Photelectrochemical Hydrogen Production

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Project ID #PDP21

Overview

Timeline

- July 2006
- August 2009
- Percent complete 40%

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 FY07 $ 309,743

Partners

- Interactions/ collaborations

1. University of Nevada, Reno
2. Arkansas NanoTechnology Center, University of Arkansas at Little Rock
3. Electrostatic and Surface Physics Laboratory, NASA Kennedy Space Center

Objectives

Overall	**Optimize surface properties of anodes for efficient Photoelectrochemical generation of Hydrogen**
2006-07	• Review interfacial charge transfer process in PEC and establish a surface engineering laboratory • Investigate nano-structured TiO_2 electrodes for photoelectrochemical conversion of light to hydrogen • Develop partnership with other institutions involved in PEC processes • Develop outreach and educational programs
2007-08	• Use Plasma Surface Engineering to control surface states for removing electron traps & improving photo-conversion efficiency • Use surface doping for interfacial photo-conversion for hydrogen generation with a minimal change in the bulk for improved durability • Correlate surface structures with light absorption and interfacial charge transfer • Measure photocurrent density for the test nano-structured TiO_2 electrodes against different bias voltages • Perform comparative efficiency analysis for different photoanodes

Milestones

Month/Year	Milestone or Go/No-Go Decision
Mar-07	Completed studies on surface modification and functional characterization of TiO_2 nanostructures. The plasma surface treatment processes were incorporated; Results demonstrated improvement of the photocurrent density of TiO_2 photo anodes.
Dec-08	Complete surface chemical characterization of plasma treated photo anode. Determine the optimum plasma treatment for removing electron traps from TiO_2 nanotubes. Dope the photoanode surface with n-type dopants for creating surface state bandgaps for an efficient photoconversion of light in the visible range
Aug-09	Analyze nanostructured TiO_2 photo anodes with different Ti based or other metal oxides semiconductors for optimum energetics for photo electrochemical hydrogen generation.

Approach

- Since PEC based production of hydrogen depends upon the interfacial kinetics dominated by the surface states, investigate the surface structures and surface states of TiO_2 photoanodes
- Remove surface contaminants and surface states that act as charge carrier traps
- Apply Plasma surface modification as a process for surface cleaning as well as surface doping of n-type dopants (N, C, Si, …)
- Test surface modified TiO2 anodes for photoelectrochemical generation of hydrogen

Approach (contd.)

- Measure the density of the surface states and the distribution of surface bandgaps
- Measure light absorption vs λ (wavelength)
- Measure photocurrent conversion efficiency (IPCE vs λ)
- Measure corrosion resistance
- Determine photo-generated carrier concentration decay by using the rf-conductivity measurements
- Perform multi-dimensional analysis: cost, durability, efficiency and environmental factors
- Develop partnership with a private enterprise

