Photelectrochemical Hydrogen Production

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Overview

Timeline

- July 2006
- August 2009
- Percent complete 70%

Barriers

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

Budget

- Total project funding $
  - DOE share $ 890,998
    - **Hydrogen Production $297K**
    - **Hydrogen Storage $ 594K**
  - Contractor share $381,543
- Total funding received in FY08 $ 324,721

Partners

- Interactions/ collaborations

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

Objectives

Overall	**Optimize surface properties of photoanodes for efficient generation of Hydrogen**
2006-07	**• Study interfacial charge transfer process in PEC** **• Investigate the roles of surface states and nano-structures of TiO_2 electrodes to minimize Surface traps** **• Develop partnership with other institutions involved in PEC processes** **• Develop outreach and educational programs**
2007-08	**• Remove surface contaminants & surface traps by plasma surface treatments** **• Dope TiO_2 electrodes with N using plasma treatments** **• Improve light absorption cross section and interfacial charge transfer rate** **• Measure photocurrent density of nano-structured TiO_2 electrodes with simulated solar radiation**

Objectives

Overall	**Optimize surface properties of anodes for efficient generation of Hydrogen**
2008-09	• **Synthesize nanostructured photoanodes, use metal silicides and metal oxides: Start with $TiSi_2$.** • **Optimize interfacial charge transfer phenomena for efficient diffusion of the minority carriers to the interface,** • **Use layered electrodes of $TiSi_2$ and TiO_2,** • **Minimize photocorrosion of $TiSi_2$ electrodes with a transparent coating of high corrosion-resistant TiO_2 electrodes, and** • **Develop processes for synthesizing nanostructured, layered electrodes of $TiSi_2$ and TiO_2**

Rationale

- Absorption of photons, separation of charge carriers, and redox reaction for hydrogen generation- all take place in the interface between the semiconductor electrode and the electrolyte.

- Optimization of interfacial charge transfer process is essential for improved solar-to-hydrogen conversion.

- $TiSi_2$ has a bandgap ranging from 3.4 eV to 1.5 eV and it can be used to 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, C, Si)

- Test surface modified Nanostructured $TiSi_2$ and TiO_2 anodes for photoelectrochemical generation of hydrogen

Experimental procedure

- Electrochemical synthesis of TiO_2 nanorods by anodization of Ti film
- Plasma surface modification of TiO_2 nanorods using Nitrogen plasma
- Characterize surface structure
- Measure photocurrent density and analyze the treated and untreated photoanodes

