

## II.G.13 Nanotube Array Photoelectrochemical Hydrogen Production

Rikard Wind

Synkera Technologies Inc.  
2605 Trade Centre Ave. Suite C  
Longmont, CO 80534  
Phone: (720) 494-8401 x111  
E-mail: rwind@synkera.com

DOE Manager

HQ: Eric Miller  
Phone: (202) 287-5829  
E-mail: Eric.Miller@hq.doe.gov

Contract Number: DE-FG02-07ER84871

Consultant:

John Turner  
National Renewable Energy Laboratory (NREL)  
Golden, CO

Project Start Date: August 15, 2008

Project End Date: August 15, 2011

### Fiscal Year (FY) 2011 Objectives

- Development of photoelectrochemical (PEC) material with required composition and architecture to achieve 5,000+ hour lifetime, 2.0 eV bandgap, and >10% conversion efficiency in the prototypes.
- Conformally deposit indium tin oxide (ITO) and Pt quantum dots inside nanoporous anodic aluminum oxide (AAO).
- Achieve bandgap  $\leq 2.0$  eV.
- Develop large area PEC samples.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AA) PEC Device and System Auxiliary Material

(AC) Device Configuration Designs

### Technical Targets

This project is conducting studies of PEC hydrogen production by creating a hybrid design that combines multiple layers of materials to simultaneously address issues of durability and efficiency. As part of this effort, techniques are being developed that can manufacture devices at commercial scales. The overall goal of this project is to create a PEC device that meets or exceeds the DOE 2018 PEC hydrogen production targets in Table 1.

**TABLE 1.** Progress towards Meeting Technical Targets for PEC Hydrogen Generation

Characteristic	Units	2013 Target	2018 Target	Synkera 2011 Status
Usable Bandgap	eV	2.3	2.0	2.06
Chemical Conversion Efficiency	%	10	12	Not available
Solar to Hydrogen Efficiency	%	8	10	1.1%
Plant Durability	hr	1,000	5,000	Not available

### FY 2011 Accomplishments

- Produced conformal transparent conductive oxide (TCO) and TiO<sub>2</sub> nanotubes in a layered manner inside pores of AAO.
- Demonstrated deposition of platinum nanodots inside the TCO and TiO<sub>2</sub> nanotubes.
- Demonstrated direct bandgap of 2.06 eV in Pt coated TiO<sub>2</sub>.
- Developed new process for depositing highly conductive ITO inside AAO.
- Demonstrate 4x current increase for ITO-based PCE versus previous results.
- Demonstrated conformal deposition of WO<sub>3</sub> inside AAO nanopores.



### Introduction

The cleanest method of hydrogen production is the use of sunlight to electrochemically split water into hydrogen and oxygen. Advances in photoelectrode materials are required to make PEC hydrogen production practical. Current materials representing the state of the art in this area suffer from significant lifetime limitation, bandgaps poorly matched with the solar spectrum, and low conversion-efficiency. The project aim is to develop and commercialize next-generation PEC materials that incorporate an innovative three-dimensional nanostructured architecture and a tailored bandgap.

### Approach

The material architecture includes high-density, high-surface-area arrays of nanotubes formed inside the pores of the honeycomb-like, self-organized matrix of nanoporous AAO. The approach utilizes a synergistic combination of two technologies developed by the project team: (1) synthesis and integration of AAO with the required

porous structure; and (2) conformal atomic layer deposition (ALD) of materials inside the high-aspect-ratio pores to produce nanotubes with atomically controlled thickness of coaxial layers. The approach results in up to a 1,000-fold increase of the cross-section available for light absorption and the surface area available for electrochemical reactions, thus significantly increasing the hydrogen yield per area of the electrode.

The PEC materials developed in this project include a catalytic layer, surrounded by a layer of light absorbing material, surrounded by an outer shell of TCO (Figure 1). The architecture provides a long vertical path length for light absorption with a short lateral path length for efficient charge separation.

## Results

Previously during this project we demonstrated that AAO membranes with larger pore periods and diameters were most effective as PEC scaffolds. All the development of PEC materials was conducted on free standing 13 mm diameter AAO coupons. In order to create functional PEC devices capable of meeting the cost targets for hydrogen, two issues must be addressed: 1) the area of AAO must be scaled up; and 2) the PEC device must be integrated into a system capable of capturing the generated hydrogen.

Synkera has addressed these two issues by creating 1"×5" AAO membranes that are integrated with an aluminum rim (Figure 1). The challenge in this effort was to create membranes with large pore diameters in this format and to anneal them to the required temperature prior to ALD. We have achieved both of these goals with 100% yield.