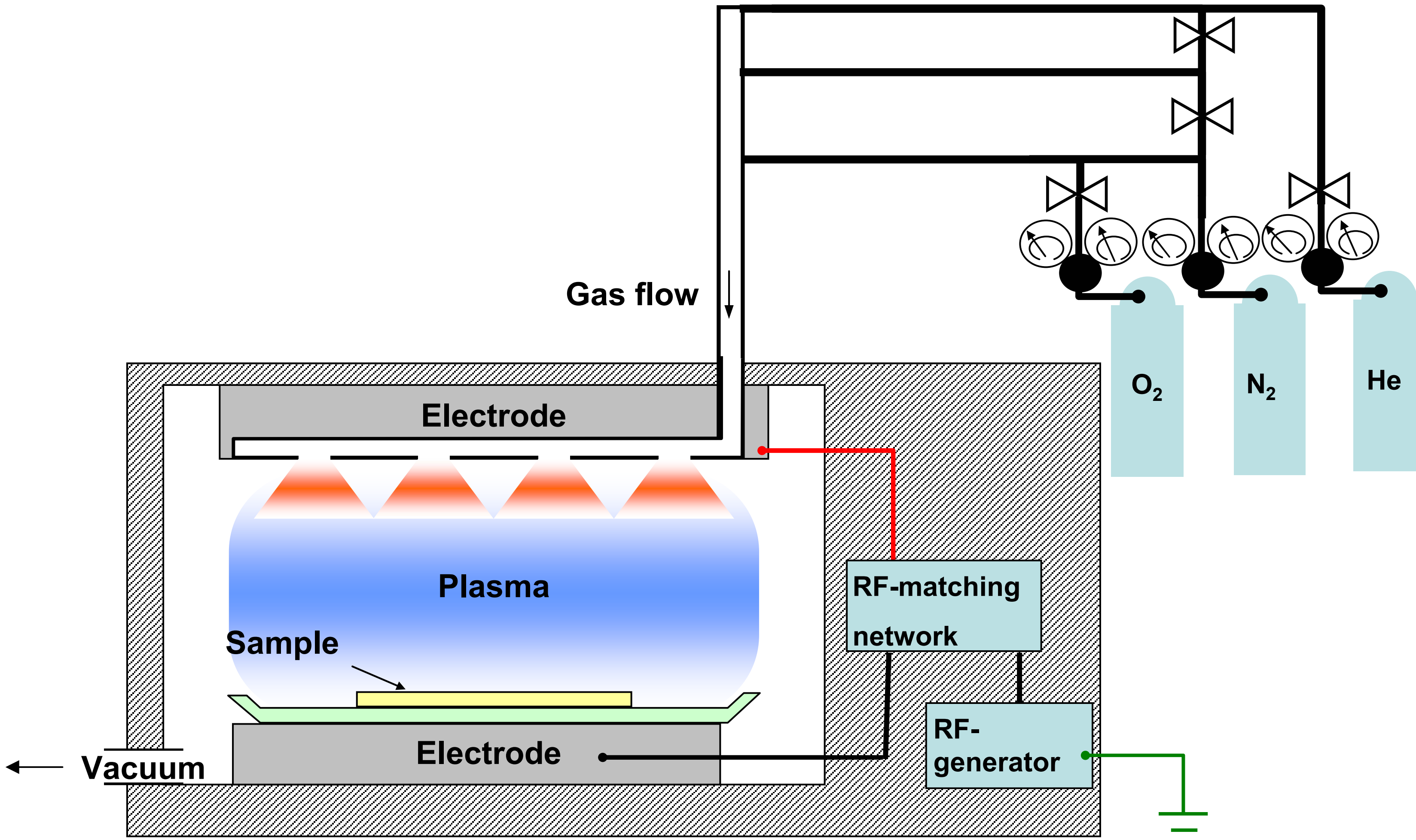
Plasma surface modification
Experimental Setup

- Plasma surface modification was performed using low-pressure Oxygen, Nitrogen and Helium plasma, 13.56 Mhz rf 200 W plasma, Operating pressure 150 mtorr

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

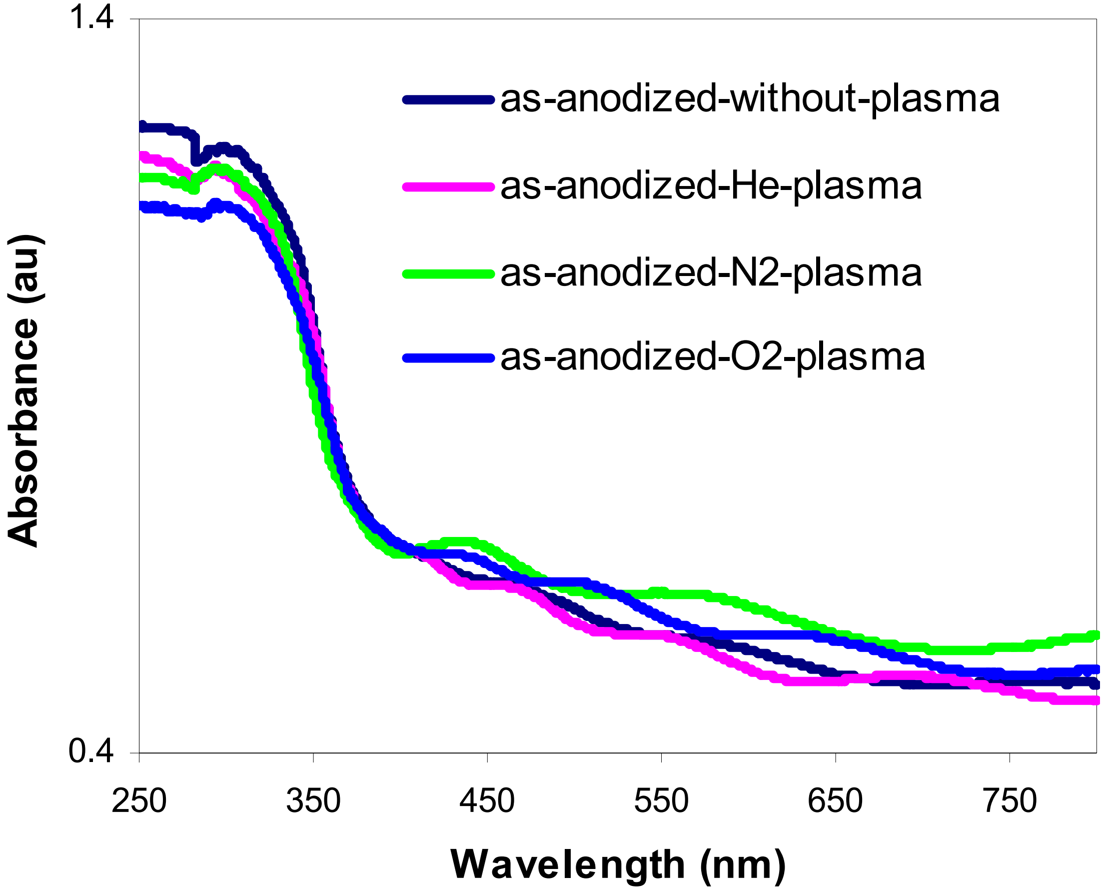
- Plasma treated samples were sent to UNR for analysis

