PEC Based Hydrogen Production by Using Self-Cleaning Optical Windows

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Overview

Timeline

- August 2006
- July 2011
- Percent complete 90%

Barriers

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

Budget

- Total project funding
- DOE Total share $ 891,000
  - Hydrogen Production $297K
  - Hydrogen Storage $594K;
- Contractor share $222,750

Partners

- Interactions/ collaborations

  1. University of Nevada, Reno

  2. Arkansas Nanotechnology Center, UALR

  3. NASA Kennedy Space Center

  4. Boston University

Optimize surface properties of photoanodes and optical windows for efficient generation of Hydrogen with minimum losses

- Improve photocatalytic properties of photoanodes by (a) removing contaminants and unwanted surface states, (b) doping photoanode surface with nitrogen for creating oxygen vacancies and vacant acceptor states to enhance oxidation of water,
- Study interfacial charge transfer process iusing $TiSi_2$ photoanode anodes with a corrosion protective layer of TiO_2 thin film,
- Synthesize nanostructured photoanodes,
- Optimize surface structure of nanotubular electrodes for maximizing photocurrent density, and
- Develop an optical system with self-cleaning solar window with antireflection coatings

Rationale

- No single semiconductor electrode has been found to provide both high light absorption in the visible spectrum and corrosion resistance

- Interfacial processes needs optimization: photon absorption, charge separation, minimization of charge traps

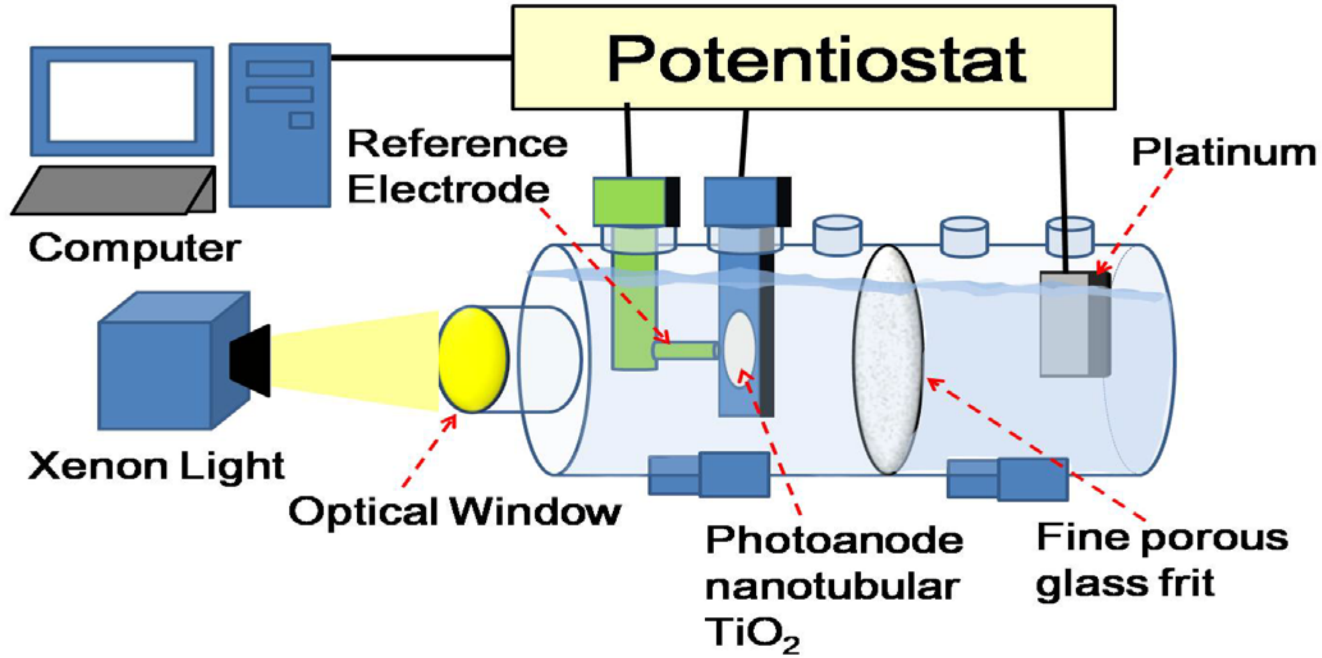
- Heterostructure electrodes such as $TiSi_2$ can harvest the visible and UV spectrum of solar radiation. Transparent TiO_2 electrode layer can be used to minimize photocorrosion

- Loss of photon flux by reflection and dust deposition on optical windows needs to be minimized.

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
- Develop self-cleaning optical windows with antireflection (AR) coatings for high efficiency transmission of photon flux to the photoanodes

