

II.C.5 Metal Oxide Semiconductor Nanotubular Arrays for Photoelectrochemical Hydrogen Generation

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(AJ) Synthesis and Manufacturing

Technical Targets

The project is aimed at conducting fundamental materials and device studies related to the development of metal oxide semiconductor nanotubular arrays for PEC hydrogen generation that have high efficiency. Insights gained from these studies will be applied toward the design and synthesis of hydrogen generation materials that meet the following DOE hydrogen production targets:

- Cost: \$4/gasoline gallon equivalent (gge) at plant gate by 2020
- Cost: \$5/gge at plant gate by 2017
- Efficiency: 15% efficiency by 2020

FY 2013 Accomplishments

- Developed hierarchical TiO₂ nanotubes (H-T-NT) nanolace-type TiO₂ nanotubes (T-NT) in a single anodization step.
- Developed a method to extend the visible light absorbance of tantalum oxynitride nanotubes.
- Developed new synthesis techniques for higher order one-dimensional titania nanotube architectures which demonstrate enhanced PEC water splitting.



Overall Objectives

Develop high efficiency hybrid-semiconductor nanotubular materials for hydrogen generation by water splitting

Fiscal Year (FY) 2013 Objectives

- Enhance visible light absorption of metal oxide nanotubes
- Develop new synthesis techniques for enhanced photoelectrochemical (PEC) performance

Technical Barriers

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

(AE) Materials Efficiency - Bulk and Interface

(AF) Materials Durability - Bulk and Interface

(AG) Integrated Device Configurations

INTRODUCTION

Increasing global energy demand requires the development of new sustainable and environmentally friendly energy storage and conversion systems [1]. Solar energy has the potential to play a significant role in meeting our energy demands. Solar-assisted water splitting to generate hydrogen as an energy carrier is one of the options, and utilizes the two most abundant resources, namely, solar energy and water [2]. Successful implementation of solar-based energy systems can possibly lower the cost of hydrogen to be comparable to gasoline prices [3]. PEC water splitting was first demonstrated in 1972 using TiO₂ [4]. Other metal oxides such as ZnO, WO₃, and Fe₂O₃ have been investigated for PEC water splitting [5-7]. However, TiO₂ remains the most studied material for this reaction as it retains several desirable properties such as chemical and optical stability as well as being environmentally benign.

The use of highly ordered, one-dimensional nanostructures of TiO_2 , such as nanotubes, has gained much attention over the past decade due to their inherently large surface area and unidirectional flow of charges. More specifically, T-NT formed via anodic oxidation of titanium metal have demonstrated superior performance over its nanoparticle counterpart in charge transport [8]. The use of hierarchical type T-NT has demonstrated enhanced performance over plain T-NT in photovoltaic and PEC applications. The common synthesis technique adopted for growing hierarchical-type T-NT involves a two-step anodization process. First, T-NT are grown on a Ti substrate and subsequently removed via ultrasonication for a long duration, leaving a patterned Ti substrate.

APPROACH

The project approach is to increase visible light utility of metal oxide nanotubes by examining new synthesis techniques and to study the effect of surface treatment and effect of light irradiation during synthesis. Then, characterization of the prepared materials is conducted to gain a fundamental understanding of the materials properties. The materials are then evaluated for their PEC behavior by using them as photoanodes in a PEC setup. Finally, the stability of materials in the presence and absence of irradiation is studied using electrochemical methods combined with electron microscopic analysis and spectroscopic methods.