Schematic of low-pressure plasma reactor used for surface modification



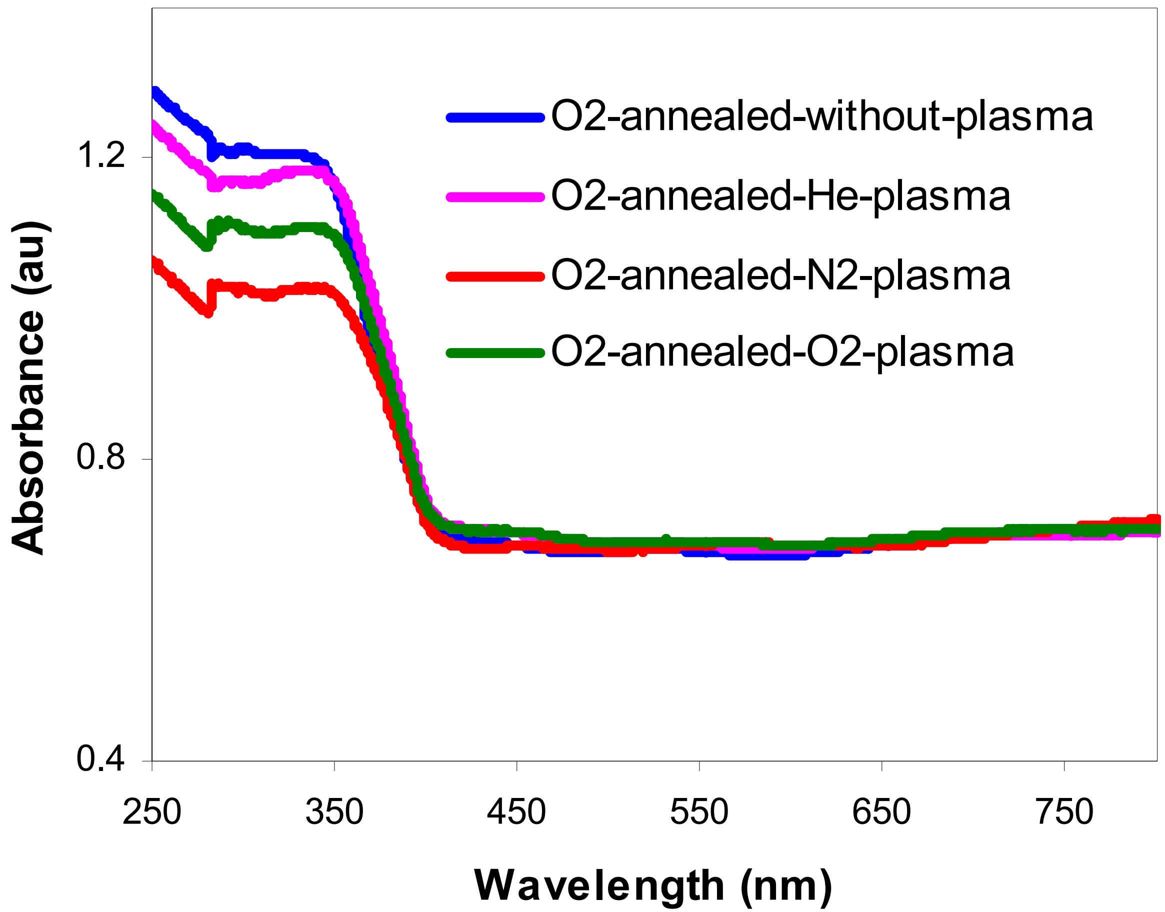
Laboratory set up for photoelectrochemical testing showing solar simulator (A), photo electrochemical cell (B) and potentiostat (C)