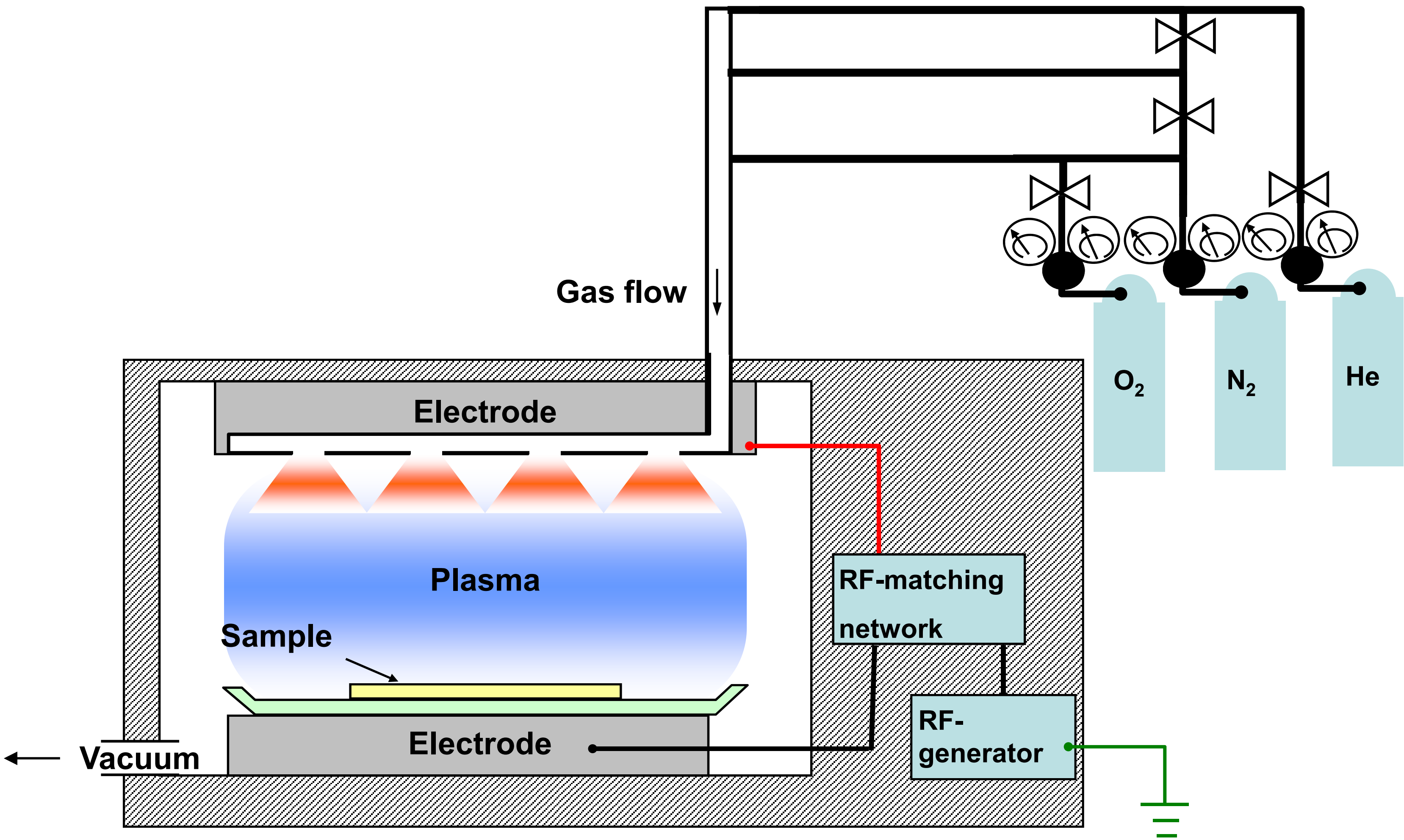
Plasma surface modification

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

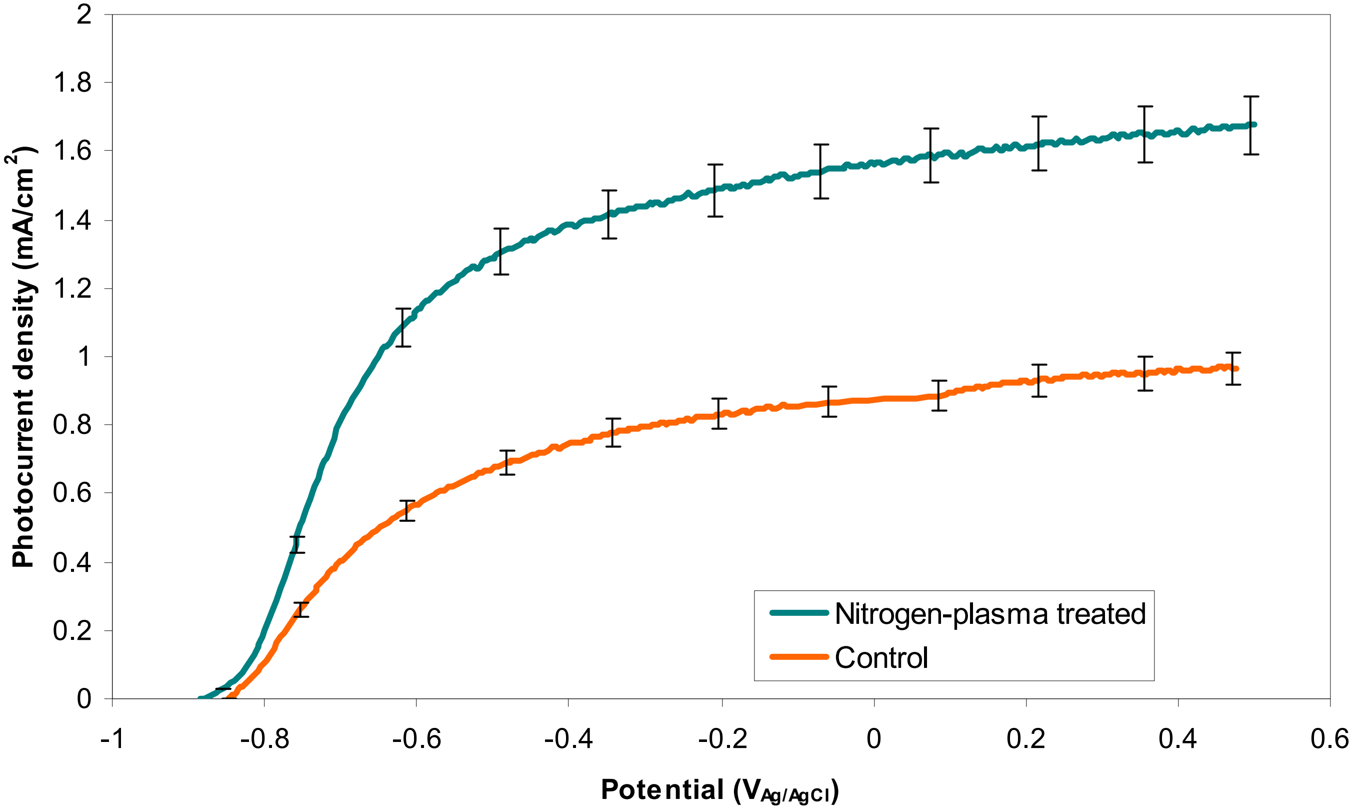
- Samples were exposed to plasma for 10 minutes in each test run

