

II.1.2 Nanotube Array Photoelectrochemical Hydrogen Production

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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 following DOE 2018 PEC hydrogen production targets:

- Usable bandgap: 2.0 eV
- Chemical conversion efficiency: 12%
- Solar to hydrogen efficiency: 10%
- Plant durability: 5,000 hours

Accomplishments

- Produced conformal transparent conductive oxide (TCO) and TiO₂ nanotubes in a layered manner inside pores of anodic aluminum oxide (AAO).
- Demonstrated photocurrent on PEC devices without applying an external potential.
- Demonstrated ability to reduce bandgap of TiO₂ to 2.5% without affecting conductivity.
- Demonstrated conformal deposition of GaN inside AAO as a separate light absorbing material.



Objectives

- Determination of optimal template geometry for photoelectrochemical (PEC) water splitting using TiO₂ as a test bed material.
- Development of additional absorber materials with required composition and architecture to achieve 5,000+ hour lifetime, 2.0 eV bandgap, and >10% conversion efficiency in the prototypes.
- Evaluation of approaches for integration of developed materials into a self-contained system.
- Formation of partnerships for bringing the technology to the market.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell 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

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). In addition, the light absorbing material can also have a vertically graded composition to allow for a vertically graded bandgap for maximum light absorption. The architecture provides a long vertical path length for light absorption with a short lateral path length for efficient charge separation.

Results

During this project we have produced AAO membranes with a variety of pore dimensions and pore densities. Pore diameters ranged from 13 to 300 nm, with corresponding pore periods from 20 to 500 nm. Subsequently, TCO and TiO₂ were deposited conformally inside the pores to form hollow PEC tubes and the materials were tested for PEC efficiency. These studies showed that the larger pore periods were more effective as PEC scaffolds and all subsequent tests were performed on these larger period samples.

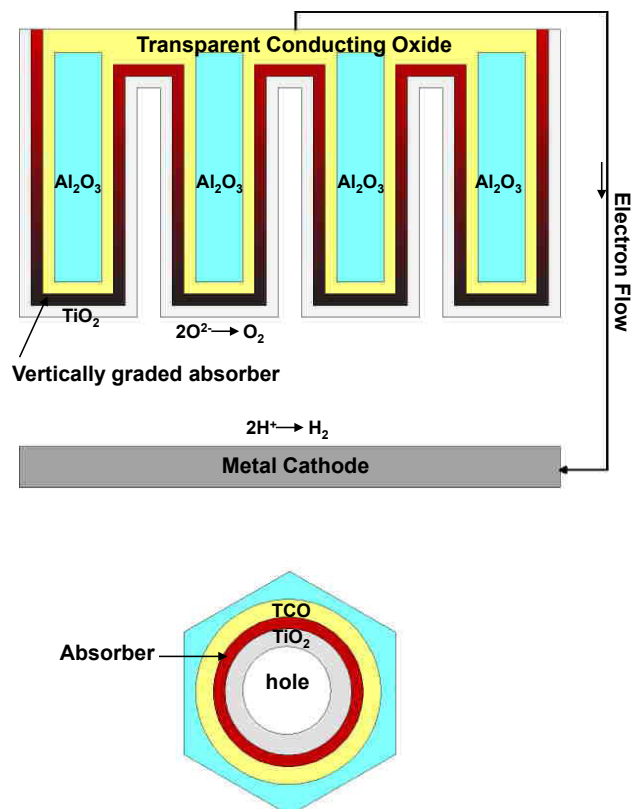


FIGURE 1. Arrays of PEC Nanotubes with a Vertically-Graded Absorber

In order to meet the cost targets for hydrogen from PEC, we also performed a scale-up effort to increase the size of our AAO membranes. Figure 2 shows an anodization cell of sufficient capacity to support large membranes (up to 10"x17") as well as large batches of smaller membranes. Further membrane production of larger format membranes will be completed in this cell.

In addition to our efforts to scale up the anodization cell, we also expanded our ALD reactor to accommodate up to seven different precursors. Two of these precursors are on a separate dosing line specifically designed to handle the low vapor pressure precursors used for TiO₂ deposition. The efficacy of this new reactor design has been demonstrated by depositing highly conformal, pinhole-free layers inside the pores of AAO.

Figure 3 shows the photocurrent in chopped light as a function of the applied potential for our nanostructured PEC samples as well as flat samples with



FIGURE 2. Scaled-Up Anodization Cell

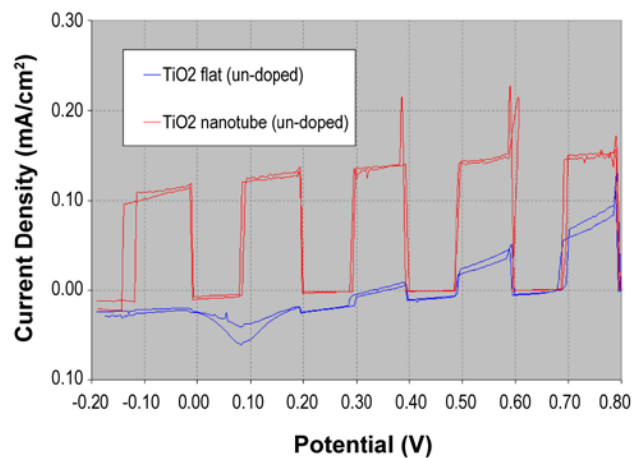


FIGURE 3. Photocurrent as a Function of Applied Potential on Flat and Nanostructured PEC Sample

materials deposited in identical conditions. Peaks in the current are due to the light incident on the sample and the valleys between are due to no illumination on the sample. A Ag/AgCl reference electrode was used which has a potential of ~ 0.22 V vs standard hydrogen electrode. Therefore, the far left axis in Figure 3 represents zero applied bias. For the flat sample, there is no current when the applied bias is low, however, for the nanostructured sample there is an appreciable current even without an applied bias. This is a very promising result for this architecture.