Photoelectrochemical characterization



- 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

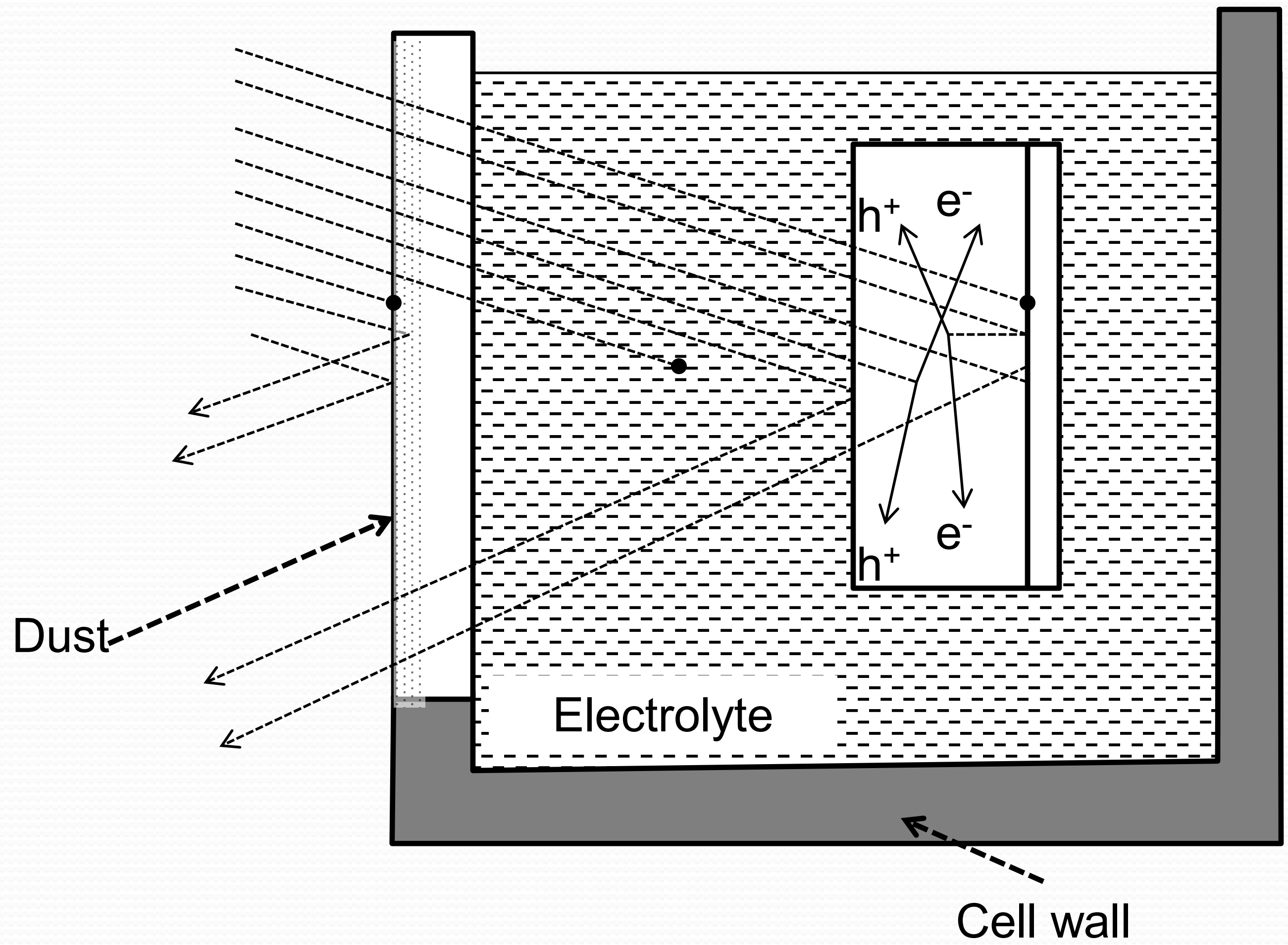
Transmission of sunlight to PEC yhrough optical windows, concentrators and fiber optics

Transmission losses:

- Reflection loss
- Scattering and absorption due to dust deposition
- Fiber optic transmission
- Absorption in the electrolyte

Transmission losses of sunlight

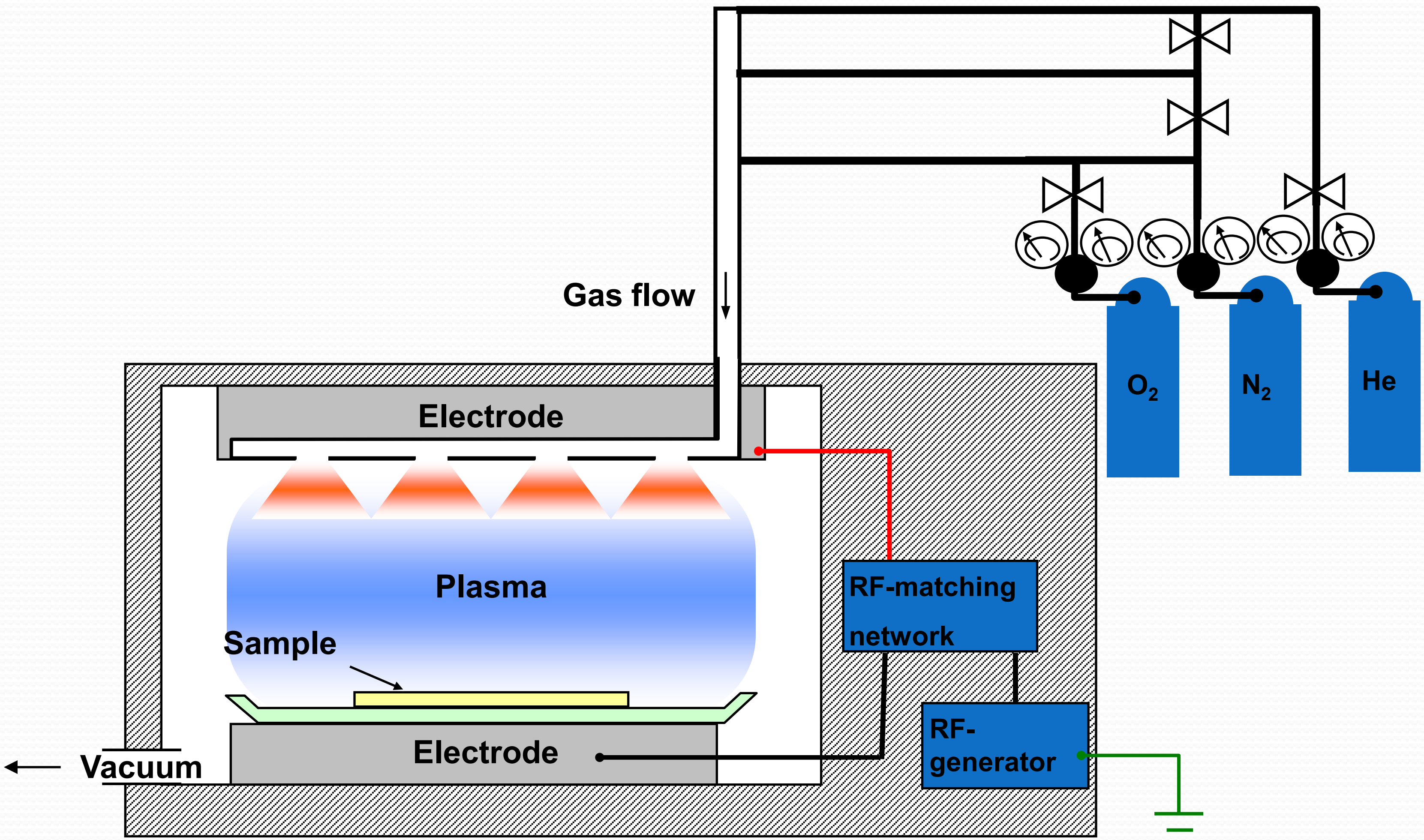
Loss caused by reflection, dust deposition and by electrolyte