In earlier efforts we explored nitrogen and carbon doping of  $\text{TiO}_2$  to reduce the bandgap of the material. We were able to reduce the bandgap from 3.1 eV to 2.5 eV



**FIGURE 1.** Annealed 1"×5" AAO Membranes Supported by Aluminum Rim

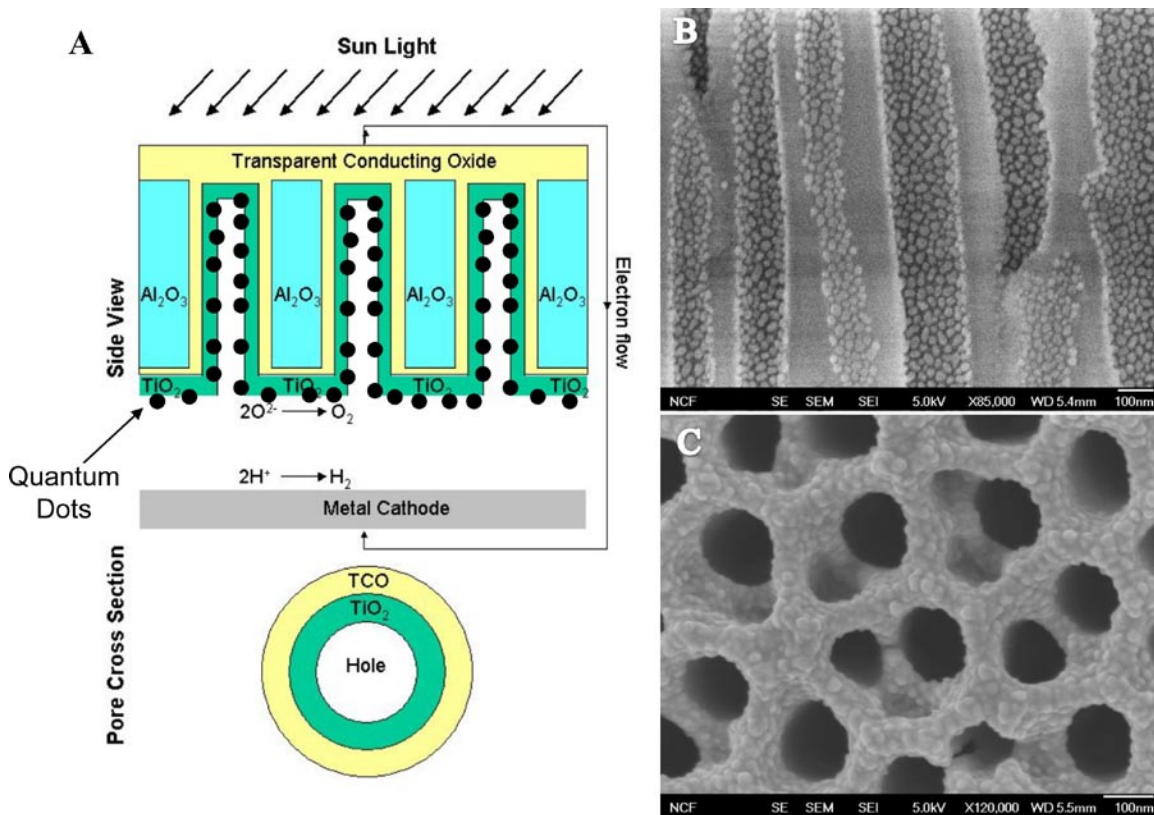
using nitrogen doping. Additional efforts at nitrogen doping did not lead to further reduction in the bandgap. In order to overcome this limitation we explored Pt quantum dots as a means of decreasing the bandgap. Figure 2A shows a conceptual drawing of the AAO cross section. The nanoporous AAO is first conformally coated with a TCO (to form TCO nanotubes) and provide a path for the generated electrons to reach the cathode. Inside the TCO, nanotubes of  $\text{TiO}_2$  are deposited to produce the catalytic surface. Finally platinum quantum dots are deposited on the  $\text{TiO}_2$  surface. Figures 2B and 2C show scanning electron microscope side and top views of the AAO after 100 cycles of Pt ALD. Both views suggest that Pt ALD forms polycrystalline domains similar to the domains formed during metallic tungsten ALD on oxide surfaces [1]. Experience with tungsten ALD suggests that the Pt ALD proceeds via the formation of individual islands that coalesce as the number of cycles increases. By only depositing a few cycles of Pt on the  $\text{TiO}_2$  surface, individual quantum dots of Pt can be obtained.

PEC samples consisting of aluminum doped zinc oxide (the TCO),  $\text{TiO}_2$ , and a few ALD cycles of Pt were prepared (Figure 2A). These samples were sent to our consultant at NREL for analysis. NREL performed photocurrent spectroscopy by measuring the photocurrent while scanning the light wavelength from 550-900 nm. Direct electronic transitions are found by plotting the square of the normalized photocurrent (NPC) and extrapolating the linear regime to the abscissa (Figure 3). The figure shows that the PEC material had a direct bandgap of 2.06 eV. Additionally, plots of the square root of the NPC showed an indirect bandgap of 1.71 eV.