DR-UV-VIS spectra for as anodized sample



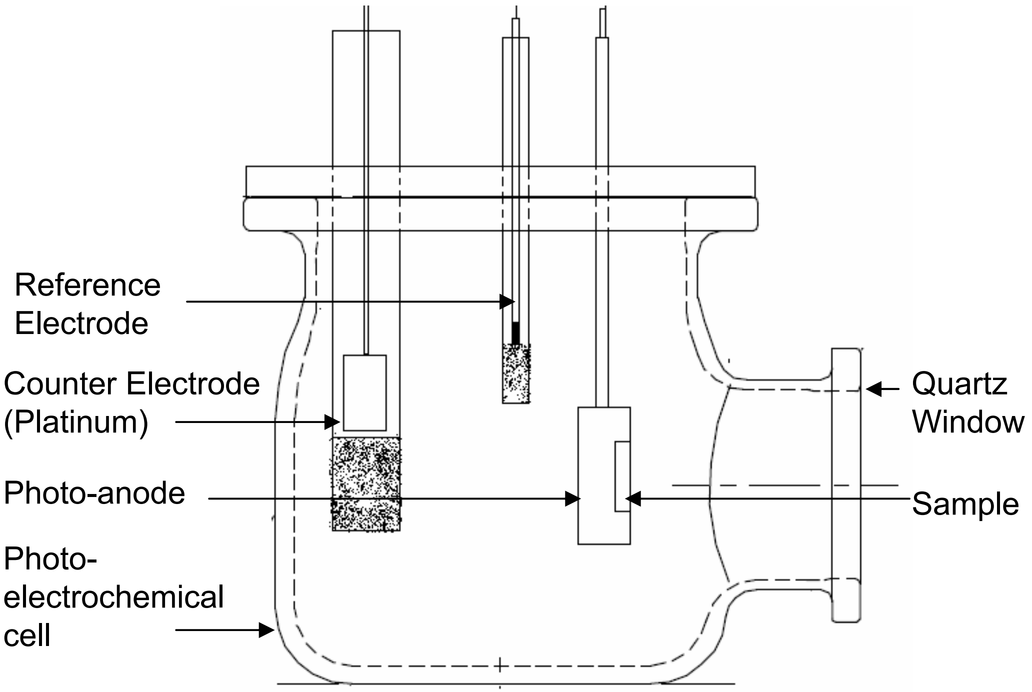
No significant difference was observed in absorbance of plasma treated and untreated oxygen annealed samples in visible region