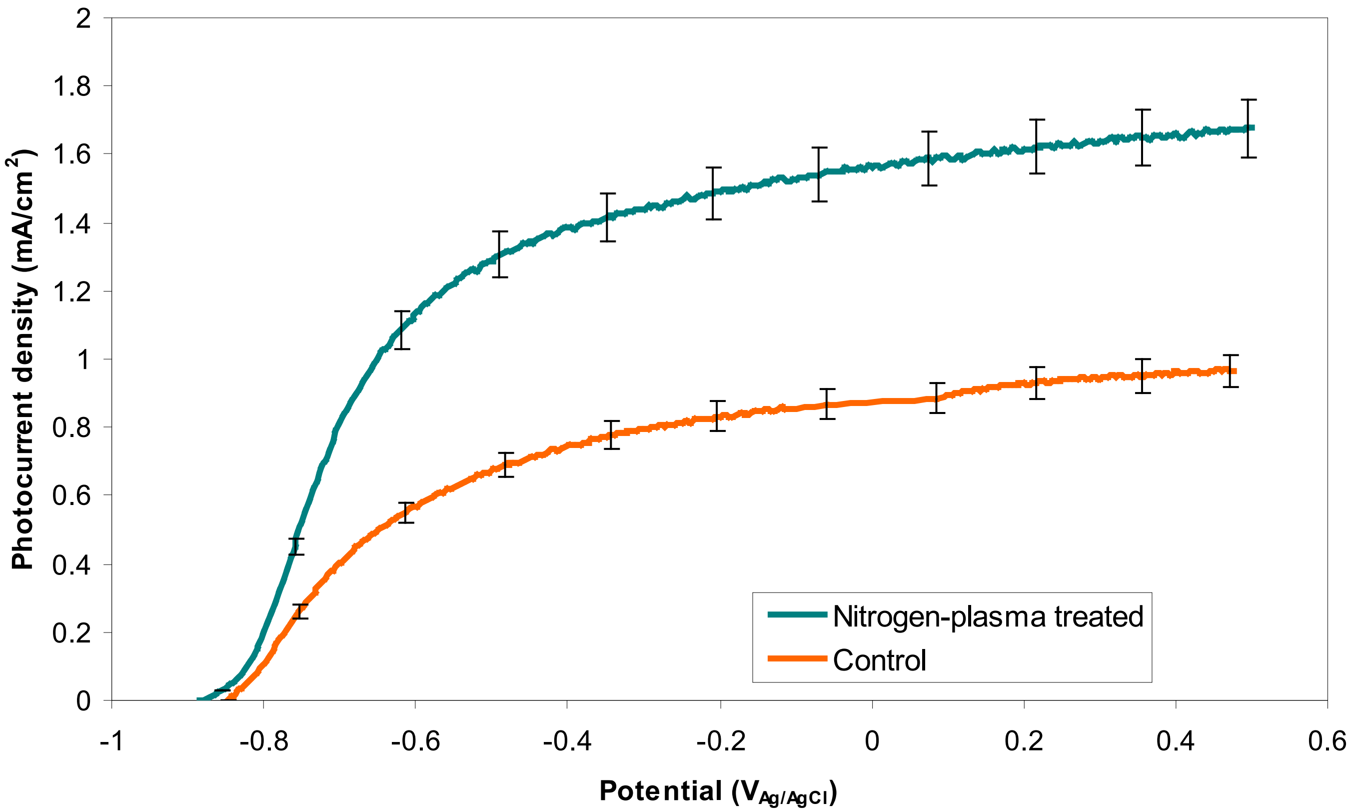
Plasma surface modification for removing contaminants and charge carrier traps

- Plasma surface modification was performed using low-pressure Ar/He plasma followed by Nitrogen plasma [13.56 MHz rf, 200W at an operating pressure of 150 mtorr]
- Samples were exposed to plasma for 10 minutes in each test run
- Ar/He plasma removed surface contaminants and charge carrier traps
- Nitrogen plasma provided substitutional doping (n-type) of TiO_2 at the surface creating oxygen vacancies
- Untreated and nitrogen plasma treated samples were tested for photocurrent density

