

## II.G.7 PEC-Based Hydrogen Production with Self-Cleaning Solar Concentrator\*

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\*Congressionally directed project

- Hybrid tandem heterostructured PEC suffer from inefficient charge carrier transfer process across the semiconducting electrode/electrolyte junction due to the presence of interfacial energy traps, and lattice constant mismatch between layered semiconductors.
- Other nanostructured devices involving oxynitrides, such as  $(\text{Ga}_{0.88}\text{Zn}_{0.12})(\text{N}_{0.88}\text{O}_{0.12})$  with co-catalysts, such as  $\text{Rh}_{2-x}\text{Cr}_x\text{O}_3$  shows considerable promise for hydrogen production but the cost of the materials and toxicity involved in some cases show further studies are needed to synthesize electrodes for commercial hydrogen production.

### Technical Targets

Solar-to-hydrogen efficiency: 10% by 2015 by developing photoanodes having efficient light absorption in the visible range by reaching quantum yield of 30% at 600 nm and long-term corrosion resistance for commercial-scale  $\text{H}_2$  production.

### FY 2011 Accomplishments

- Synthesized nanotubular  $\text{TiO}_2$  photoanodes with stepped voltage anodization and surface modification of  $\text{TiO}_2$  photoanodes with He plasma which minimized charge carrier traps and contaminants.
- Surface cleaning and doping of the photoanode with helium plasma treatment followed by nitrogen plasma followed by He plasma treatment, to form  $\text{TiO}_{2-x}\text{N}_x$  at the surface thus leaving the bulk semiconductor for high electron conductivity and created oxygen vacancies at the surface for improved photocurrent density.
- Increased photocurrent density by more than 80% by plasma treatments and enhanced light absorption by 55% with modified nanotubular structure by step-voltage anodization compared to the untreated  $\text{TiO}_2$  photoanodes.
- Synthesis of tandem heterostructured layered electrodes with lower bandgap layer (e.g.  $\text{WO}_3$ ,  $\text{TiSi}_2$ ) behind a wide bandgap semiconductor (e.g.  $\text{TiO}_2$ ) facing the electrolyte.
- Development of self-cleaning solar concentrator for operating the PEC devices at irradiance level of 10 sun for enhancing hydrogen generation rate.



### Introduction

Hydrogen is an ideal renewable chemical fuel yet its production by splitting water using sunlight has been

### Fiscal Year (FY) 2011 Objectives

- Synthesize nanostructured  $\text{TiO}_{2-x}\text{N}_x$  photoanodes and tandem heterostructured photoanodes with  $\text{WO}_3$  and  $\text{TiSi}_2$  to improve absorption of light in the visible spectrum in conjunction with  $\text{TiO}_2$  film at the outer surface forming interface between the solid electrode and the liquid electrolyte.
- Improve photocatalytic properties of photoanodes by plasma treatments for (a) removing contaminants and unwanted surface states, (b) doping the photoanode surface with nitrogen to create oxygen vacancies and vacant acceptor states to enhance oxidation of water, and (c) optimizing surface structure of nanotubular electrodes for increasing photocurrent density.
- Design optical system with self-cleaning Fresnel-lens based solar concentrator to operate the photoelectrochemical (PEC) electrode at 10 sun irradiance.
- Optimize surface structure of the layered electrodes for minimizing the charge carrier traps.

### Technical Barriers

- Metal oxide semiconductor photoanodes, such as  $\text{TiO}_2$ , extensively studied for hydrogen production, cannot provide both the needed light absorption in the visible spectrum and yet provide resistance to photocorrosion.

one of the most formidable challenges for the last several decades [1–6]. While the potential advantages of PEC-based production of hydrogen have not yet been realized recent developments show emergence of new nanostructural designs of photoanodes and choices of materials with significant gains in photoconversion efficiency [7–16]. Significant efforts are being made for reaching the quantum yield of 30% and long-term durability needed for commercial production.

$\text{TiO}_{2-x}\text{N}_x$  meets nearly all the requirements for PEC-based hydrogen production with respect to its abundance, environmental safety, and durability [7], except for its wide bandgap and consequent poor absorption of sunlight in the visible spectrum. Until now, no single compound semiconductor photoanode has been found which satisfy both the critical needs of light absorption and the long-term durability against photocorrosion. For example, tantalum oxide and gallium nitrides have demonstrated better results for hydrogen production but their cost would be more than 50 times the cost of  $\text{TiO}_2$  based catalyst [7]. Other nanostructured devices have surpassed the performance of  $\text{TiO}_2$  for water splitting, but these materials involve, for example, La-doped  $\text{NaTaO}_3$  and oxynitrides, such as  $(\text{Ga}_{0.88}\text{Zn}_{0.12})(\text{N}_{0.88}\text{O}_{0.12})$  with co-catalysts,  $\text{Rh}_{2-x}\text{Cr}_x\text{O}_3$  showing considerable promise for hydrogen production [15, 16] but the cost of the materials and toxicity involved in some cases are of concern.

