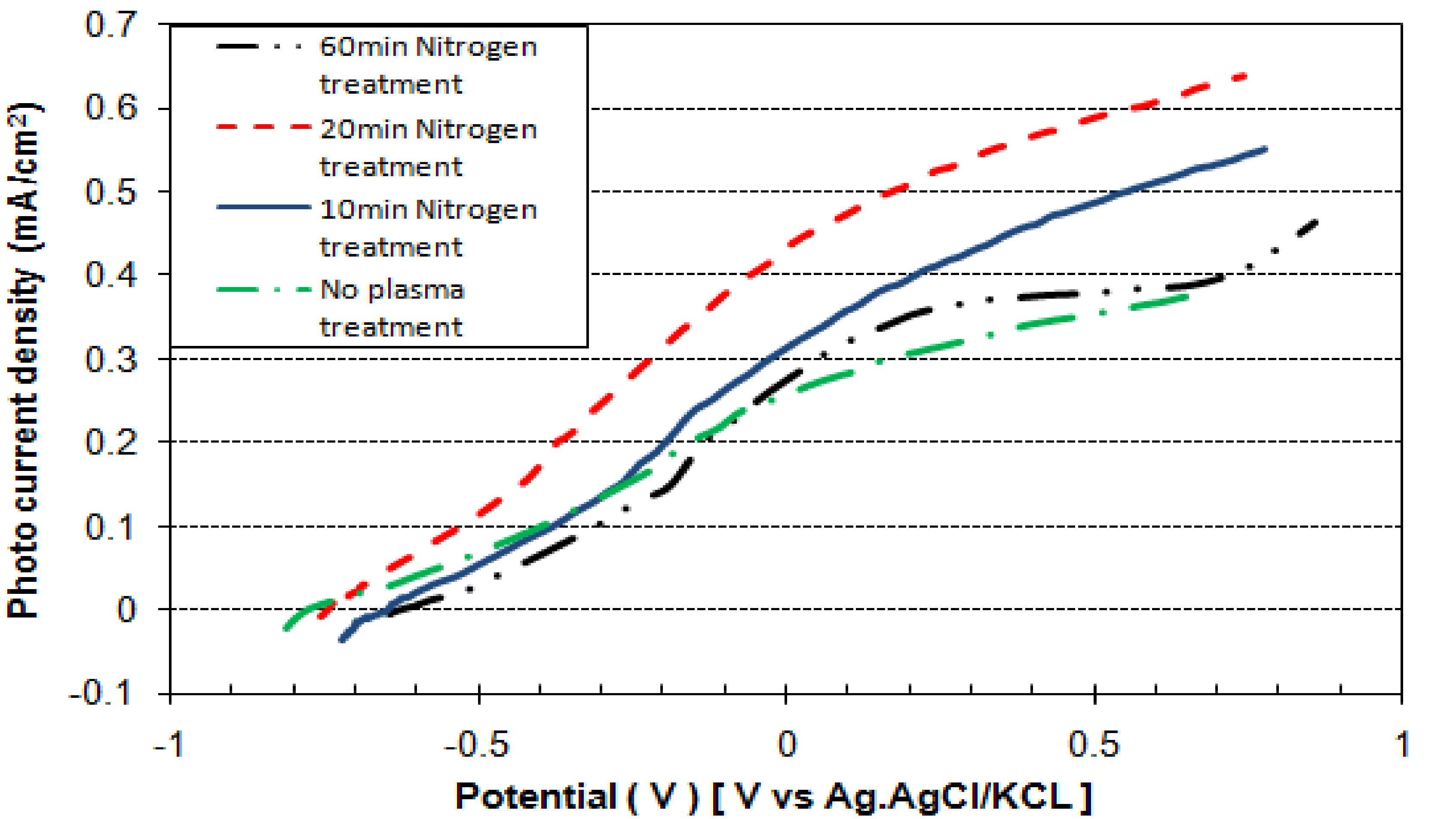




Close Spacing Open spacing

Patterned nanotubular structure for maximizing light absorption

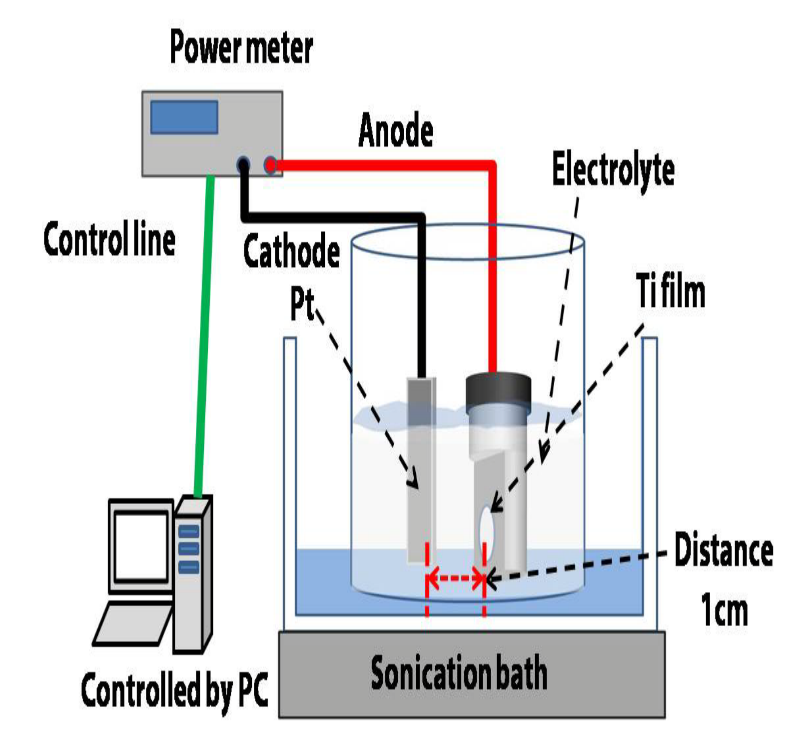
Result- Photocurrent vs. bias voltage



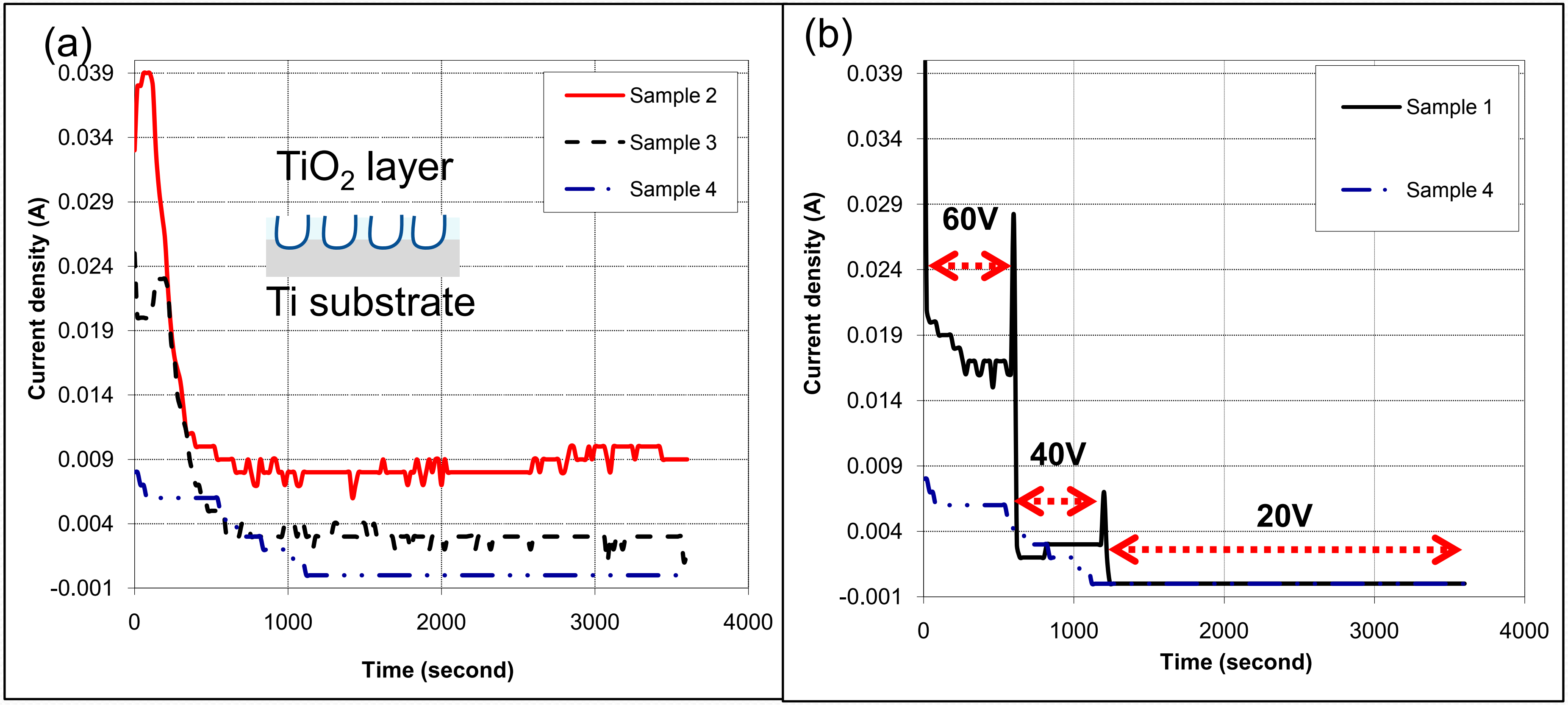
- Photocurrent density vs. bias voltage plotted for anodized samples after plasma treatment for different time periods in nitrogen atmosphere. Anodization was performed at 20V for 60 min and all samples were annealed

Equipment for anodization

- Anodization