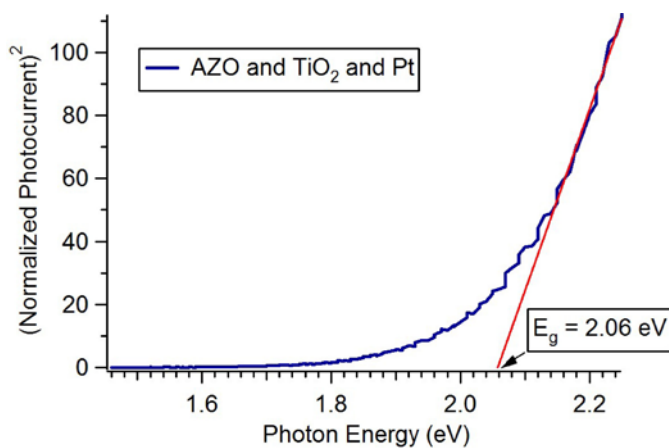
Additional tests at NREL using colored glass filters used to estimate wavelength dependent photoresponse. The Pt-coated PEC samples demonstrated the largest magnitude response to chopped illumination from photons with wavelengths longer than 695 nm ( $h\nu < 1.78$  eV) while bare  $\text{TiO}_2$  had none. This result confirms photocurrent spectroscopy results that these configurations are visible-light active, and is responsive to photon energies below what would be expected from pure  $\text{TiO}_2$ .

In other recent efforts Synkera has developed a new ALD chemistry for deposition of highly conductive ITO conformally inside the pores of AAO. PEC samples were made using ITO and  $\text{TiO}_2$  and compared to AZO/ $\text{TiO}_2$  samples as well as AZO/ $\text{TiO}_2$ /Pt samples. Figure 4 shows the photocurrent for all three types of samples during chopped light experiments conducted at Synkera. The figure shows that the photocurrent is four times higher for the ITO samples compared to the AZO samples and two times higher than the samples modified by Pt. The reason for the much higher current is unclear, but will be further explored during the last two months of the project.

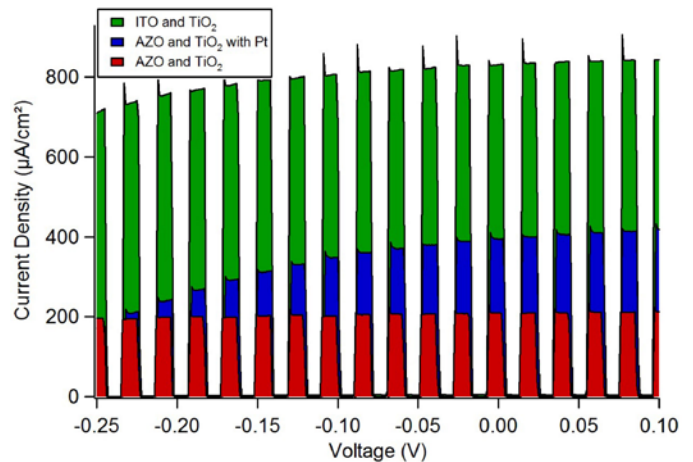
Synkera has also just completed samples that have  $\text{WO}_3$  as the photocatalyst instead of  $\text{TiO}_2$ . These samples are undergoing evaluation.



**FIGURE 2.** A: Conceptual drawing of PEC nanotube architecture with quantum dot catalyst. B: Side view of AAO after 100 cycles of Pt ALD. C: Top view of AAO after 100 cycles Pt ALD.



**FIGURE 3.** Photocurrent Spectroscopy Data Performed at NREL (Pt-coated PEC devices show a bandgap of 2.06 eV)



**FIGURE 4.** Photocurrent comparison in 0.1 M KOH (pH 13) on PEC samples with ITO/ $\text{TiO}_2$ , AZO/ $\text{TiO}_2$ /Pt, and AZO/ $\text{TiO}_2$  as a function of applied potential (vs. Ag/AgCl electrode) under 1 sun illumination with chopped light.

## Conclusions

We have developed a nanostructured PEC material that is manufactured using scalable techniques. We have successfully completed an intermediate scale up of the AAO scaffold for PEC applications. We have demonstrated a

visible light photoresponse in our PEC samples. We have also demonstrated significantly enhanced photocurrent by using ITO to replace the AZO in the device.

### Future Directions

- Complete testing of WO<sub>3</sub> PEC samples.
- Fabricate samples of ITO/TiO<sub>2</sub>/Pt.
- Measure long-term stability of best performing PEC sample.
- Manufacture large area PEC sample.

### Patents Issued

1. On August 30<sup>th</sup> 2010 we resubmitted a U.S. Provisional Patent Application No. 61/174,577 entitled “ENERGY CONVERSION DEVICES AND METHODS FOR MAKING SAME.” This patent covers the architecture described in this project as well as related architectures for photovoltaics and other applications.

### FY 2011 Publications/Presentations

1. We presented a poster on this work on May 10<sup>th</sup> 2011 at the DOE Hydrogen and Fuel Cells Program, and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting.

### References

1. R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, “Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al<sub>2</sub>O<sub>3</sub>”, *J. Appl. Phys.* **105**, 074309 (2009).