Common to most of current investigations, are the studies on: (1) effects of nanostructural surface morphology (nanorods, nanotubes), (2) reduction of interfacial charge carrier traps, (3) increase in the effective surface area for enhancing light absorption at semiconductor-electrolyte interface, and (4) optimum level of sunlight irradiance for operation of the PEC devices at their maximum efficiency. The studies reported here are focused on the interfacial aspects of the PEC-based hydrogen production and optimization of solar irradiance at the photoanode surface.

## Approach

To address the problem related to the wide bandgap of  $\text{TiO}_2$ , one approach is to develop a hybrid nanostructured photoanode (Figure 1) comprised of thin-film layers of semiconductors with lower bandgap (e.g.  $\text{WO}_3$ ,  $\text{TiSi}_2$ ) behind a wide bandgap semiconductor (e.g.  $\text{TiO}_2$ ) facing the electrolyte [15]. Similar photoanodes can be synthesized with nanotubular structures with outer layer of titanium dioxide ( $\text{TiO}_2$ ) covering nanotubes of  $\text{WO}_3$ ,  $\text{CdS}$  or  $\text{TiSi}_2$ . The low bandgap semiconductors have high efficiency in light absorption covering the visible solar spectrum while  $\text{TiO}_2$  provides corrosion protection. The layered nanotubular electrodes can be arranged in a patterned array for trapping sunlight more effectively compared to the densely packed nanotubular structures, providing large illuminated area effective for electrolysis. While the nanostructure greatly improves the interfacial surface area and light absorption, the efficiency of the charge carrier transport across the

interfaces and removal of charge carrier traps at the semiconductor-electrolyte interface need to be investigated for different heterostructures including layered films, nanotubes and nanoparticles.

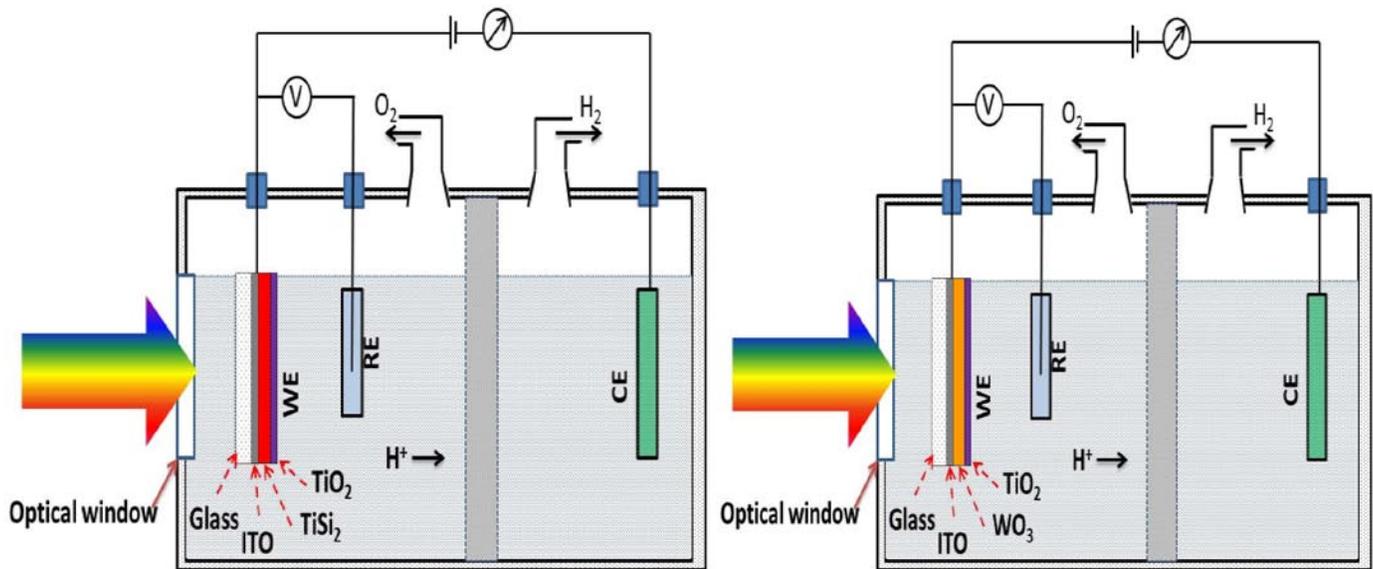
Interfacial charge carrier transfer phenomena govern the PEC-based hydrogen generation process. Studies on the role of surface and interface states in the charge carrier transport and the necessity for matched lattice structure in using heterostructured semiconductors (such as  $\text{TiO}_2$  and  $\text{TiSi}_2$ ) have been reported in the literature [7], however, the chemical and physical control mechanisms for mitigating the losses due to the presence of charge carrier traps and for minimizing photocorrosion of the electrodes are yet to be established.