  - The dimensions of the nanotubes can be easily varied (Length, wall thickness and internal diameter)
- Two-electrode electrochemical cell
- The electrolyte consisted of 0.5 wt % NH4F + ethylene glycol + 0.2 % by vol DI water
- Room temperature anodization at a constant potential

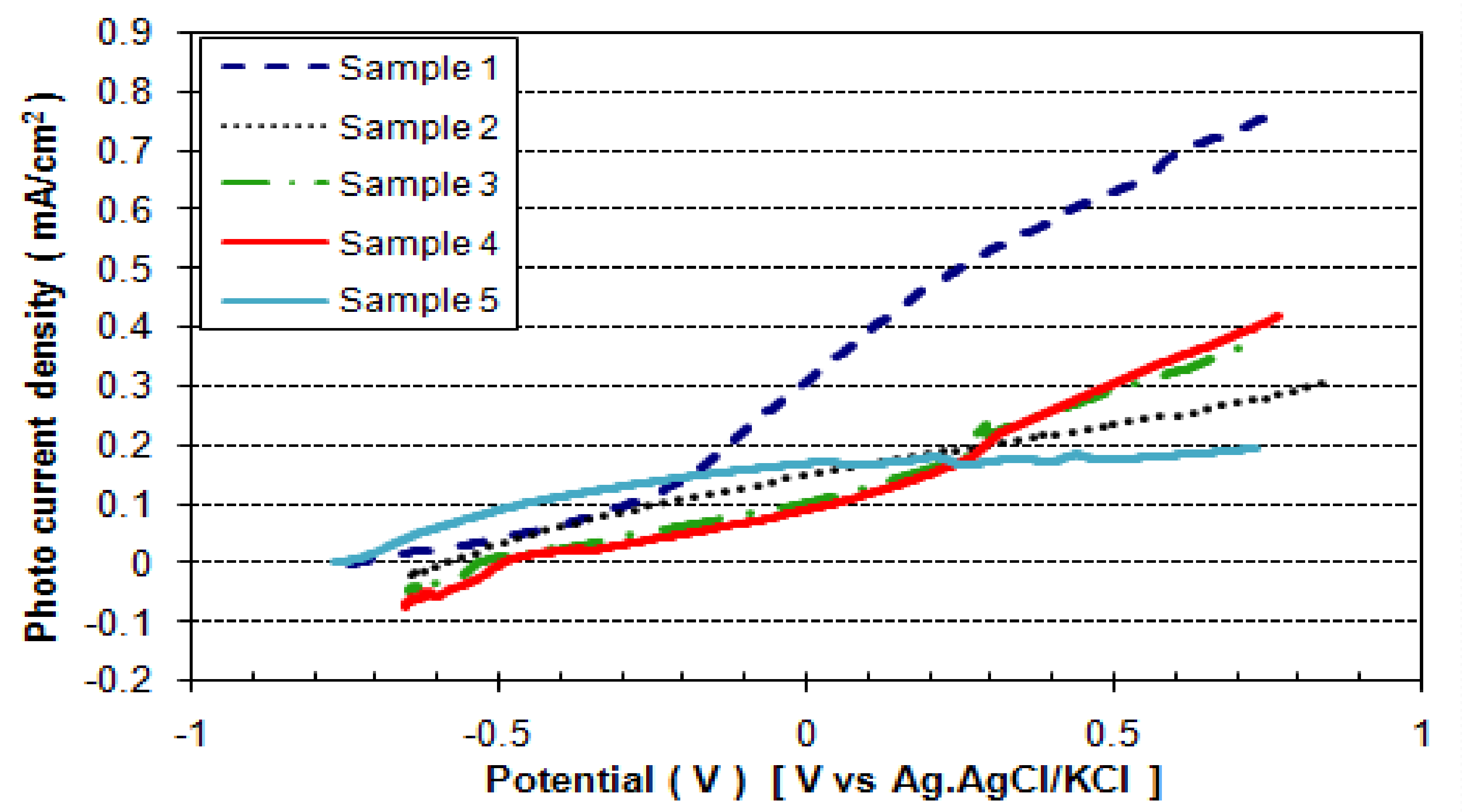


Results-current transients during anodization



- Current density vs time during anodization; (a) constant voltage anodization at different voltage levels, (b) step voltage anodization at 60V-40V-20V compared with constant 20 V anodization