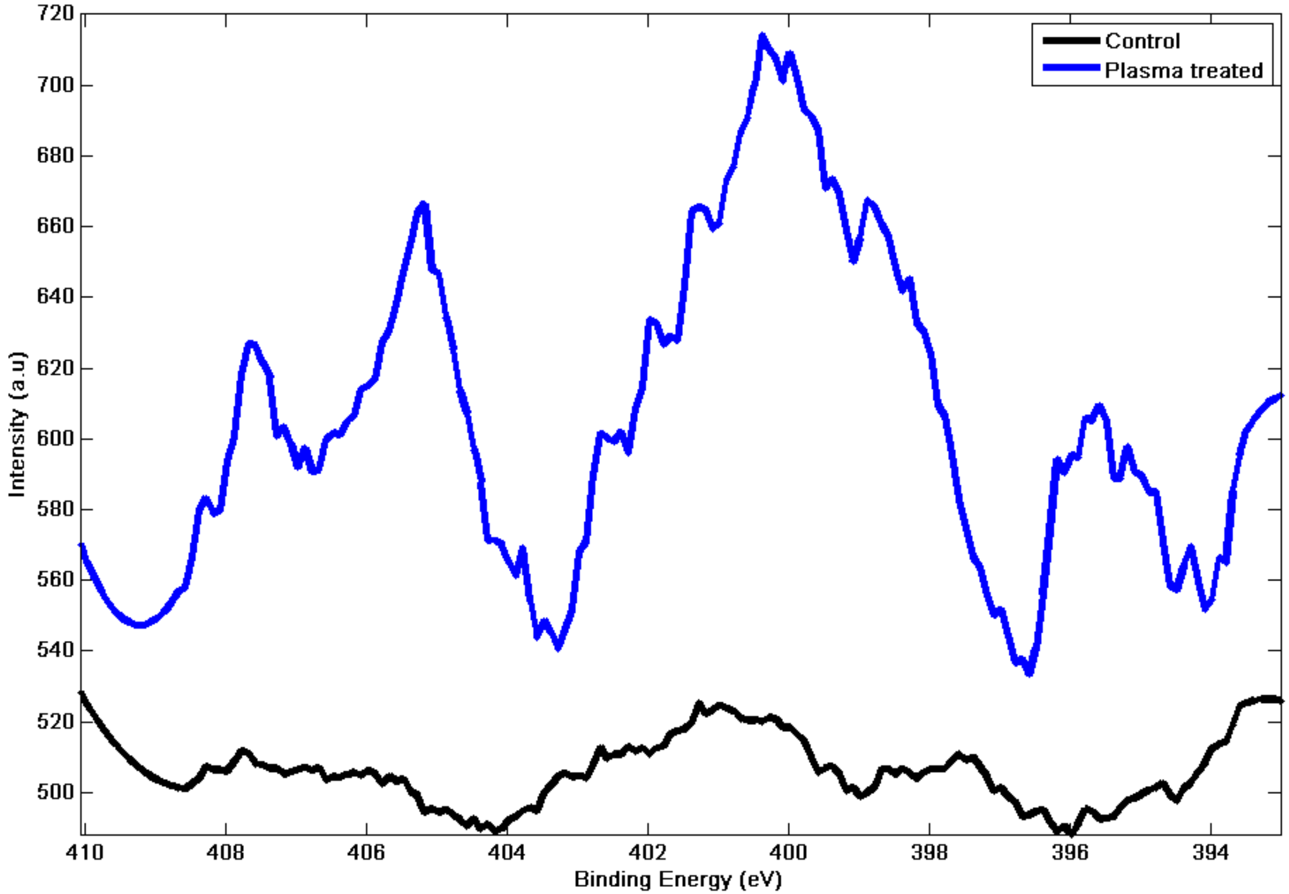
Schematic of low-pressure plasma reactor used for surface modification



Photocurrent density measurements for control and nitrogen plasma treated titania photoanodes