Optimization of the optical system for illuminating photoanode at the desired irradiance level with solar concentrator is needed for obtaining maximum efficiency at a low cost. For collecting sunlight at the maximum level it is necessary to use a solar concentrator with self-cleaning properties to avoid loss of light transmission efficiency due to the deposition of dust. It is expected that large-scale PEC-based hydrogen production facility will take place in semi-arid and desert locations where irradiance level is high but these places are often the dustiest locations.

## Experimental Studies and Results

Our experimental studies consisted of: (1) synthesis nanotubular  $\text{TiO}_2$  photoanodes by anodization of Ti foil followed by annealing under oxygen atmosphere; (2) surface modification of  $\text{TiO}_2$  photoanodes with He plasma for removing organic contaminants and charge carrier traps; (3) surface doping of the photoanode surface with nitrogen plasma to form  $\text{TiO}_{2-x}\text{N}_x$  (Figure 2a) and creating oxygen vacancies at the surface thus leaving the bulk semiconductor pristine in its crystalline  $\text{TiO}_2$  structure for high electron conductivity for improved photocurrent density [17]; (4) optimization of the structure of the nanotubes by varying anodization voltage for increasing light absorption; (5) development of layered electrodes of  $\text{WO}_3$ ,  $\text{TiSi}_2$  and  $\text{TiO}_2$ ; (6) analysis of the photoanode structures (Figure 2b) using X-ray photoelectron spectroscopy (XPS); and (7) evaluation of surface-modified nanostructured photoanodes for PEC generation of hydrogen.

The test photoanodes prepared for evaluating the photoelectrolytic properties were annealed under both oxygen and nitrogen atmospheres achieve crystallization of  $\text{TiO}_2$  in its anatase form. The PEC apparatus used for measuring photocurrent density of the test photoanodes under dark and illuminated conditions consisted of: (1) a potentiostat/galvanostat electrochemical instrument Model 283, (2) a Xenon lamp ( $30 \text{ mW/cm}^2$ ), (3) a 60 mm-diameter quartz optical window, and (4) a reference electrode ( $\text{Ag/AgCl}$ ) placed close to the photoanode. The electrolyte used was 1M KOH (pH~14) + de-ionized water solution. The experimental arrangements are shown in Figure 1.



**FIGURE 1.** Experimental arrangement for PEC generation of hydrogen using different photoanodes (a) hybrid  $\text{TiSi}_2$  and  $\text{TiO}_2$  electrode (left) and (b) hybrid  $\text{WO}_3$  and  $\text{TiSi}_2$  electrode (right). A Pt counter electrode was used in both cases. WE, RE, and CE denote working electrode, reference electrode, and counter electrode respectively. The glass plate is coated with indium tin oxide (ITO) to form a transparent conductive substrate for depositing photoanodes.

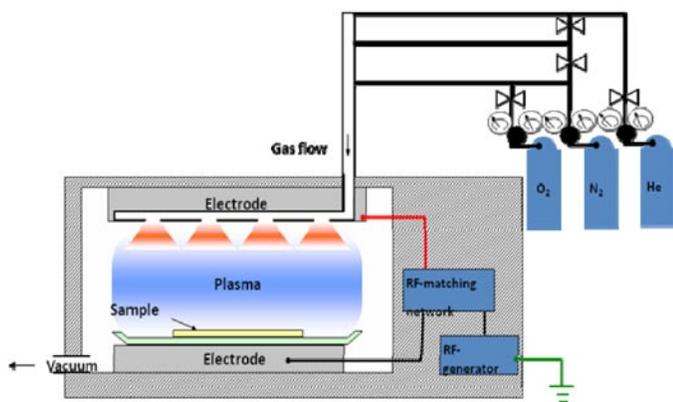
An electrodynamic screen was developed for operating solar concentrators using Fresnel lens with self-cleaning properties against deposition of dust on the sunlight collector surface [8]. A transparent electrodynamic screen can remove the dust layer in less than two minutes without any need for water or mechanical method for cleaning.