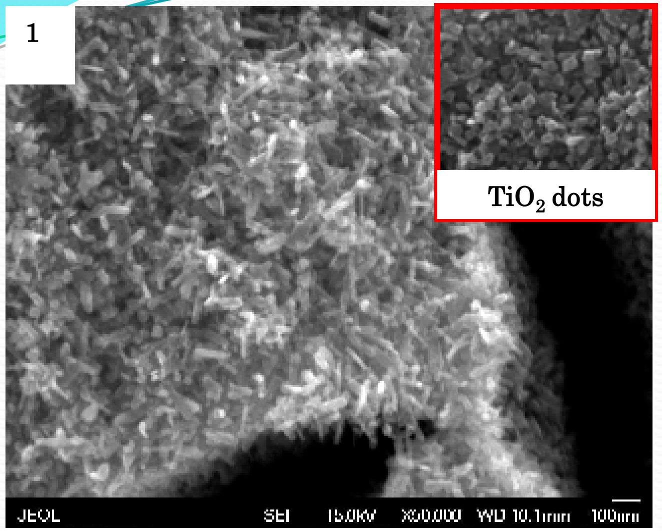
Photocurrent density vs. anode nanostructure



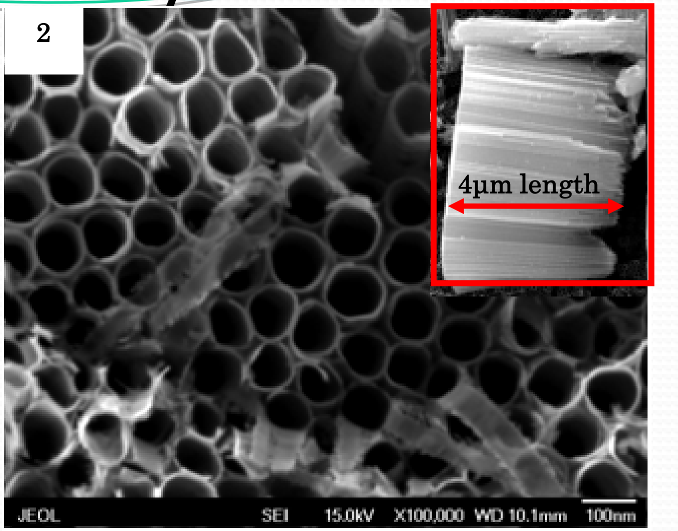
Photocurrent density vs bias voltage plotted for samples anodized at different voltages

Stepped voltage anodization resulted in 55% higher current compared to the value of potocurrent at a constant voltage anodization

SEM image of TiO_2 nanotubular array

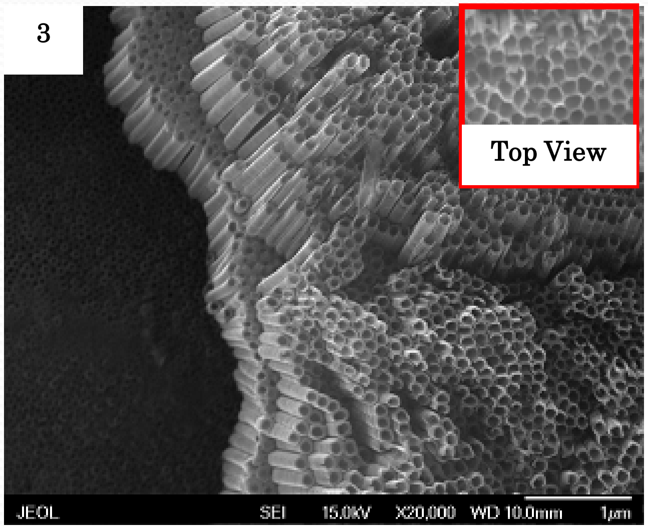


•The nanotube;
- •Average length 4 μm
- •Average diameter 100 nm
- •Average wall thickness 5 nm
- •Average center to center spacing of 150 nm



•The nanorod;
- •Average length 100nm
- •Average width 10nm
- •Average hight 10nm

•The nanodot
- •Average 10 nm of square of side.