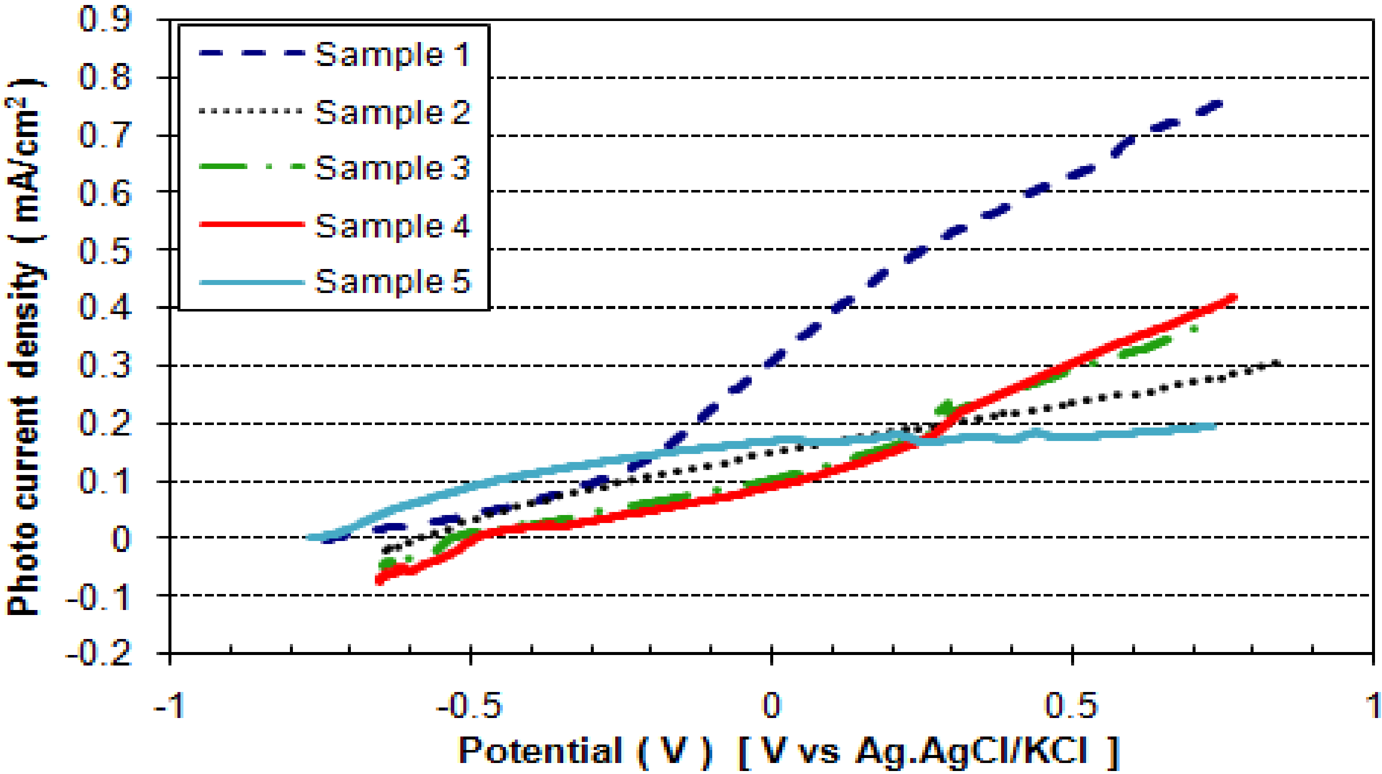
Sample description	OCP (bright), $V_{Ag/AgCl}$	Current at -0.2 V ($mA\ cm^{-2}$)	Current at 0.2 V ($mA\ cm^{-2}$)
Control	-0.85	0.83	0.93
N_2 plasma treated	-0.97	0.94	1.68



XPS spectrum (a) Control and (b) Nitrogen-Plasma treated TiO_2 photoanodes

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

Photocurrent density vs. anode nanostructure



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

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

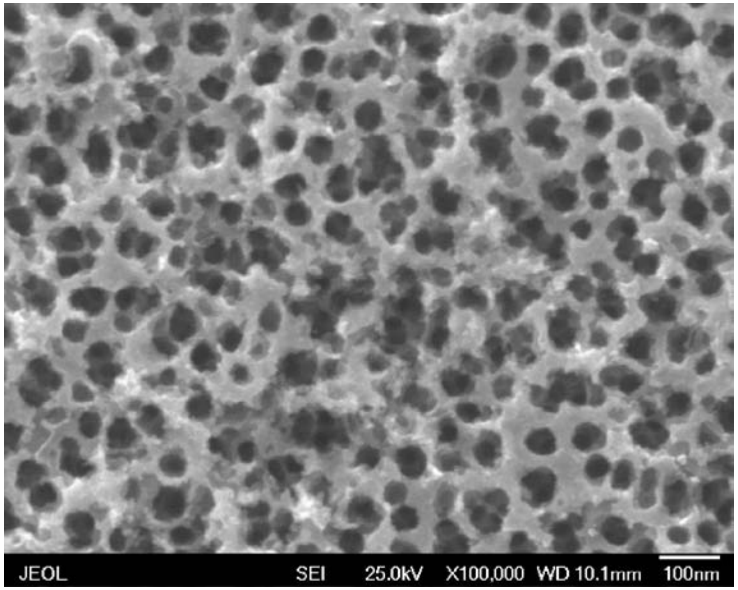
Stepped voltage anodization resulted in 55% higher current compared to the value of photocurrent at a constant voltage anodization

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 $TiSi_2$.