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

Schematic of low-pressure plasma reactor used for surface modification



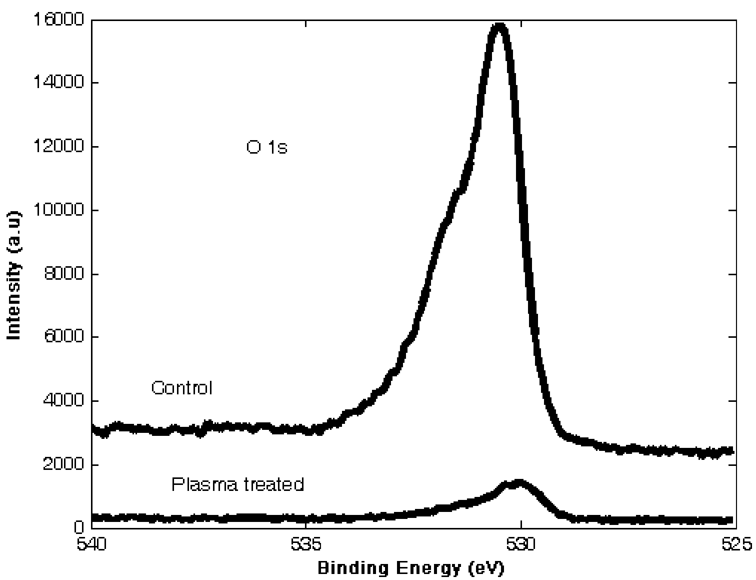
Photocurrent density measurements for control and nitrogen plasma treated titania photoanodes