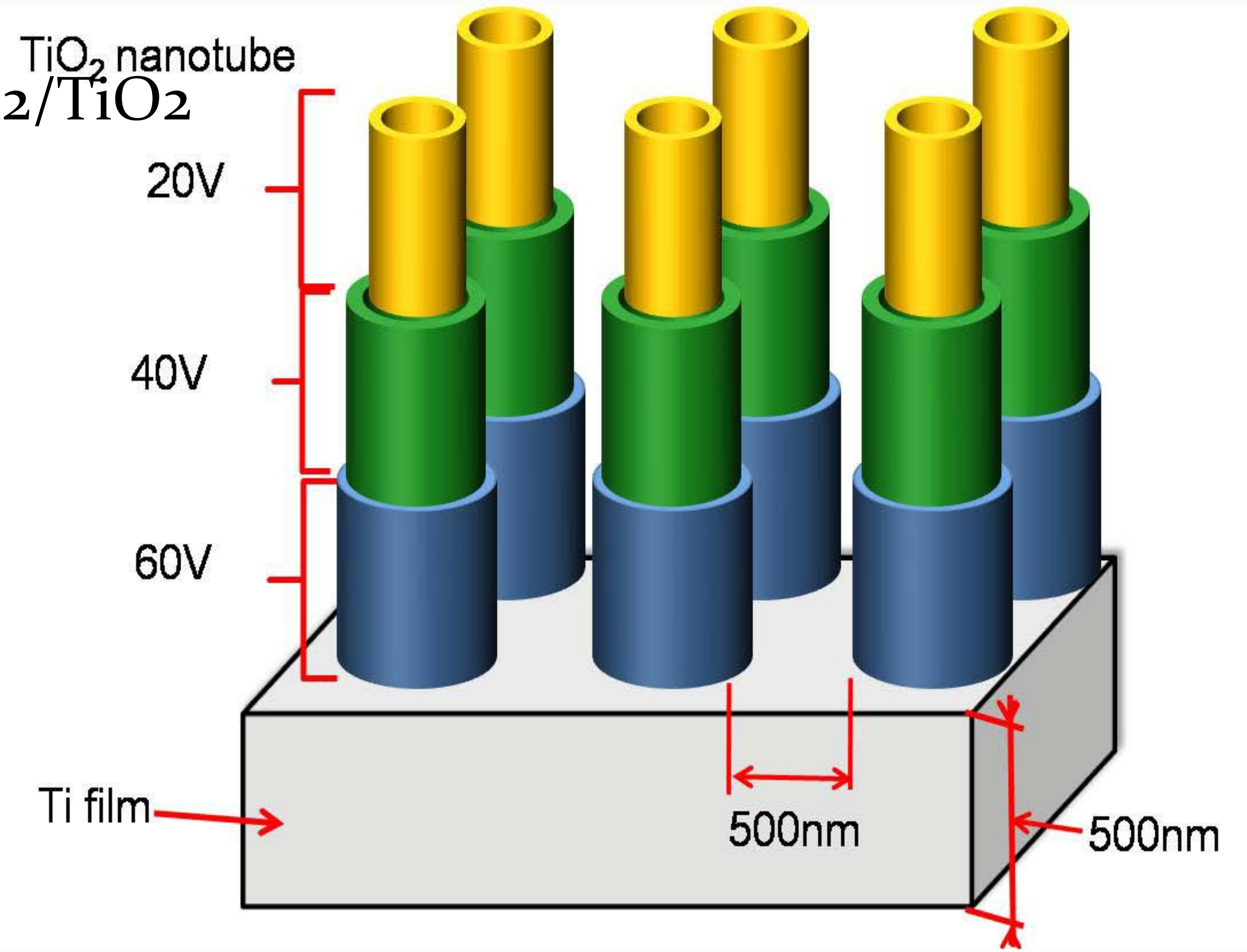


•The three successive stage nanotube;
- •Average length 4μm
- •Average diameter 100nm
- •Average wall thickness 5nm
- •Average center to center spacing of 150 nm

SEM image showing the TiO_2 sample anodized in a fluoride based electrolyte at three different voltage settings: (1) constant potential 20V (Fig.2a), (2) constant potential 60V (Fig.2b), and (3) stepped voltage potentials, 60V-40V-20V (Fig.2c)

Layered Nanotubular Arrays

TiO2/TiSi2/TiO2



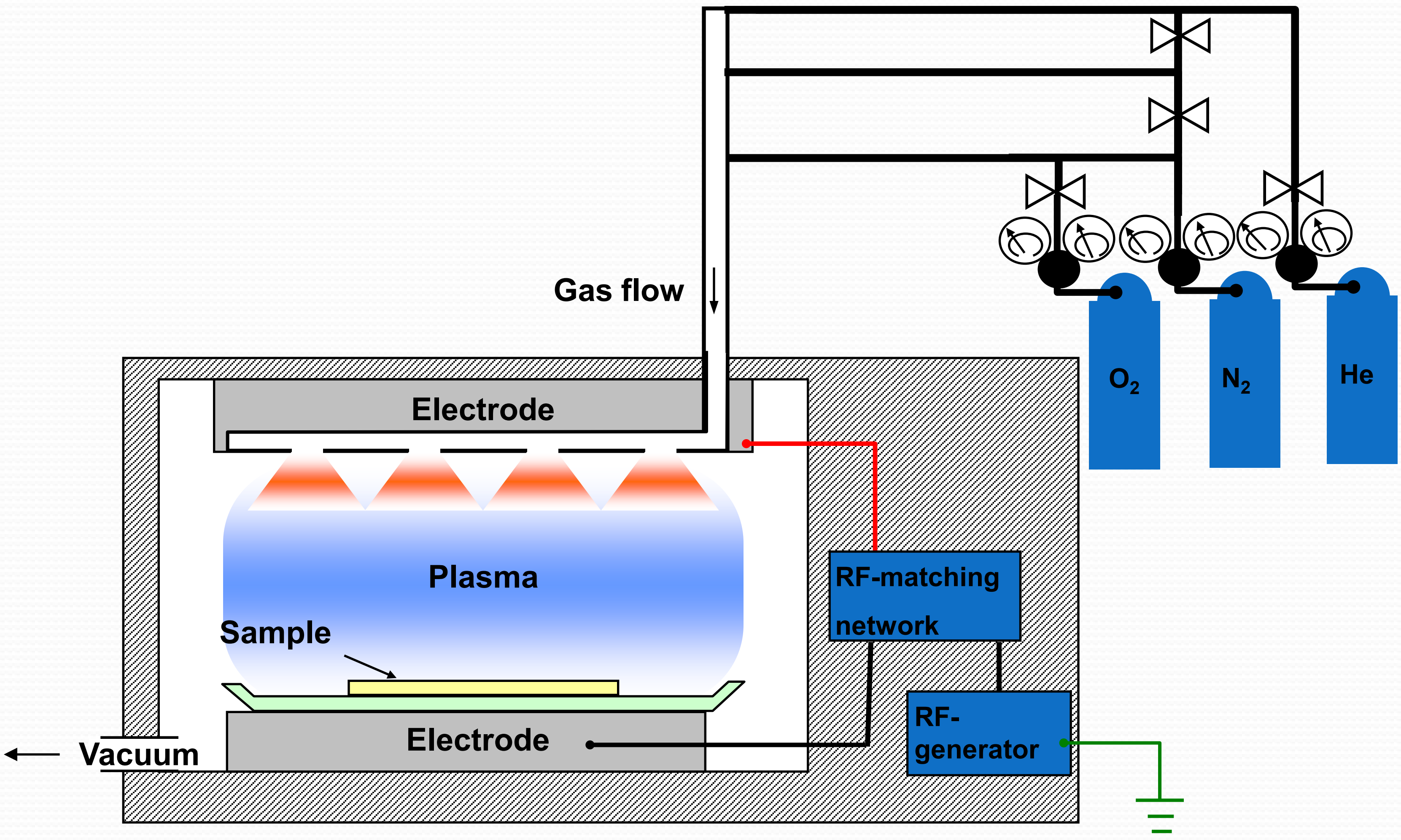
Plasma surface modification

- Plasma surface modification was performed using low-pressure Nitrogen plasma [13.56 MHz rf 200 W plasma at an operating pressure 150 mtorr]