DR-UV-VIS spectra for oxygen annealed samples

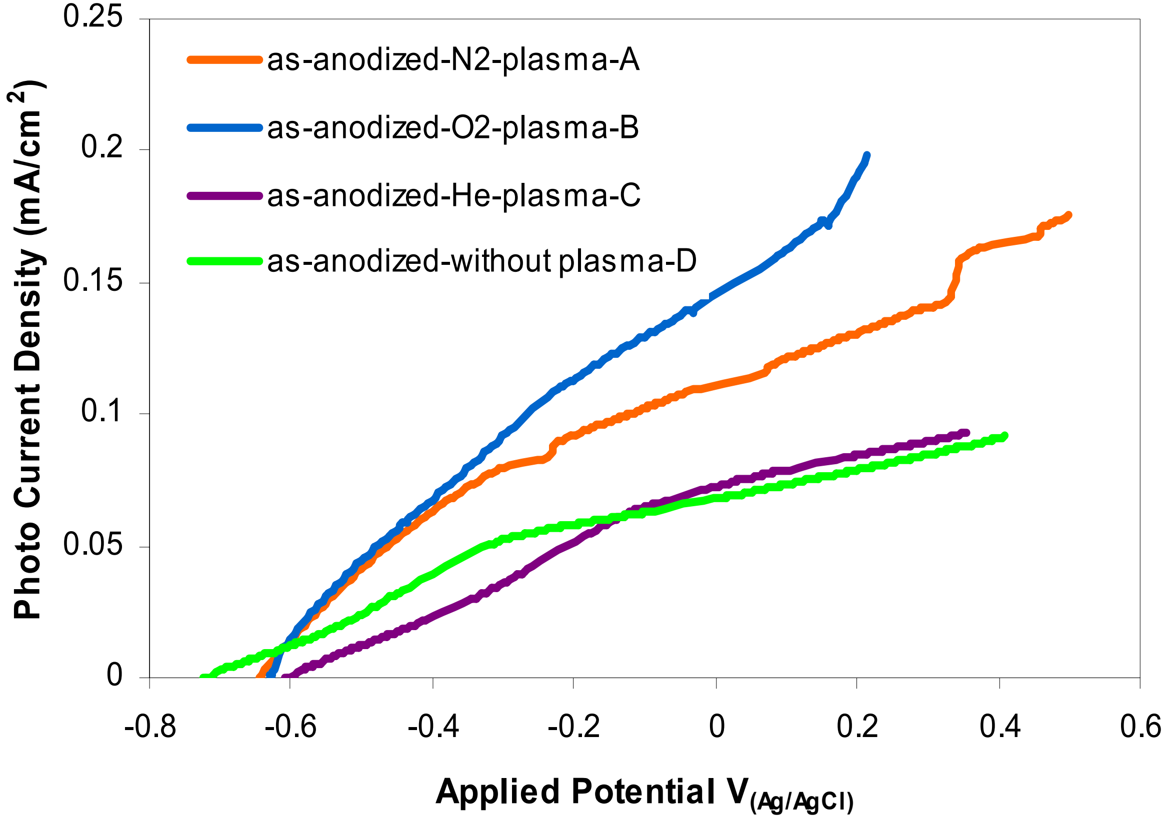


No significant difference was observed in absorbance of plasma treated and untreated oxygen annealed samples in visible region