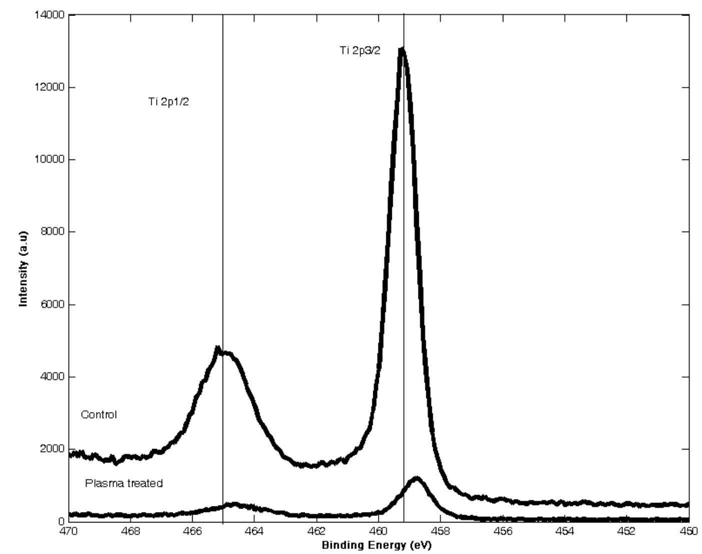


Technical Accomplishments

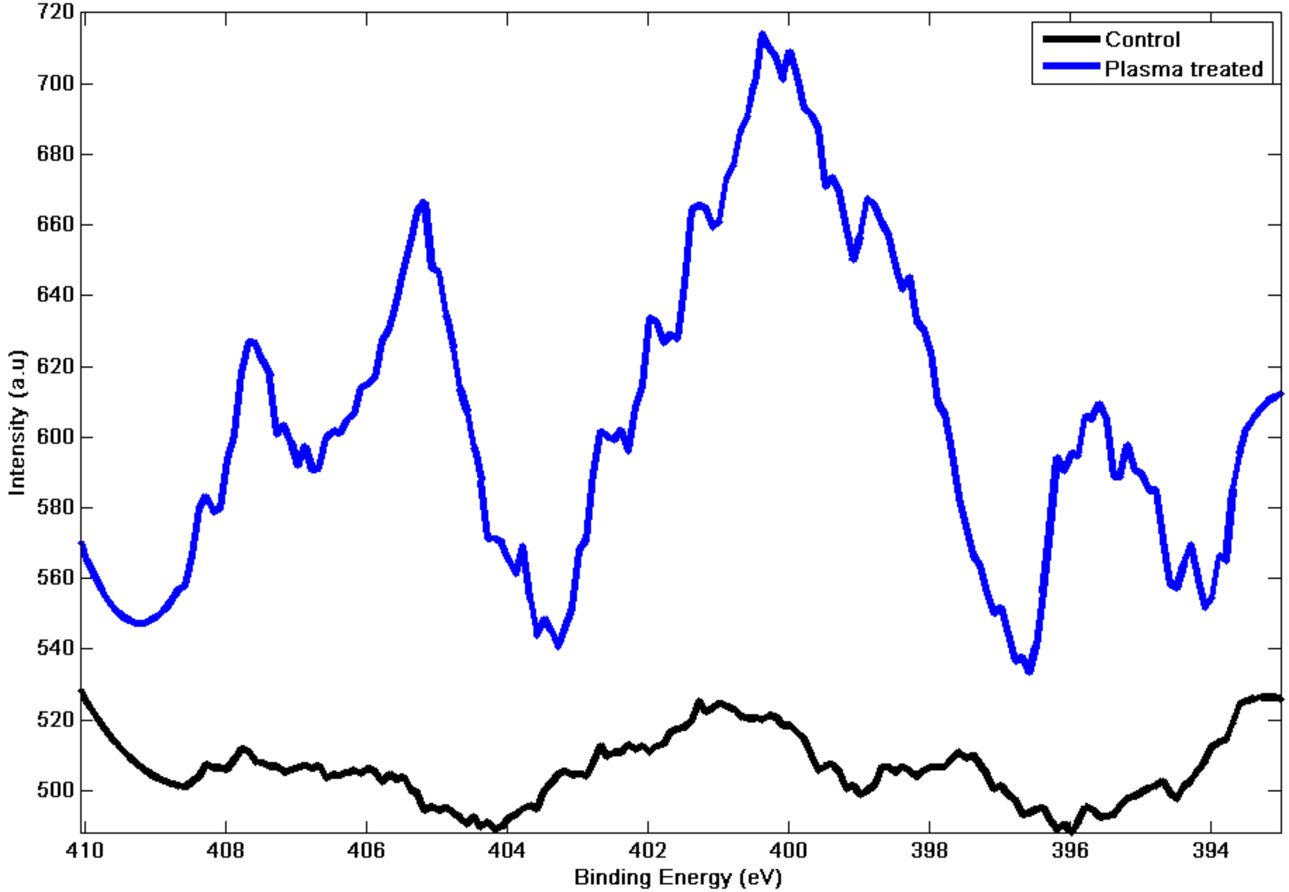
- **Plasma surface modification and surface doping increased photocurrent density of titania nanotubular electrodes**
- **Synthesis of TiO_2 nanorods**
- **Synthesis of $TiSi_2$ based heterojunction electrodes**
- **Photoelectrochemical hydrogen production with a high photocurrent density**

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

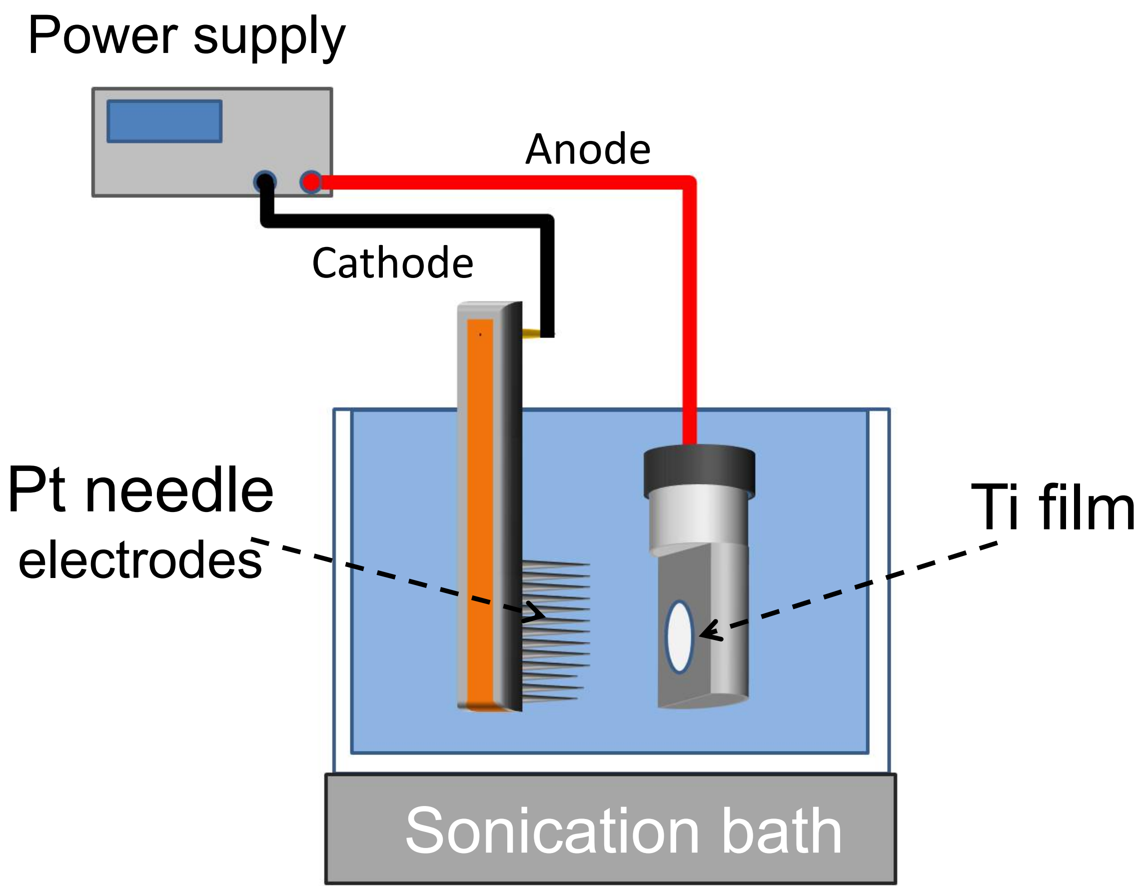
The narrow scan N 1s spectrum is demonstrated in peaks at 400 and 396 eV, which have been ascribed to presence of nitrogen in lattice structure either as substitutional dopant for O, or as interstitial dopant