RESULTS

Figures 1 and 2 show scanning electron microscope (SEM) images of the T-NT and hierarchical type titania nanotubes (H-T-NT). The etching treatment anisotropically removes a small layer of Ti resulting in a rippled surface of titania. As nanotube formation depends on the local electric field and solution diffusion rate [9], the etching treatment prior to anodization provides a discontinuous surface where the electric field is not uniform and becomes localized at the grains. The current during the anodization was observed to stabilize rapidly, implying an initial oxide layer had already formed (via etching). The existing oxide layer that is formed is relatively smooth as the etching treatment results in the exposure of small grains. The initial pitting mechanism for nanotube formation occurs at the wells of the surface. The smooth surface from the etching treatment results in a more uniform distribution of electric field, yielding a porous top layer to the nanotubes (inset Figure 2). Previous reports show anodization of a specially processed Ti foil smoothed via mechanical polishing resulted in a nanoporous layer [10]. However, the etching treatment of the Ti substrates creates a random surface of exposed grains, which is not an entirely uniform surface. This treatment results in a

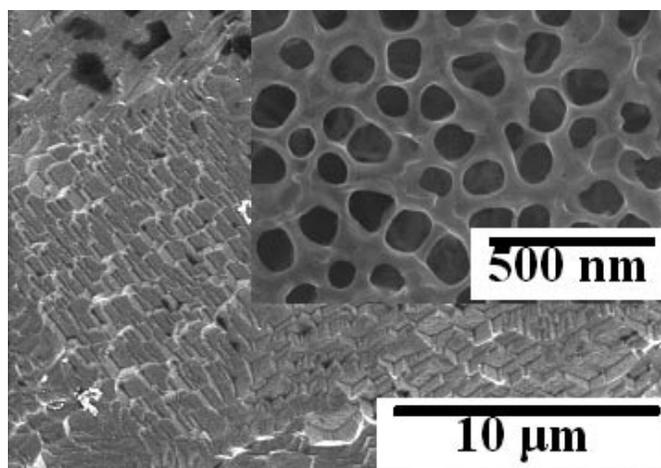


FIGURE 1. SEM Image of Plain T-NT

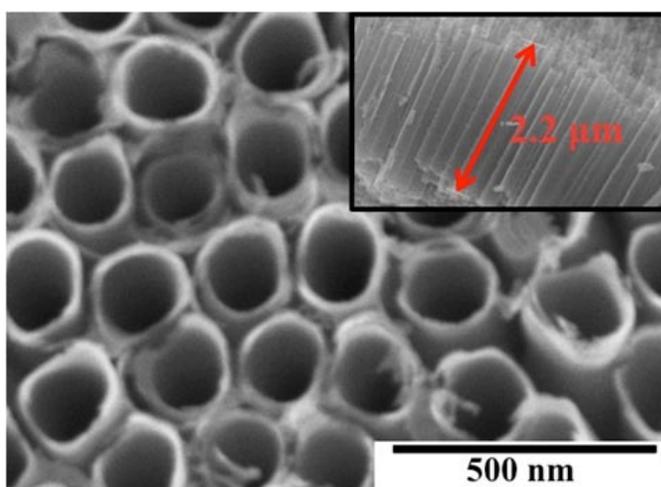


FIGURE 2. SEM image of etched Ti surface before anodization. Inset shows the formation of H-T-NT.

larger distribution of pore sizes within the nanoporous layer formed on top of the nanotubes. Longer etching treatments of the Ti substrates forms a thicker native oxide layer prior to anodization. It was observed that the nanoporous layers become qualitatively thicker with longer etching treatments. Figure 3 shows SEM images of H-T-NT and nano-grass type titania nanotubes (N-T-NTs). Anodization at elevated temperatures increases the reaction kinetics of not only nanotubular formation, but also the chemical dissolution of the nanotubes as well (due to solvated F^- species). Etching of the tops of the nanotubes leads to inhomogeneous nanotube formation. As the walls of the nanotubes become too thin, they collapse on themselves due to capillary forces during rapid drying. Larger examination of the N-T-NT samples shows qualitatively more nanoglass with increased anodization temperature.