Schematic of the photo-electrochemical cell used for testing samples

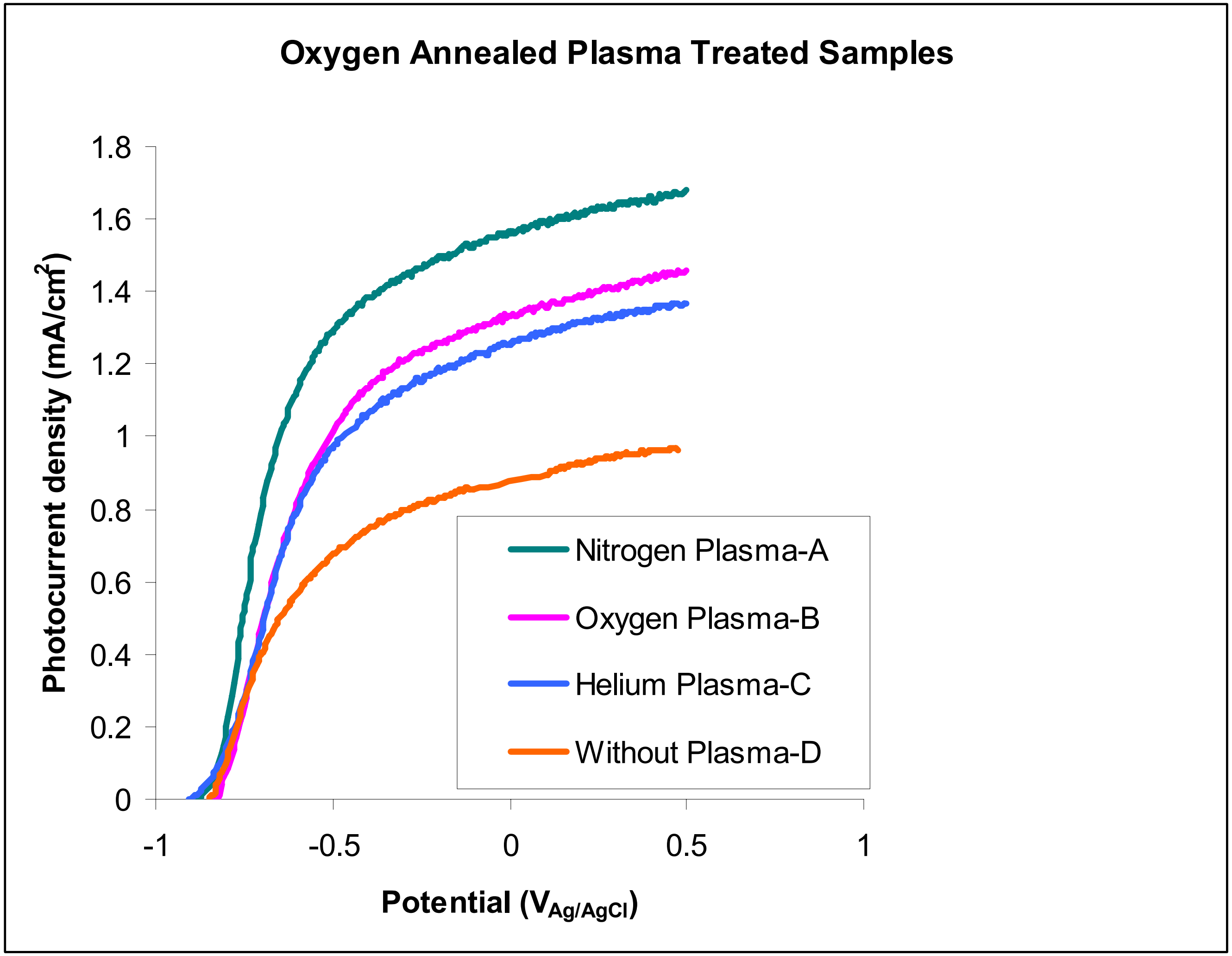


Functional characterization of as anodized samples prepared in acidic solution



Photocurrent for as anodized samples prepared in acidic solution.

Functional characterization of oxygen-annealed samples prepared in acidic solution



Photocurrent for oxygen-annealed samples prepared in acidic solution.

Results

- O/Ti ratio decreased from 3.32 for control to 2.80 after N plasma treatment, indicating removal of some physisorbed oxygen from the surface by plasma treatment. Nitrogen plasma replaced O atoms by N atoms. XPS data show incorporation of N in Lattice.
- It was also observed that Nitrogen concentration on the TiO_2 surface increased from 0.24% in the control to 0.96% after nitrogen plasma treatment.
- Nitrogen plasma increased photocurrent density of nano-tubular TiO_2 Photoanodes with and without Oxygen annealing process. When annealing was performed in Oxygen, the photocurrent density increased approx. 10 folds, from 0.16 mA/cm^2 to 1.6 mA/cm^2.

Discussion

- 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.

- The effective work function of insulators such as TiO_2 depends strongly upon the surface states and weakly upon the bulk bandgaps. Potentially, each surface atoms can also serve as electron traps causing nonradiative recombination of charge carriers.

Discussion (contd.)

- It is therefore essential to perform surface engineering to (1) remove surface contaminants and potential electron traps, (2) dope surface atoms so that the effective work function, after reaching equilibrium with the bulk band gaps, provide the desired photo-conversion properties, and (3) obtain surface structure to provide maximum optical absorption.

Future Work

- Determine optimum plasma treatment methods for surface modification of TiO_2 photoanodes.

- Characterize surface states of TiO_2 photoanodes by determining density of states, surface bandgaps & work function, 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 (contd.)

- Establish methods of surface state modification and characterization under normal operating conditions of PEC.

- Improve optical coupling of incident radiation and characterize photoelectrochemical properties of photoanodes as a function of wavelengths (near UV and visible) and radiation intensity.

Project Summary

Relevance: Develop cost effective and efficient photoanode material for optimizing photoelectrochemical hydrogen production

Approach: Plasma surface modification for removing surface contaminants and electron traps and for doping the surface with n-type dopants

Technical Accomplishment and Progress: Demonstrated enhanced photocurrent density with oxygen annealed photoanodes with surface doping with nitrogen

Collaboration: Active partnership with University of Nevada, Reno and Arkansas Nanotechnology Center

Proposed future research: Quantitative determination of plasma treatments needed for optimizing photoelectrochemical generation of hydrogen

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