Synthesis of TiO_2 Nanorods: Effect of Cathode Geometry

- Modify the electric field distribution between cathode and anode in the electrochemical synthesis of nanorod or nanotube structures using needle electrodes:

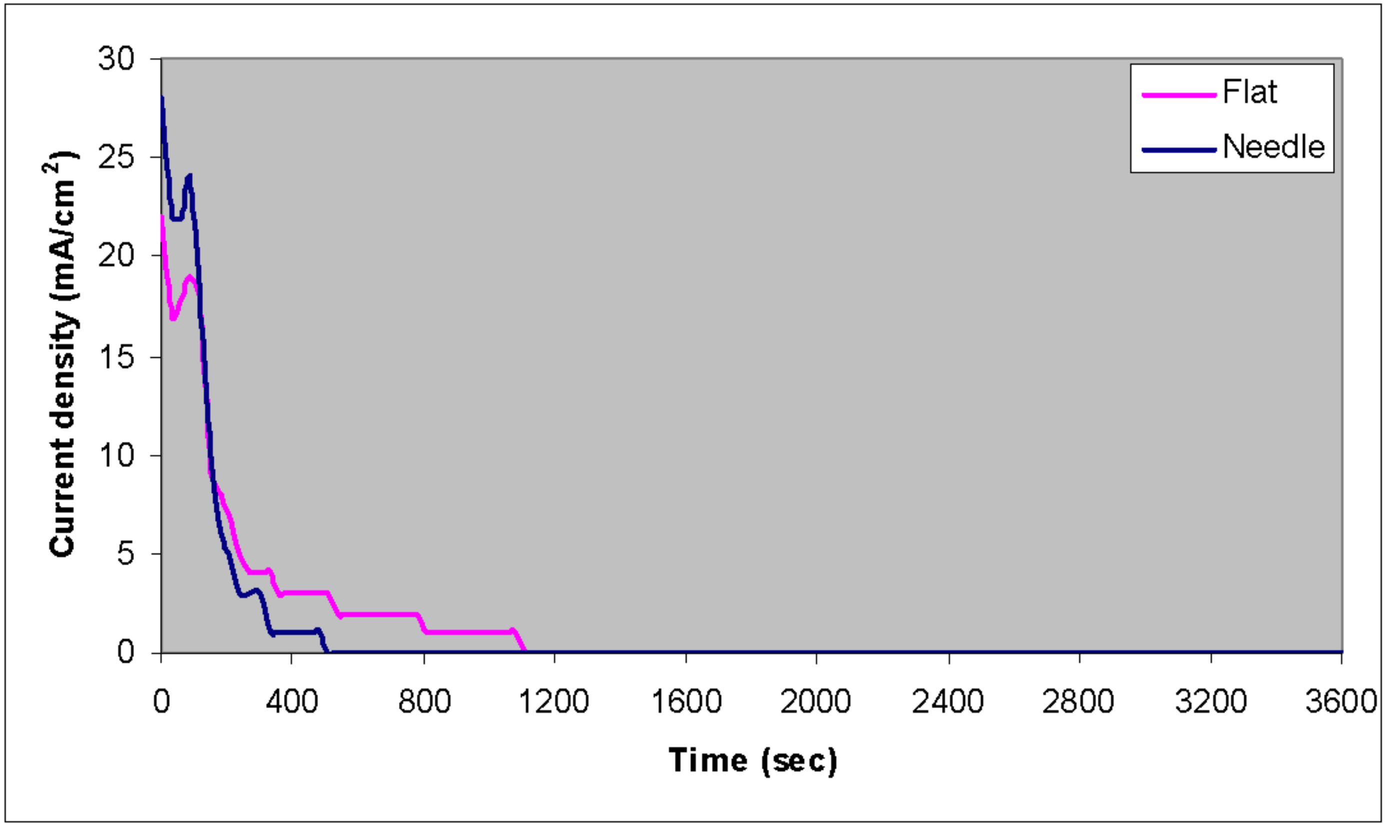
(1) Make the interelectrode spacings to be comparable to the wavelength of the visible radiation for maximizing light absorption and