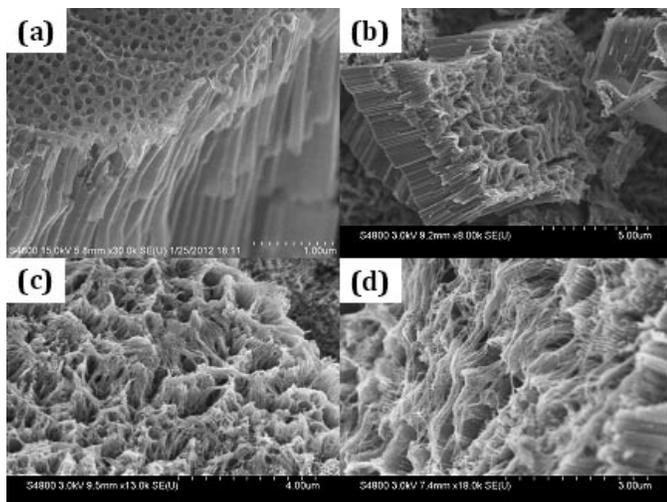


FIGURE 3. SEM Images of (a) H-T-NT, (b) N-T-NT Prepared at 40°C, (c) 50°C, and (d) 65°C

PEC Activity

The PEC enhancement of the hierarchical nanotubes over plain nanotubes can be attributed to an increased surface area for light harvesting and electrolyte surface coverage as well as improved charge separation. Wang, et al., [11] studied the ultraviolet photoelectron spectroscopy of hierarchical and plain titania nanotubes. The study found the work function difference between the plain nanotubes and hierarchical nanotubes to be 0.05 eV, which is sufficient for improving charge separation. The nanoring/nanoporous layer on top of the tubes serves as an electron transporter for effective charge separation and rapid transport of photogenerated charges [11]. These results are further supported by the electrochemical impedance spectroscopy and Mott-Schottky studies conducted on hierarchical titania nanotubes by Zhang and Wang [12], in which they reported a reduction in charge transfer resistance between the semiconductor/electrolyte interface in conjunction with an increased charge carrier density. In a similar manner, the same argument can be said for the N-T-NT regarding improved PEC activity. However, as the layer of the nanograss becomes thicker (due to increased anodization temperature, *vide supra*) the PEC activity drastically decreases.

CONCLUSIONS AND FUTURE DIRECTIONS

The observed behavior may be attributed the entangled nanograss interfaces which act as recombination centers. The photo-induced electrons and holes have a more tortuous diffusion path within the nanograss increasing their probability or recombining within the volume of the nanograss. A similar trend was observed when the nanoporous layer on H-T-NT samples was thicker due to longer etching treatment. Future studies would include:

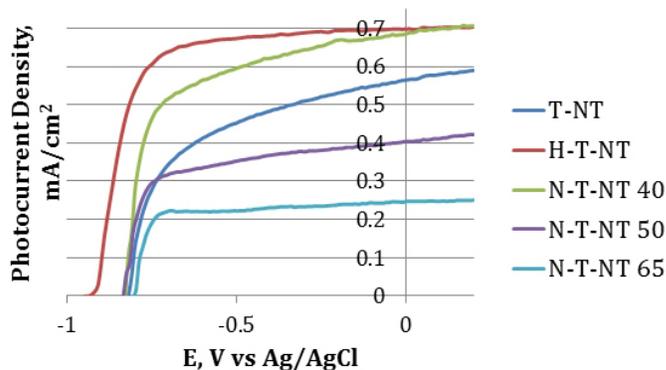


FIGURE 4. Potentiodynamic plot of various substrates under AM 1.5 irradiation in 1 M KOH electrolyte. The anodes were anodically polarized from open-circuit potential to 0.2 V (vs Ag/AgCl) at 10 mV/s.

- Electrochemical impedance spectroscopy studies on these samples would give information on the electrolyte/photoanode interface charge resistance as well as the charge carrier density.
- Stability studies in the presence and absence of irradiation.
- Materials will be studied using spectroscopy and microscopy.

FY 2013 PUBLICATIONS/PRESENTATIONS

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