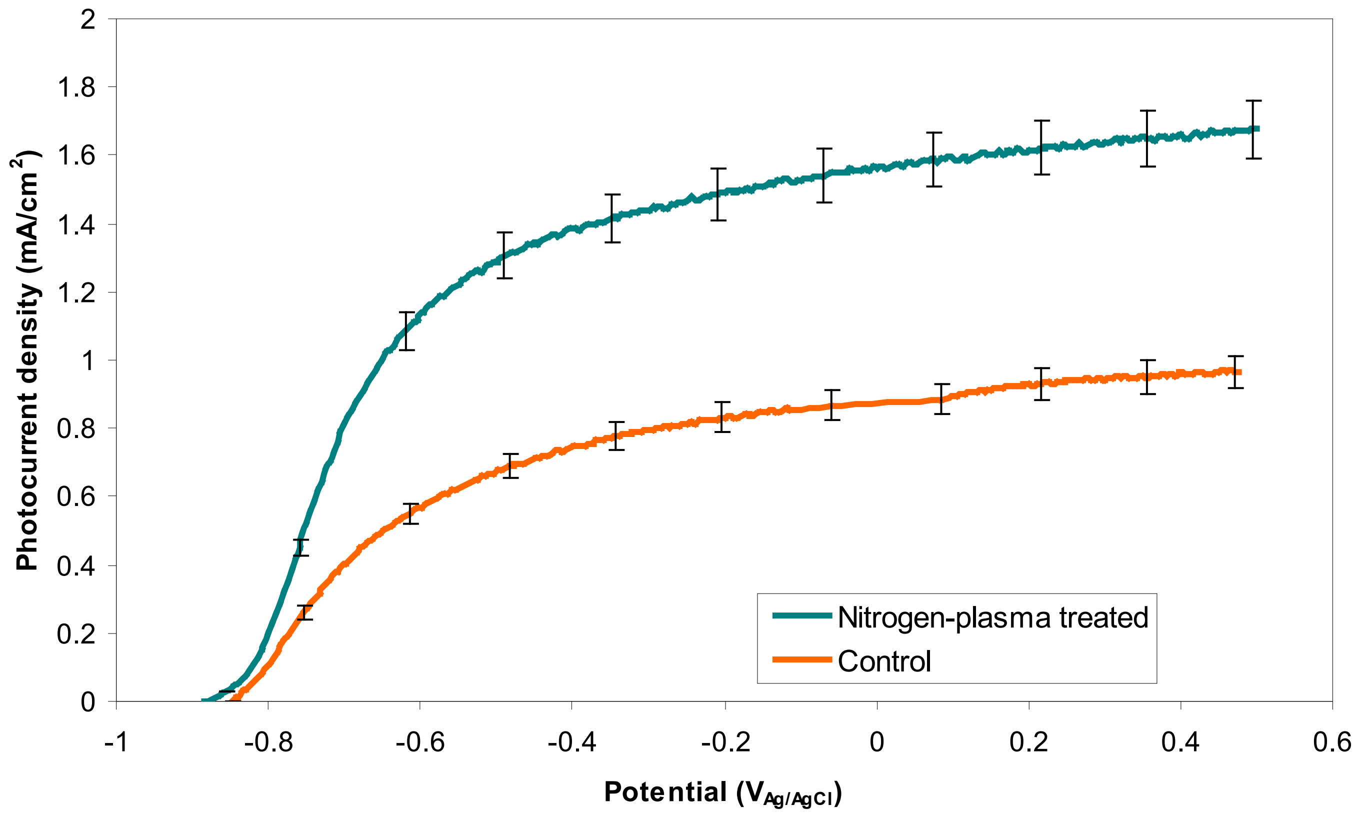
- Samples were exposed to plasma for 10 minutes in each test run

- Untreated and nitrogen plasma treated samples were tested for photocurrent density

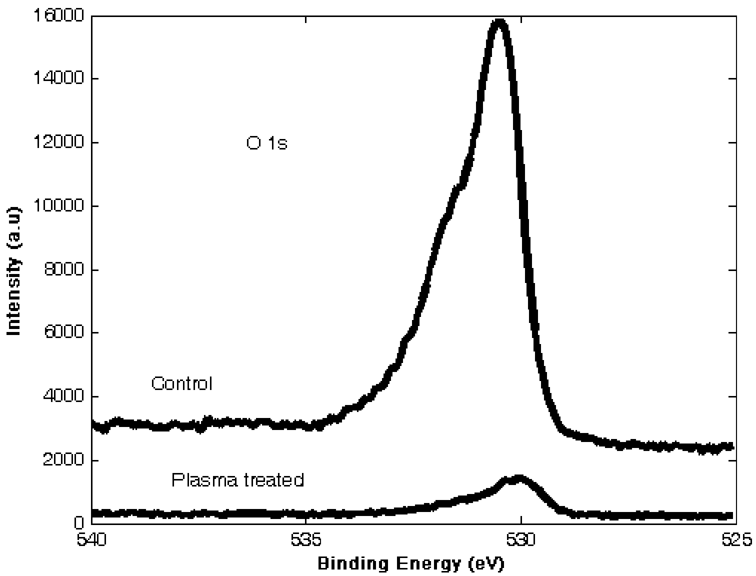
Schematic of low-pressure plasma reactor used for surface modification

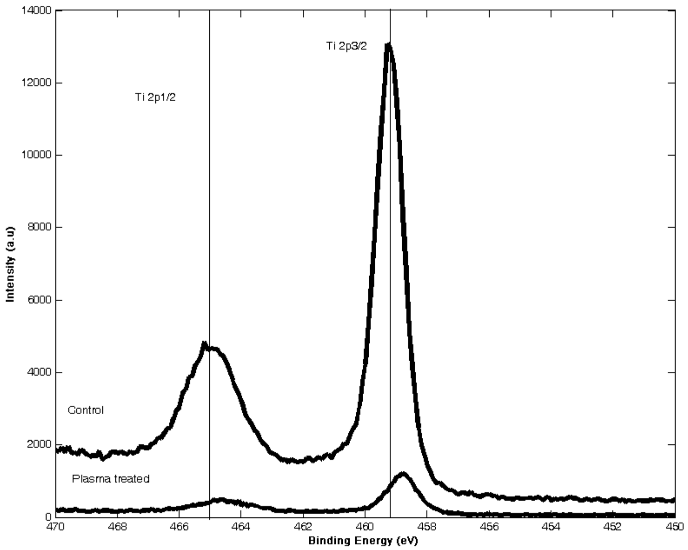


Photocurrent density measurements for control and nitrogen plasma treated titania photoanodes