(2)Minimize recombination losses.



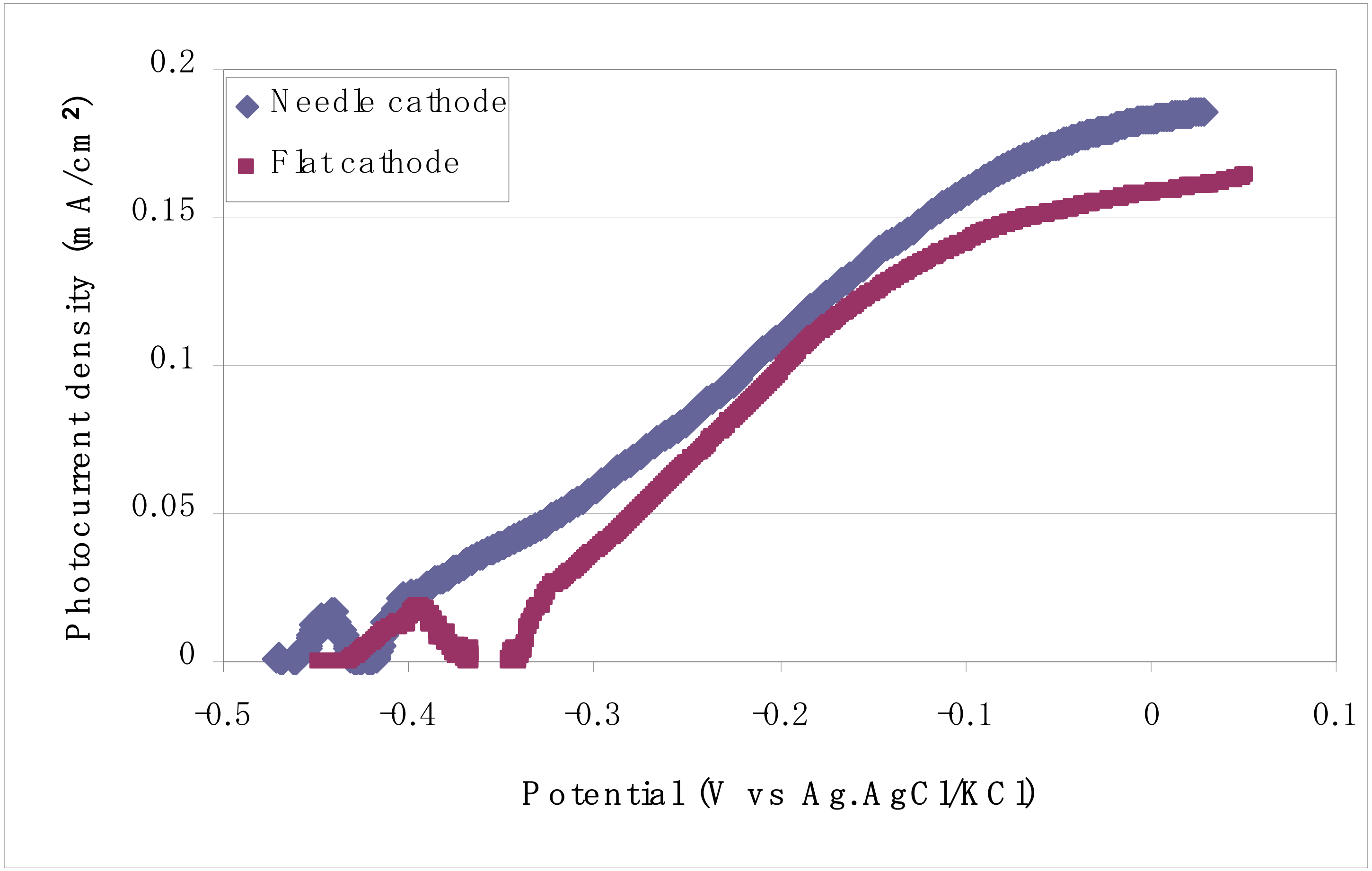
Experimental setup for the electrochemical synthesis of TiO_2 Nanorods with needle electrodes as cathode

Current transient during anodization of Ti using "needle shaped" and flat electrode.