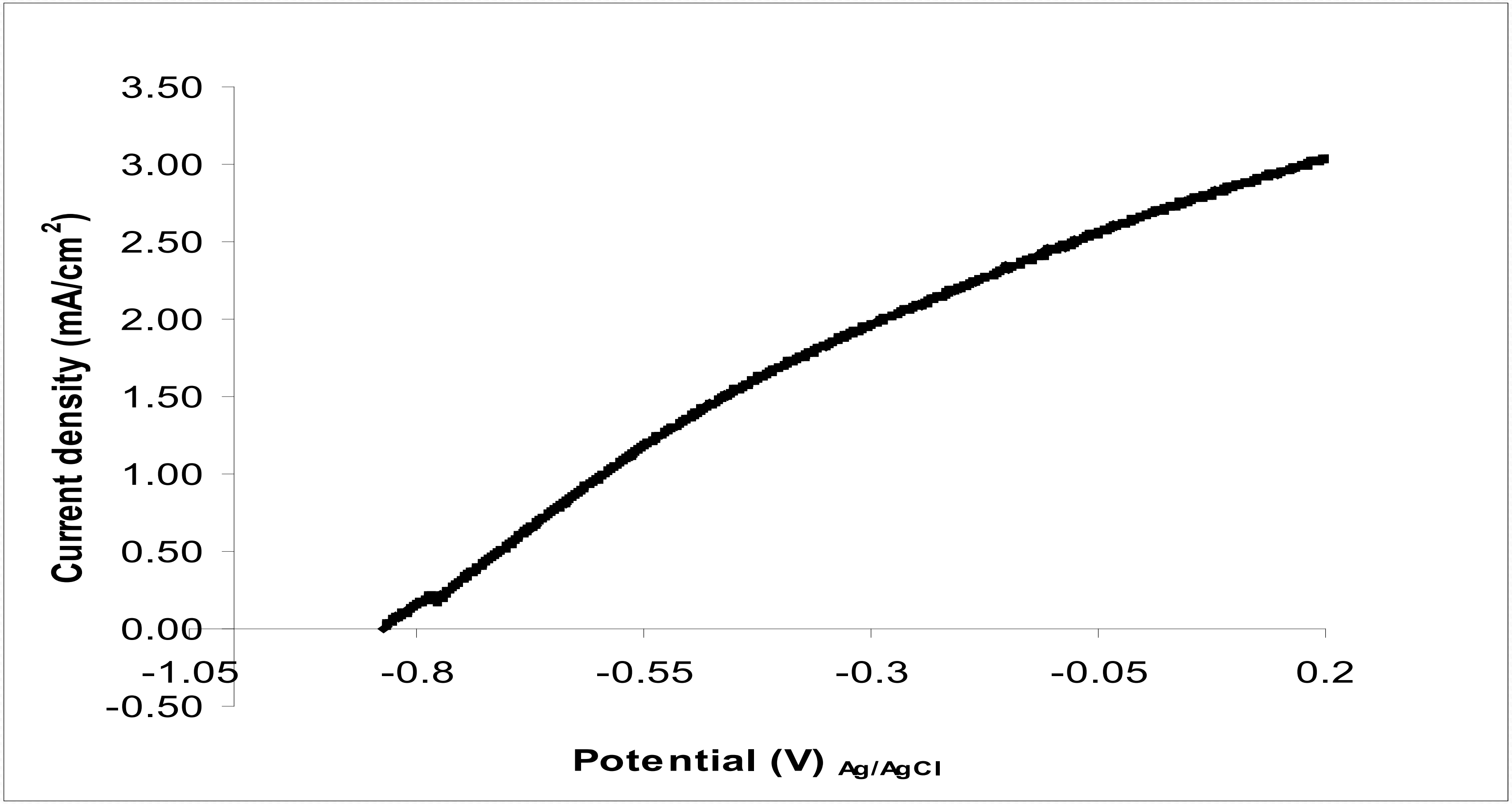
Nanoporous hybrid photoanaode

Ti_5Si_3 Film Anodization



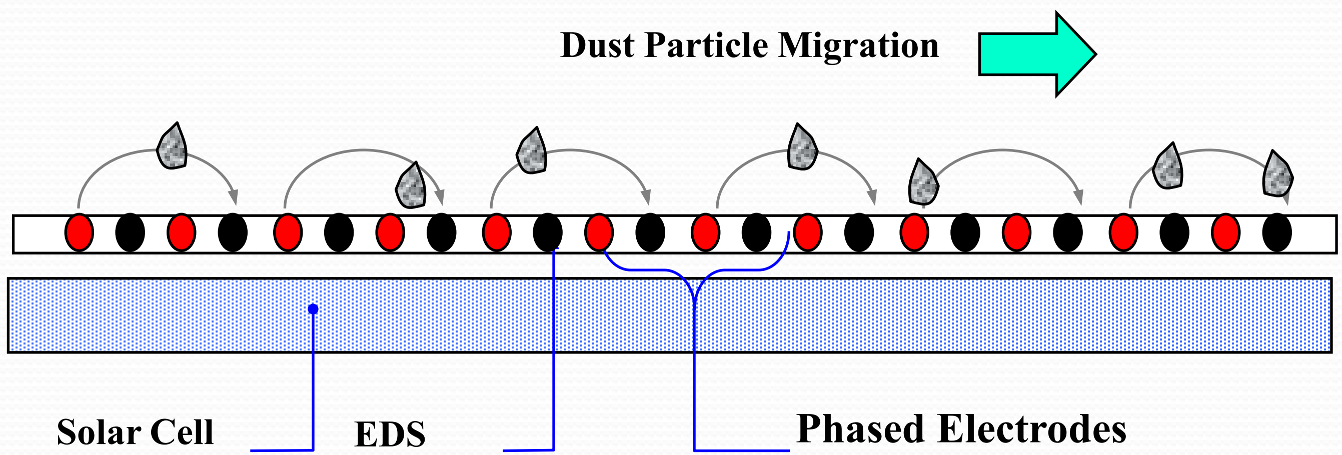
Solution: Ammonium fluoride 1.8g + DI water 22.5ml + EG 427.5ml
35V for 30 min for anodization