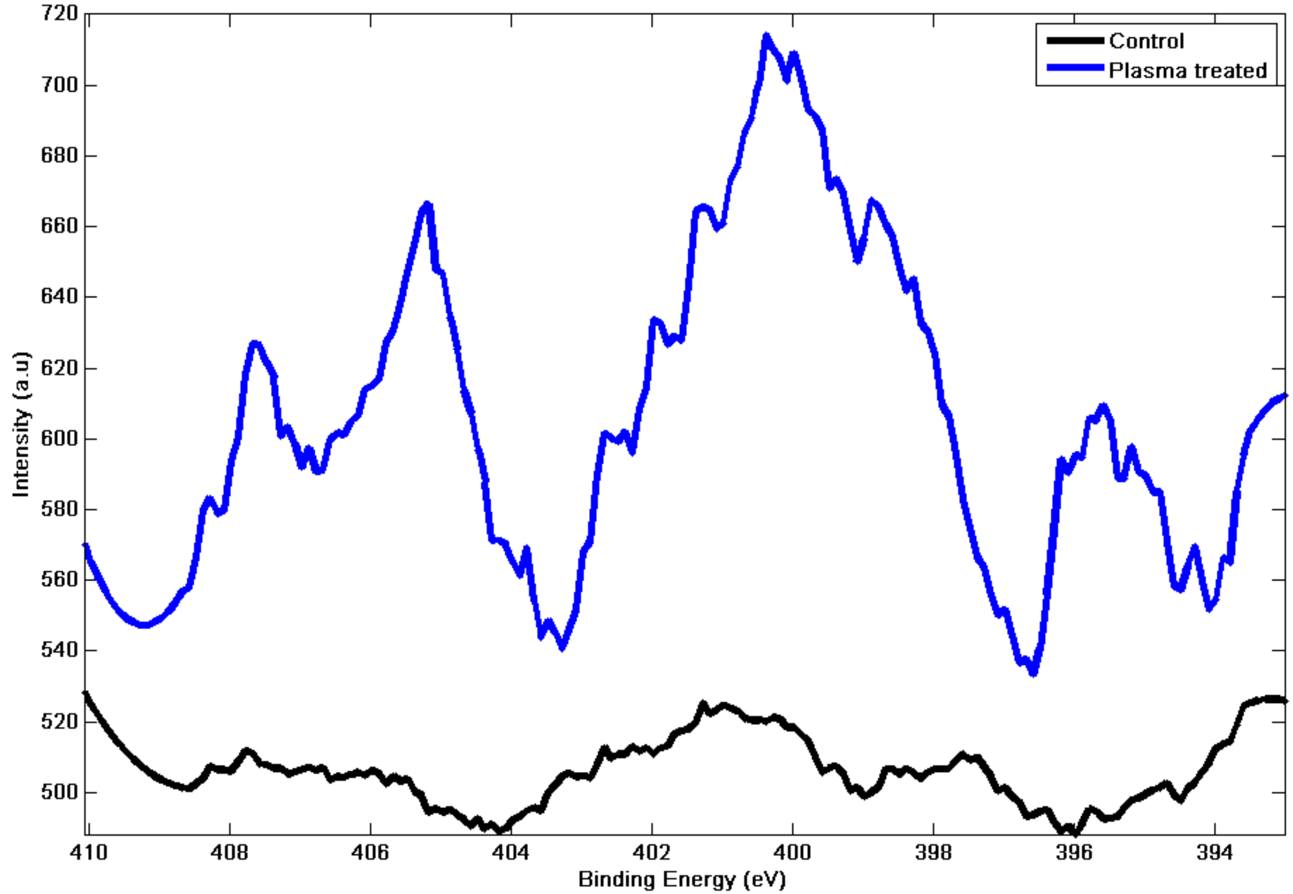


XPS Analysis of Nitrogen plasma treated TiO_2 samples





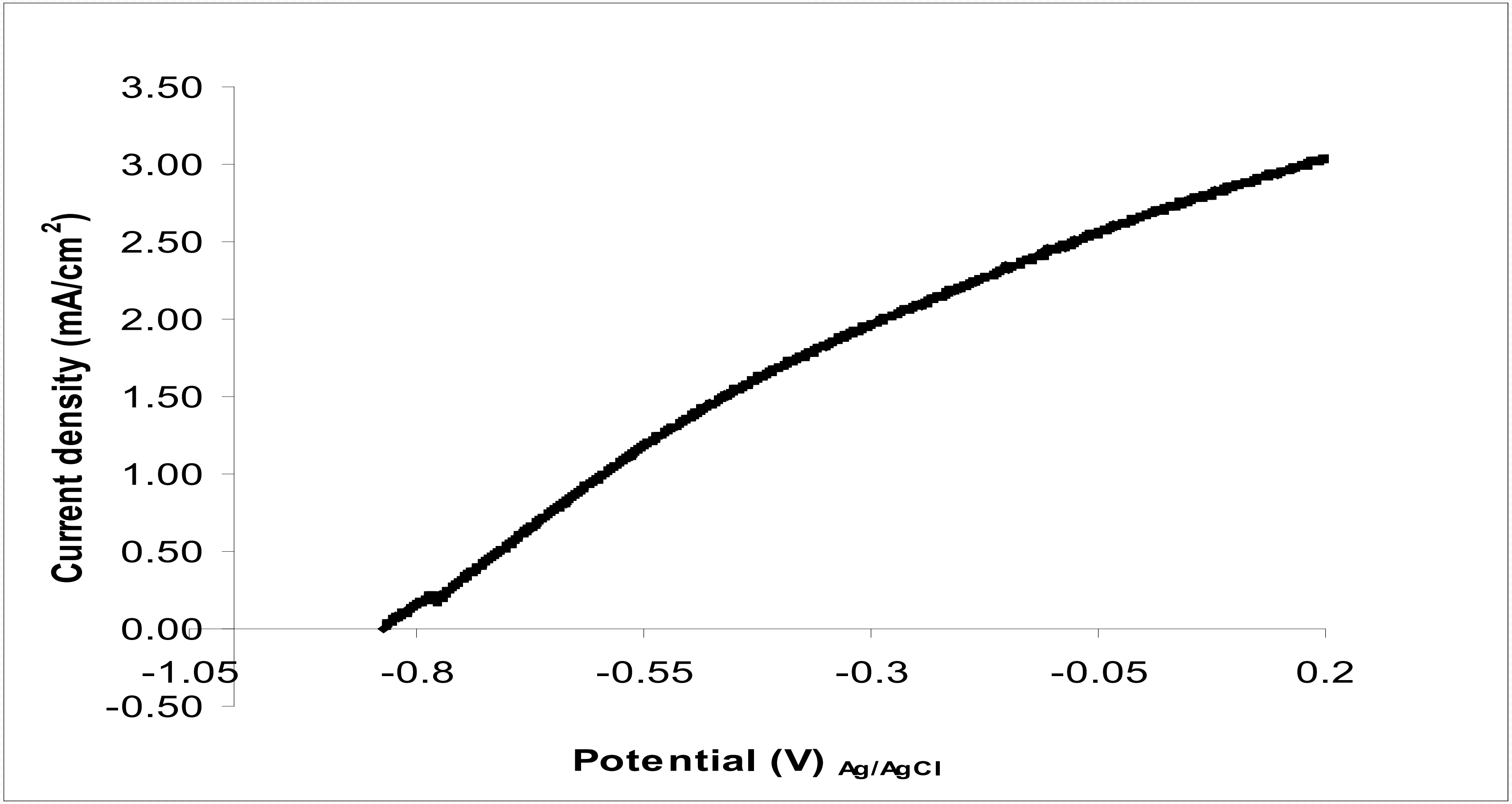
XPS spectrum of (a) Ti 2p and (b) O 1s levels for Control and Nitrogen-Plasma treated TiO_2 photoanodes