Due to point-to-plate geometry, the electric field between the electrodes was stronger
As a result the field assisted oxidation of Ti using "needle shaped" was much faster as compared to that of flat electrode.
Because of more intense field, the dissolution of metal ions was into the solution was also faster
Nanotubes were formed much faster in case of "needle shaped" electrode as demonstrated by the steady current

Photocurrent density of the titania photoanodes synthesized using Needle-shaped and Flat Cathode



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 measurement for $TiSi_2$ has shown a bandgap ranging from 3.4 eV to 1.5 eV. This bandgap spread covers the entire visible spectrum. However $TiSi_2$ is unstable in water.
•TiO_2 can serve as a passive layer to passivate TiSi2.

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

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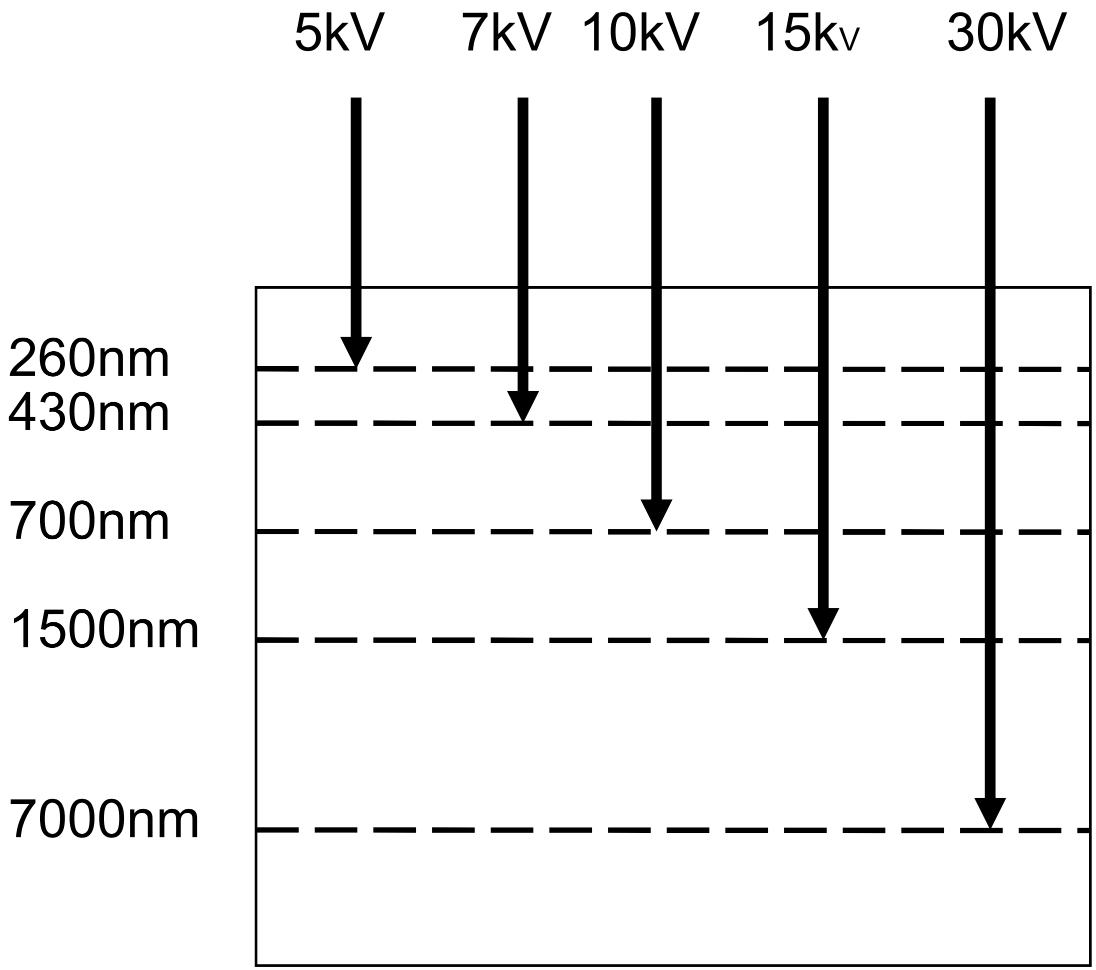