**Results**

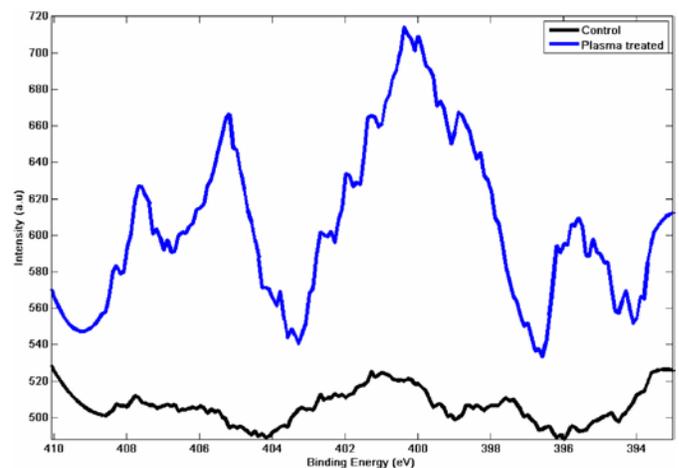
XPS analysis indicated the incorporation of N in titania lattice structure of the photoanode surface. As shown in Figures 2a and 2b, the narrow scan N 1s spectrum is demonstrated at 400 and 396 eV, which has been ascribed

to the presence of nitrogen in the lattice structure either as substitutional dopants for O, or as interstitial dopants in the  $\text{TiO}_2$  crystal structure.

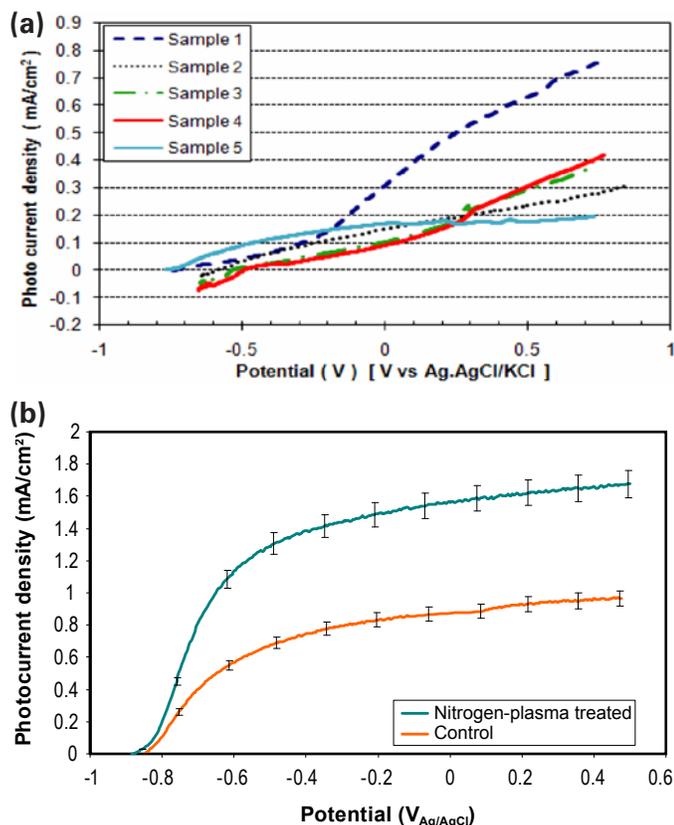
Stepped-voltage anodization was used to synthesize titania nanotubes of variable diameters. Photocurrent density vs bias voltage plotted for samples anodized at different voltages. Annealing of the photoanodes was optimized. Most significant improvement came from the nitrogen plasma treatment of titania photoanodes which resulted in 80% increase in photocurrent density. Plasma surface cleaning with helium plasma and surface doping by nitrogen plasma increased photocurrent density of titania nanotubular



**FIGURE 2a.** Schematic of low-pressure plasma reactor used for surface modification including He-plasma for surface cleaning and minimizing surface charge carrier traps followed by surface doping of with N-plasma to form  $\text{TiO}_{2-x}\text{N}_x$  at the photoanode surface.