Photocurrent Density with $TiSi_2$ Particles on TiO_2 Nanotubular Electrode

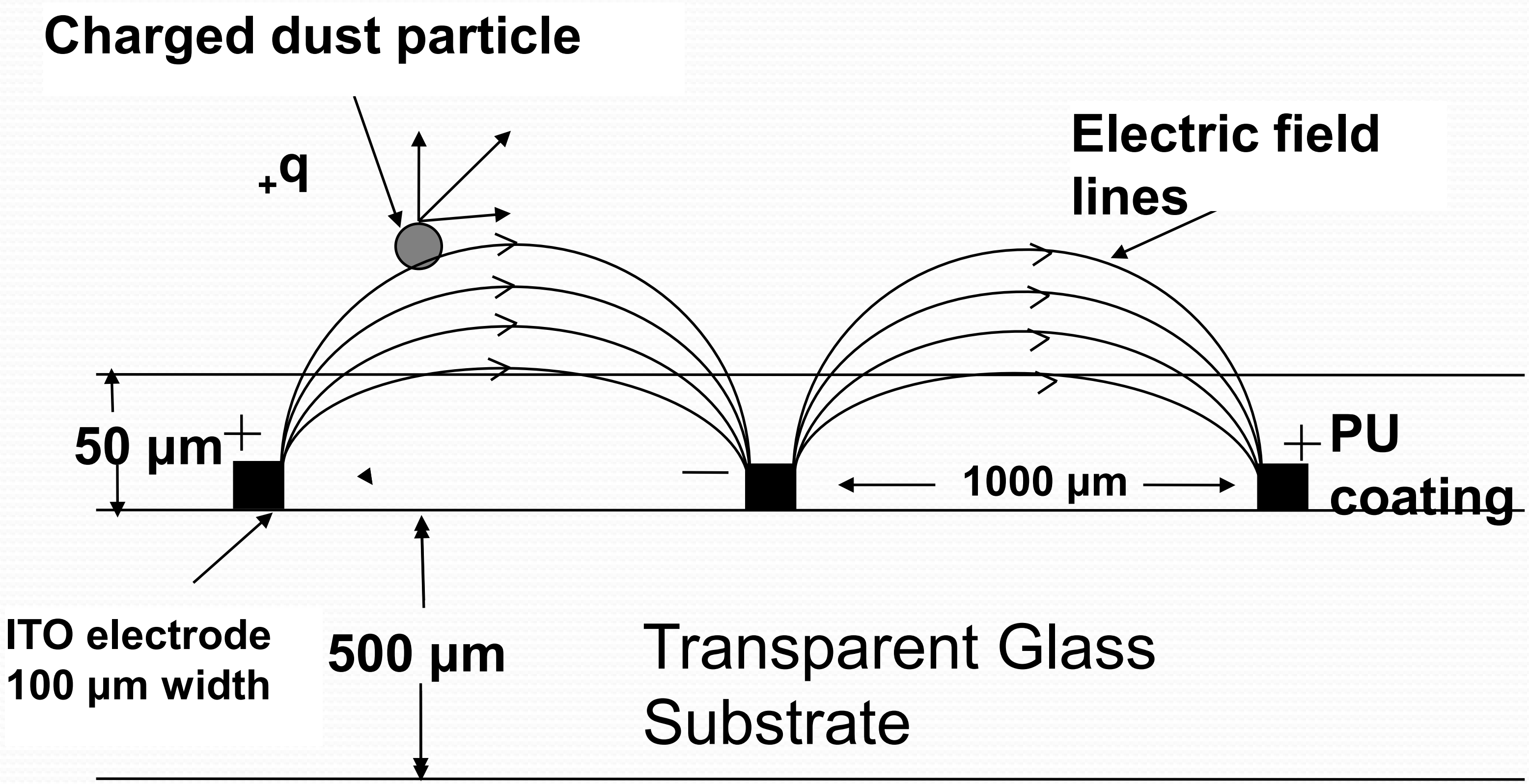


Electrodynamic Screen (EDS) & Antireflection Coatings on Optical Windows

- Dust particles are lifted by electrostatic force and moved away
- Minimizes reflection losses
- Improves solar-to-hydrogen generation efficiency



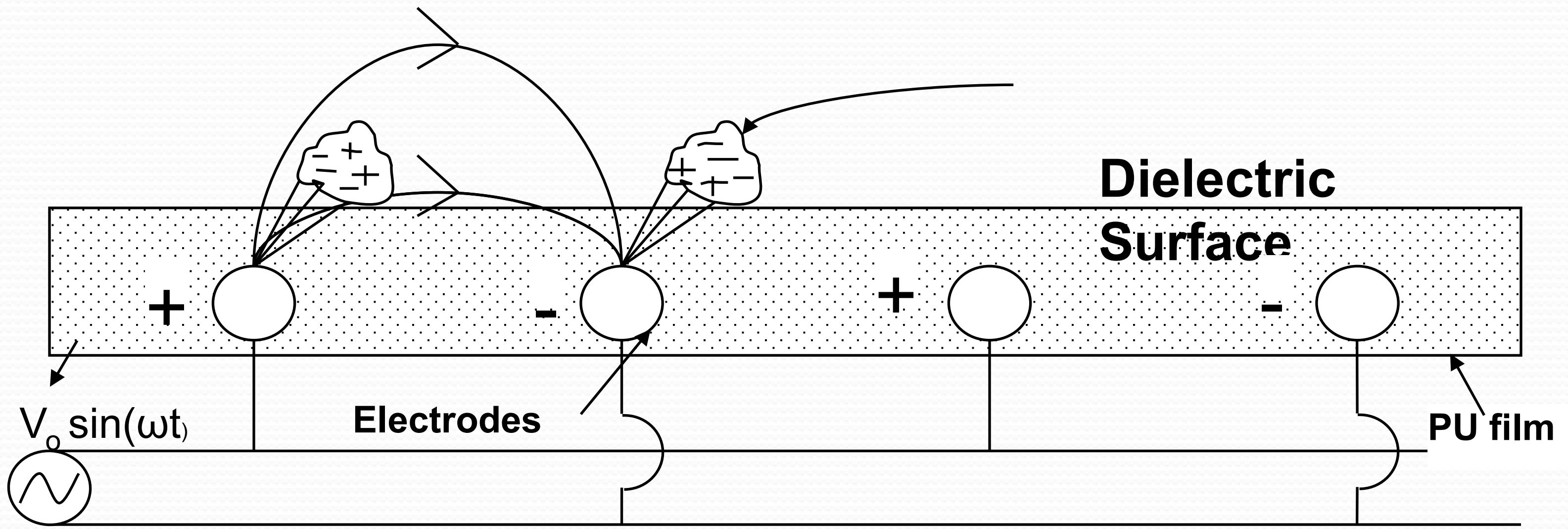
Dust Removal Mechanism



$$m_{\mathrm{p}}\frac{\mathrm{d}V_p}{\mathrm{d}t} + 6\pi\eta r V_p(\bar{r},t) = qE_0(\bar{r})\cos\omega t + F_{\mathrm{ext}}$$

This alternating Coulomb force kicks dust particles upwards and away. The traveling wave causes all of the deposited dust to slide off of the screen.