In earlier efforts we explored nitrogen and carbon doping of TiO_2 to reduce the bandgap of the material. We were able to reduce the bandgap from 3.1 eV to 2.5 eV using nitrogen doping (Figure 4). These samples were prepared before the ALD reactor was modified and this was the best that could be achieved at the time. In more recent efforts we have developed a chemistry for the deposition of TiN. By combining this chemistry with the TiO_2 chemistry, we anticipate that we will be able to achieve larger doping densities and lower the bandgap to the required 2.0 eV.

In addition to modifying the TiO_2 bandgap, we have also explored the use of a separate absorber material, as shown in Figure 1. We used the expanded ALD reactor to manufacture PEC samples consisting of an outer conductor, a GaN absorber, and a TiO_2 catalytic layer. These samples were extensively tested by our collaborators at the National Renewable Energy Laboratory.

The open-circuit potential (OCP) (measured vs. the reference electrode) shifted negative with the application of broadband illumination from a 250-Watt tungsten lamp. The negative shift in OCP indicates these material configurations behave n-type, making them photoanodes.

Photocurrent spectroscopy was performed and indicated an indirect bandgap transition for these

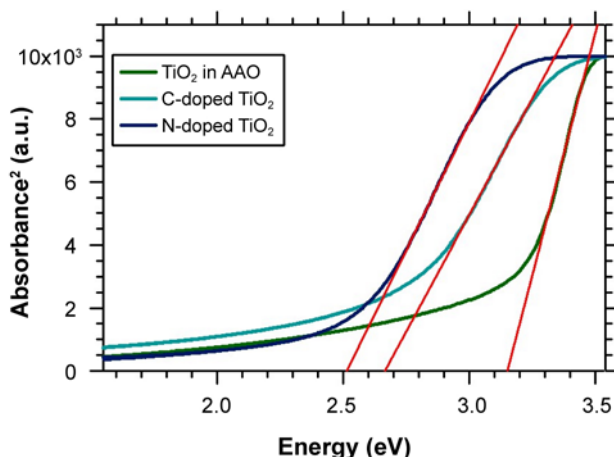


FIGURE 4. Bandgap Reduction of TiO_2 using N and C Doping

materials. GaN (bulk) is known to have a direct electronic transition at an energy of 3.4 eV, so the absorption of visible light is an encouraging result. That the transition is indirect is less encouraging. One possible explanation for the low-energy indirect transition observed could be mid-gap defect states in the GaN. These defect states limit the utility of the as-deposited GaN as an absorber material.

The reason the GaN/ TiO_2 electrodes didn't generate significant photocurrent is likely due to non-ideal band alignment at the GaN/ TiO_2 heterojunction. If the valence band (VB) of the GaN is above the VB of TiO_2 , holes from the GaN have an energy barrier that would prevent them from injecting into the VB or TiO_2 where they would be available for oxidation on the electrode surface. A similar argument could be made for electrons in the conduction band (CB) if the CB of GaN is above the CB of TiO_2 . X-ray photoelectron spectroscopy measurements by Hansen [1] of a GaN/ TiO_2 heterojunction suggest the latter.

The visible light absorption in GaN is intriguing. It is likely that the GaN has defects or impurities that lead to the visible absorption. There are reports that solid solutions of ZnO/GaN can absorb into the visible region, but not as far into the visible as we see with these electrodes. From the two data points we have (5 nm, 10 nm) the thicker the GaN, the better the photoresponse. Though these GaN samples can absorb visible light and generate reasonable photocurrent densities, the band edges appear to preclude these electrodes as unbiased water splitting electrodes.

Currently the lifetime of the materials is low, less than 100 hours. Techniques to increase the lifetime are currently being explored.

Conclusions and Future Directions

Conclusions

We have developed a nanostructured PEC material that is manufactured using scalable techniques. The material shows a significant enhancement in photocurrent over flat anodes, and is active without the need for an applied bias. We have shown that we can lower the bandgap of TiO_2 while increasing the efficiency of PEC. We have also produced samples with GaN as the absorber, and shown that it absorbs visible light; unfortunately, the band edges are misaligned for water splitting.

Future Directions

- Investigate WO_3 as a PEC material.
- Revisit N-doping of TiO_2 as a means to push bandgap down to 2 eV.
- Measure long-term stability of nanostructured films.

- Investigate other absorber materials.
- Explore techniques for increasing robustness of films and their lifetimes.

Special Recognitions & Awards/Patents Issued

1. On May 1st 2009 we submitted 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.

References

1. Hansen et. al., J. Vac. Sci & Tech. B 23(2), p.499, 2005.