**FIGURE 2b.** XPS Spectrum (a) Control and (b) Nitrogen-Plasma treated  $\text{TiO}_{2-x}\text{N}_x$  Photoanodes

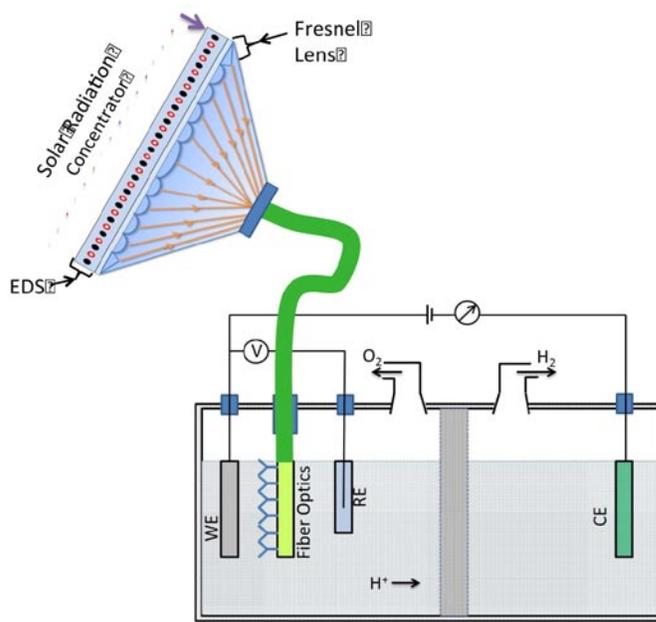


**FIGURE 3.** Photocurrent density measurements for evaluating photoanodes synthesized under different conditions. The electrolyte used was 1M KOH (pH~14) + de-ionized water solution. A Xe lamp was used to illuminate photoanodes at an irradiance level of 30 mW/cm<sup>2</sup>. (a) Photocurrent density vs. stepped voltage anodization of TiO<sub>2</sub> nanotubular electrodes; sample #1 was anodized at three steps: at 20 V for 40 min, next 40 V for 10 min, and finally 60 V for 10 min, Sample #2 was anodized in one step, 60 V for 60 min, sample #3 was anodized at 40 V for 60 min, and samples 4 and 5 were both anodized in one step at 20 V for 60 minutes. (b) Photocurrent density measurements for control and nitrogen plasma treated titania photoanodes before and after N plasma treatment to form followed by He plasma cleaning. TiO<sub>2-x</sub>N<sub>x</sub> was formed at the surface of TiO<sub>2</sub> nanotubes. Photocurrent density increased from 0.93 mA/cm<sup>2</sup> to 1.68 mA/cm<sup>2</sup> at a bias voltage of 0.2 V.

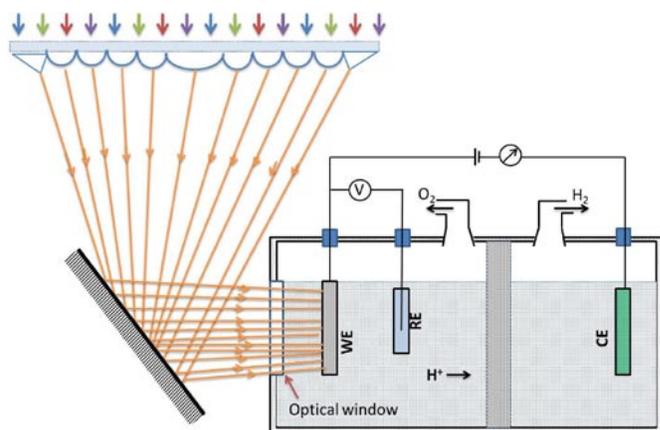
electrodes [17]. The results showed enhanced light absorption and increased photocurrent density by 55% (Figure 3).

Several deposition processes for developing heterojunction TiO<sub>2</sub>/TiSi<sub>2</sub> photoanodes have been studied; an e-beam deposition system has been used for depositing thin films of different photoanode materials. An electro spray system has been designed for electrostatic coating of TiSi<sub>2</sub> particles with nanoparticles of TiO<sub>2</sub>.

Our experimental data show that deposition of fine atmospheric dust on solar collector with surface mass density of 4 g/m<sup>2</sup> can obscure sunlight by more than 40%. Design of a self-cleaning solar concentrator has been completed with mirrors and fiber optics for illuminating the photoanode surface at 10-sun level of irradiance is shown in Figures 4a and 4b.