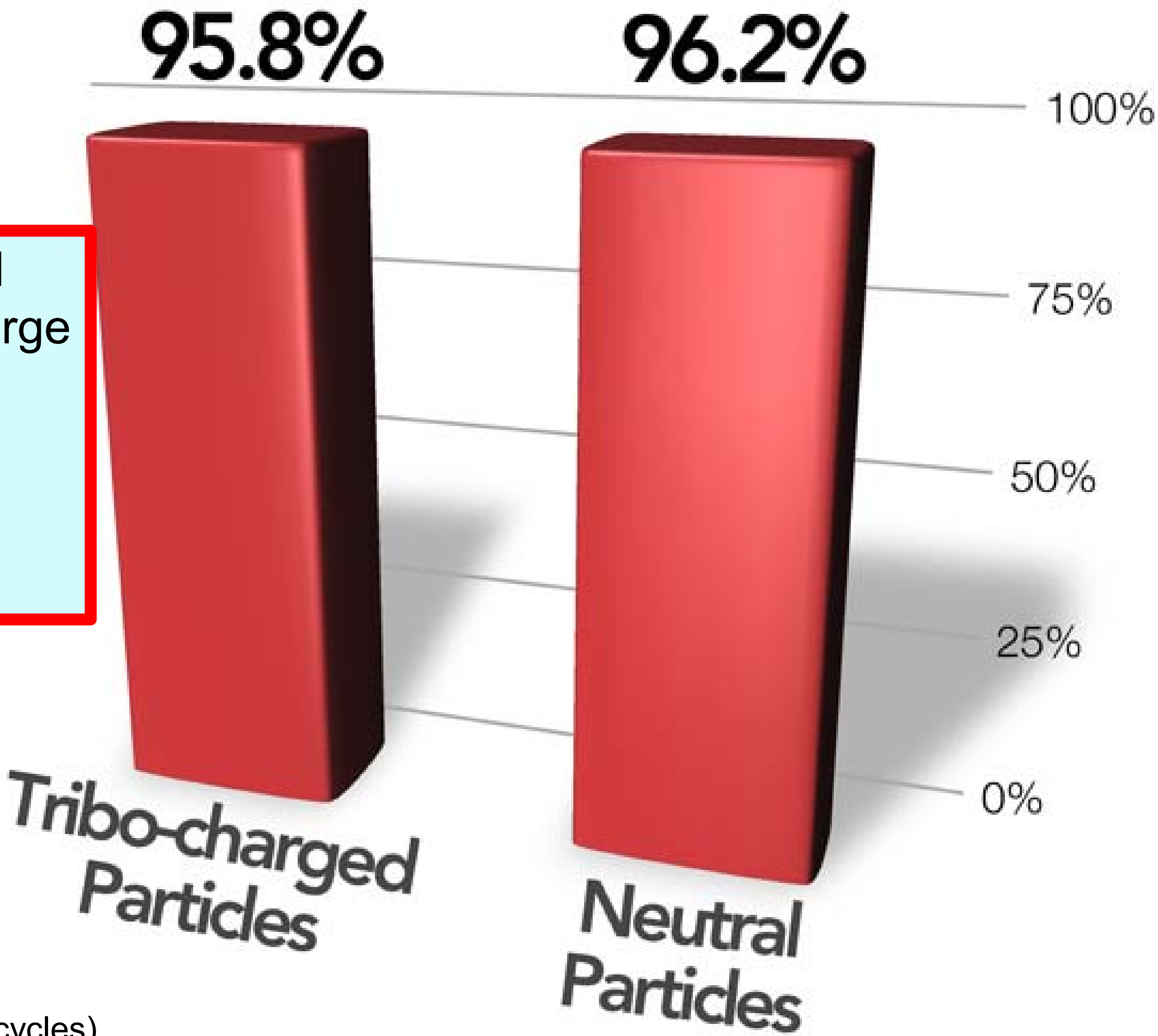
Rolling, Hopping, & Charging of Particles before Liftoff



$$\bar{F}_d = 2\pi r^3 \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \nabla |E|^2$$

Dielectrophoretic charging drives the dust off the screen by electrostatic force

Dust Removal Efficiency



With EDS and AR coating, large area optical windows can remain clean

(Over multiple cycles)

Summary

- 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.

- Stepped-voltage anodization was used to synthesize titania nanotubes of variable diameters for enhanced light absorption.

- Development of heterojunction $TiO_2/TiSi_2$ photoanodes have been studied, An e-beam deposition system was used.

- Self-cleaning optical windows can minimize photon flux losses due to dust deposition.

Technical Accomplishments

- **Plasma surface modification and surface doping increased photocurrent density of titania nanotubular electrodes**
- **Structural modification of TiO_2 nanotubes showed enhanced light absorption**
- **Synthesis of $TiSi_2$ based heterojunction electrodes has been designed.**
- **Self-cleaning AR coated windows provides efficient photon flux transmission**

Work under progress

- Develop patterned naotubular layered $TiSi_2$ and TiO_2 photoanodes.

- Characterize interfacial states between $TiSi_2/TiO_2$ /electrolyte by determining the optical absorption spectrum, durability and photocurrent density.

- Passivate interfacial states by hydrogen and nitrogen plasma treatments.

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, application of self-cleaning optical windows

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, development of self-cleaning optical windows

Collaboration: University of Nevada, Reno and Arkansas Nanotechnology Center

Proposed future research: Application of layered photoanodes, plasma treatments, passivation of interfacial states, and advanced optical systems for photoelectrochemical generation of hydrogen

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