XPS spectrum (a) Control and (b) Nitrogen-Plasma treated TiO2 photoanodes

The narrow scan N 1s spectrum is demonstrated in peaks at 400 and 396 eV, which have been ascribed to presence of nitrogen in lattice structure either as substitutional dopant for O, or as interstitial dopant

Photocurrent Density with TiSi2 Particles on TiO2 Nanotubular Electrode



Effects of Surface and Structural Modifications of TiO_2 Nanotubes

Table 1. Enhancements of open circuit potential and photocurrent density values by surface modification of oxygen-annealed samples by nitrogen plasma treatment.

Sample description	OCP (bright), $V_{Ag/AgCl}$	Current at −0.2 V (mA cm^{-2})	Current at 0.2 V (mA cm^{-2})
Control	-0.85	0.83	0.93
N_2 plasma treated	-0.97	0.94	1.68

Table 2. Structural Modifications of nanotubular TiO_2 photoanodes by changing anodization conditions of Ti foil (Stepped voltage (Sample 1) vs. constant voltage anodization)

Sample Name	Anodization Voltage and duration		
Sample 1	60 V for 10 min	40 V for 10 min	20 V for 40min
Sample 2	60 V for 60 min		
Sample 3	40 V for 60 min		
Sample 4	20 V for 60 min		
Sample 5	20 V for 60 min		

Synthesis of Titanium disilicide thin films for using composite multilayer photoanodes for Hydrogen generation

- Deposit a thin film of $TiSi_2$ using sputter coating on Ti film for 60 minutes

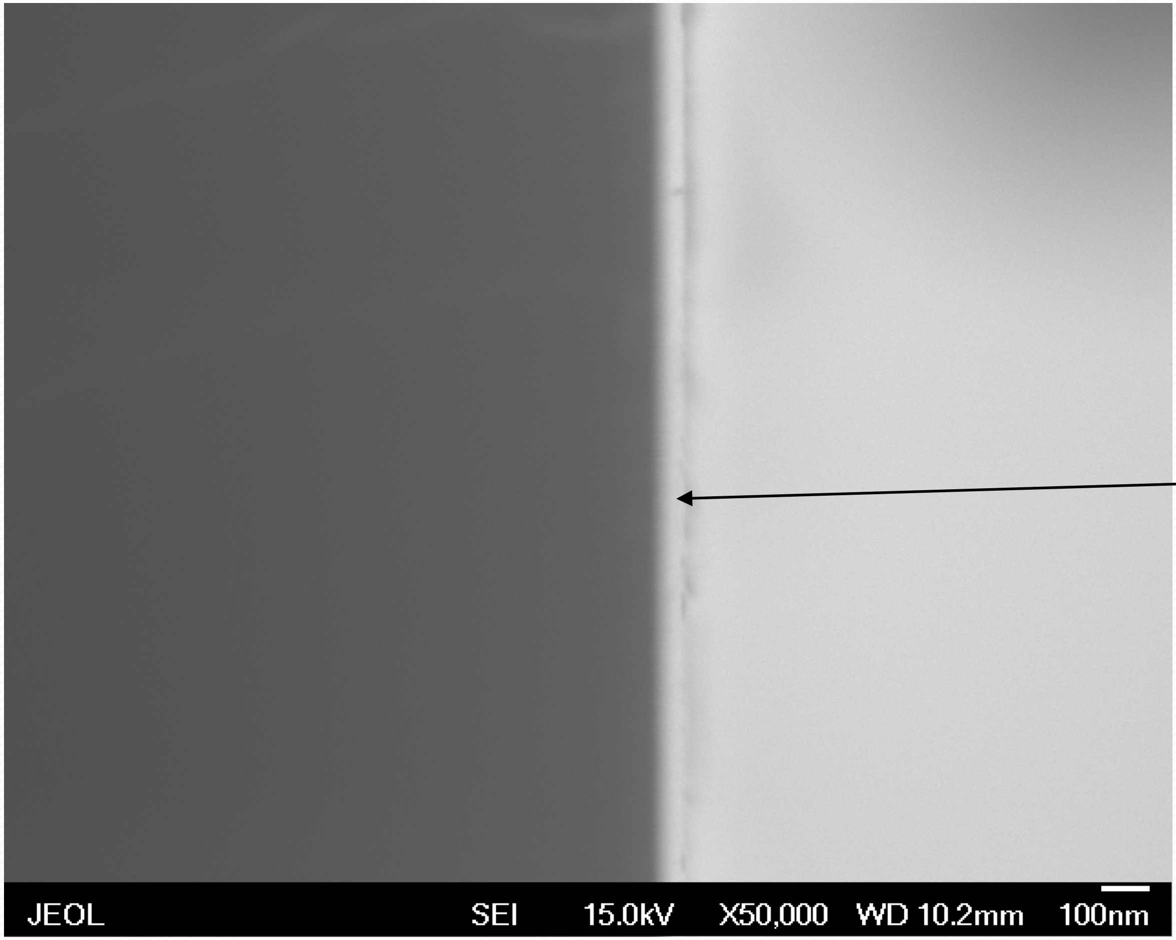
- Analyze chemical composition gradients using XPS and EDS

- Use electron beams, impinged with different energies (3, 7, 10, 15, and 30 kV) on the film to analyze chemical composition at different depths of the film