**FIGURE 4a.** Illumination of photoanode with self-cleaning solar concentrator at an irradiance level of 10 sun. A fiber optics-based light coupling is used to allow illumination of the photoanode at the front surface of the electrode to minimize reflection loss at the outer glass optical window and at the back surface of the inner indium tin oxide-coated glass substrate. An electrodynamic screen is used to remove dust deposited on the front surface of the Fresnel lens.



**FIGURE 4b.** Illumination of photoanode with self-cleaning solar concentrator at an irradiance level of 10 sun. A mirror is used to allow illumination of the photoanode at the back surface. This arrangement suffers from reflection losses at the outer glass window and the back surface of the inner indium tin oxide-coated glass substrate. There is no fiber optic coupling loss in this arrangement.

## Conclusions

Our experimental studies with plasma surface treatments with helium and nitrogen gas show a significant

increase of  $\text{TiO}_{2-x}\text{N}_x$  photoanode current density compared with the untreated surface of the electrodes. The nitrogen plasma treatment increased acceptor surface states and increased oxygen vacancies. Surface cleaning of the photoanode by low-temperature helium plasma treatment removed a major fraction of the contaminants (adsorbates) from the surface.

The present work reports the importance of systematic investigations of: (1) the morphological structure of the nanotube arrays, (2) the plasma treatment process for surface doping of  $\text{TiO}_2$  nanotubular photoanode with N for increasing oxygen vacancies, and (3) optimization of the annealing process for crystallization of  $\text{TiO}_2$  for improving photocatalytic generation of hydrogen from water. The test results show promising aspects of tuning several parameters involved in developing heterostructured photoanodes for PEC-based hydrogen production. Development and design of self-cleaning solar concentrator for increasing solar irradiance at the photoanode surface is reported.

### Plan for Future Studies

Develop: (1) hybrid nanostructured photoanode comprised of thin-film layers of semiconductors with lower bandgap (e.g.  $\text{WO}_3$ ,  $\text{TiSi}_2$ , CdS) behind a wide bandgap semiconductor (e.g.  $\text{TiO}_2$ ) facing the electrolyte, (2) patterned array of nanotubular electrodes for trapping sunlight more effectively compared to the densely packed nanotubular structures, providing large illuminated surface area effective for electrolysis, and (3) encapsulated nanoparticles of core-shell design using narrow and wide bandgap materials.

We plan to investigate the charge carrier transport process across the interfaces and removal of charge carrier traps at the semiconductor-electrolyte interface by passivation of the dangling bonds for different heterostructures, including layered films, nanotubes and nanoparticles.

Study methods for: (1) optimizing the film thickness (in the nanometer to micrometer range, to improve tunneling and charge carrier transport); (2) matching the crystalline structures of the layered semiconductors; and (3) measuring the photocurrent conversion efficiency (incident photon conversion efficiency vs  $\lambda$ ), corrosion resistance, and photo-generated carrier concentration decay rate (by using a radio frequency-conductivity probe); and (4) investigate the use of self-cleaning solar concentrator for operating the PEC at an optimum irradiance level.

### FY 2011 Publications/Presentations

#### Publications

1. Rajesh Sharma, Hidetaka Ishihara, Alexandru S. Biris, Malay K. Mazumder, "Development of surface engineered nanostructured photoanodes for enhanced photo

electrochemical processes," *IEEE Industry Applications Society 43<sup>rd</sup> Annual Meeting*, Houston, 2010.

2. Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma, Franklin Hardcastle, Ganesh K Kannarpady, Malay K Mazumder, "Electrochemical Synthesis of Titania Nanostructural Arrays and their Surface Modification for Enhanced Photoelectrochemical Hydrogen Production," *Chemical Physics Letters*, Volume 489, Issues 1-3, 1 April 2010, Pages 81-85, 2010.

3. M.K. Mazumder, A.S. Biris, R. Sharma, H. Ishihara, G. Kannarpady, and P. Girouard "PEC Based Hydrogen Production with Self-Cleaning Solar Concentrator" Poster presentation at the DOE AMR meeting at Washington D.C., May 10, 2011.

#### Patent Application

1. "Plasma Treated Nanostructured Titania Photo-anode for Hydrogen Generation" Rajesh Sharma, Alexandru Biris, Malay Mazumder, US Provisional patent application, 2010.

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**18.** Mazumder, M.K., Biris, A.S., Johnson, C.E., Yurteri, C.Y., Sims, R.A., Sharma, K. Pruessner, S. Trigwell and. Clements, *Particles on Surfaces 9: Detection, Adhesion and Removal*, Brill Publisher, 2006, pp.1-29. ISBN 90 6764 435 8.