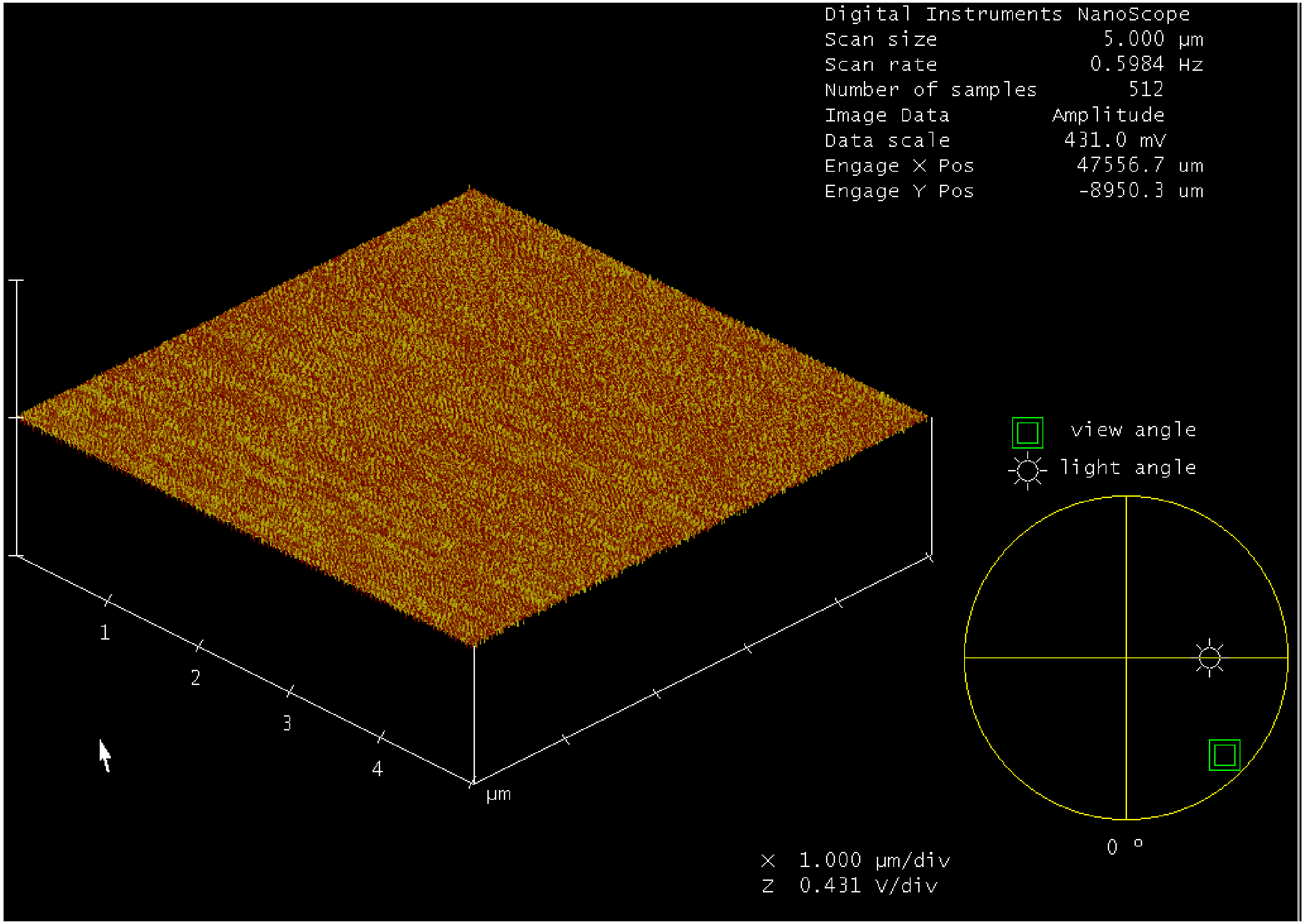
Electron beam penetration depth using Monte-Carlo simulation

Development of heterojunction $TiSi_2/TiO_2$ photoanodes

Depth [nanometer]	Composition	
	Ti [%]	Si [%]
260	43.35	23.27
430	43.4	22.9
700	47.58	17.94
1500	46.77	6.42
7000	50.85	3.25

Approximate depth profit of Titanium silicide using EDS (Energy Dispersive X-ray Spectroscopy)

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**

Work under progress:

- Develop the heterojunction photoanodes using TiO_2 as passivating layer .

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

- Perform comprehensive studies on the improvement of photoconversion efficiency by modifying surface states and surface structures with the addition of nanoparticles of Au, Pt, and other materials for improved photo-catalytic activity of TiO_2

Future Work

- **Develop multijunction electrodes to enhance the absorption of solar radiation**
- **Measure the density of the surface states and the distribution of surface bandgaps**
- **Measure light absorption vs λ**
- **Perform multi-dimensional analysis: cost, durability, efficiency and environmental factor**
- **Measure photocurrent conversion efficiency (IPCE vs λ) and Measure corrosion resistance**
- **Determine photo-generated carrier concentration decay by using the rf-conductivity probes**

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 electorodes**

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**

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