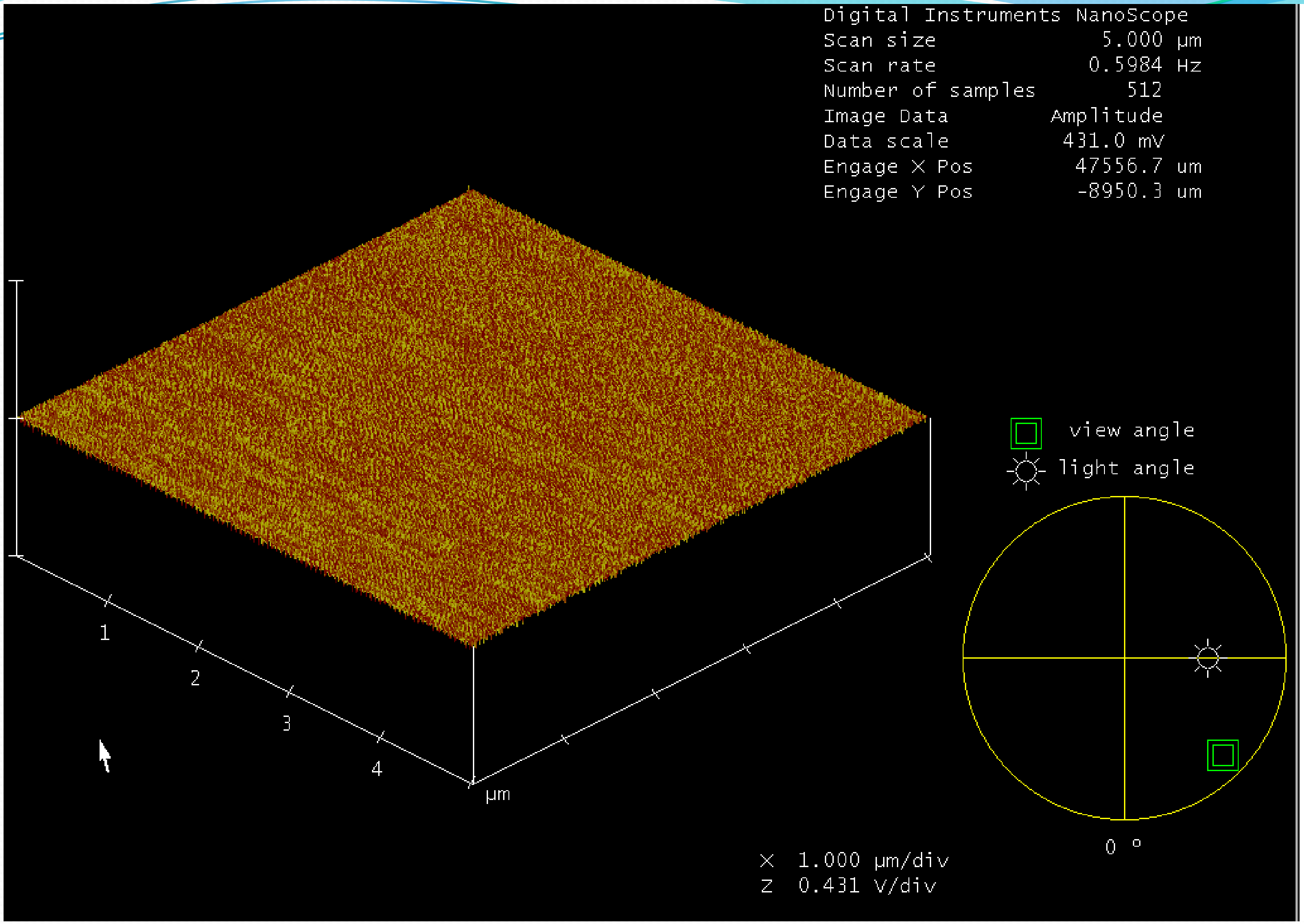
.

Development of Heterojunction $TiSi_2/TiO_2$ photoanodes

- Titanium disilicide is a promising photoanode material in photoelectrochemical hydrogen generation
- A hetrojunction $TiO_2/TiSi_2$ photoanode can harvest a significant portion of solar radiation in the visible region.
- Broadband reflectance measurements for $TiSi_2$ show a bandgap ranging from 3.4 eV to 1.5 eV. However $TiSi_2$ is unstable in water.
- TiO_2 film coatings can serve as a protective layer for $TiSi_2$.



SEM image of a titanium silicide film



AFM image of a titanium silicide film displaying high degree of uniformity

Results

- **Nitrogen plasma treatment of titania photoanodes resulted in 80% increase in photocurrent density;**

- **XPS analysis clearly indicated the incorporation of N in titania lattice structure.**

- **Electrochemical synthesis of titania nanotube arrays using needle shaped cathode improved the performance of photoanode**

- **The deposition rate of titanium silicide has been determined as a part of the process of developing heterojunction $TiO_2/TiSi_2$ photoanodes**

Technical Accomplishments

- **Plasma surface modification and surface doping increased photocurrent density of titania nanotubular electrodes**
- **Synthesis of TiO_2 nanorods**
- **Synthesis of $TiSi_2$ based heterojunction electrodes**
- **Photoelectrochemical hydrogen production with a high photocurrent density**

Work under progress:

- **Develop patterned naotubular layered TiSi2 and TiO2 photoanodes.**

- **Characterize interfacial surface states between $TiSi_2$ and TiO_2 photoanodes by determining density of states, surface bandgaps, crystallinity, optical absorption spectrum, photoconductivity, and durability.**

- **Optimize interface states and the process of layered photoanode synthesis**

Future Work

- Develop multi-junction (TiSi2 and TiO2) electrodes to enhance the absorption of solar radiation
- Analyze the density of the interface states and the distribution of surface bandgaps
- Measure light absorption vs λ
- Measure photocurrent conversion efficiency (IPCE vs λ) and measure corrosion resistance
- Determine photo-generated carrier concentration decay by using a rf-conductivity probe
- Perform multi-dimensional analysis: cost, durability, efficiency and environmental impact in PEC based hydrogen generation

Project Summary

Relevance: Develop efficient photoanode materials for optimizing hydrogen production

Approach: Plasma surface modification for removing surface contaminants and use of layered electrodes for PEC based generation of hydrogen

Technical Accomplishment and Progress: Enhanced photocurrent density with oxygen annealed photoanodes of TiSi2 and TiO2 photoanodes with surface doping of nitrogen using plasma treatments and synthesis of nanostructured electrodes

Collaboration: University of Nevada, Reno and Arkansas Nanotechnology Center

Proposed future research: Application of layered photoanodes, plasma treatments and quantitative determination of photoelectrochemical generation of hydrogen

Acknowledgements: Department of Energy, University of Nevada, Reno, NASA Kennedy Space Center, Arkansas Science and Technology Authority, and Boston University

M. K. Mazumder, mkmazumder@ualr.edu, 617 997 7049

University of Arkansas at Little Rock

Project ID #PD057

University of Arkansas at Little Rock