Design, Synthesis, and Characterization of Hematite Nanotubes for Photoelectrochemical Water Splitting.

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Introduction

The efficient storage of solar energy in the chemical bonds of hydrogen remains one of the most attractive solutions to meet growth in global energy demand in a sustainable manner. [1, 2] Photoelectrochemical (PE) water splitting is one broadly studied method to produce hydrogen due to its low cost and relative technical simplicity. Here we demonstrate the room temperature synthesis of ordered, vertical iron oxide nanotubes (NT) via electrochemical anodization. This NT morphology offers increased surface areas for light capture and one-dimensional electron transport, and reduces the NT wall thickness to dimensions within the hole diffusion distance, hence limiting recombination.[3] We describe the dependence of NT diameter on the applied voltage, with potential exploitation of this dependence in the design and synthesis of NTs with improved morphologies for significant enhancements in light harvesting. We also demonstrate variation of the PE performance with diameter of the NTs.

Experimental

A two-electrode cell was constructed, with a 0.25 mm thick Fe substrate acting as anode and a Pt foil acting as cathode. An Agilent 3674 power supply was used to apply a voltage across the electrochemical cell, with the voltage increased from 0 V to the final voltage at a rate of 25 mV/s. A Matlab software was used to remotely control the voltage input to the power supply and record the current output from the cell. To synthesize the NTs, we used an electrolytic solution composed of 2 wt. % de-ionized water, 0.37 wt. % ammonium fluoride, and 97.63 wt. % ethylene glycol. The resulting NT were typically amorphous and were crystallized via high temperature calcination in air. X-Ray Diffraction (XRD) was used to characterize the crystalline structure; hematite is the desired photoactive phase. Scanning Electron Microscopy (SEM) was used to characterize surface morphologies of the NTs. Linear Sweep Voltammetry (LSV) in a 1 M KOH electrolyte was used to evaluate the PE performance of the NTs, with the photoelectrode as the working electrode, a Pt foil as counter-electrode, and a Hg/HgO reference electrode.

Results and Discussion

Scanning electron micrographs (Fig. 1) demonstrated the presence of ordered NTs, with outer diameters ranging from 55 to 70 nm, and varying linearly with final voltage inputs in the 30 V – 60 V range (Fig. 2). The linear variation leads to the prospect of easy generation of more complex NT morphologies, like layered, and sinusoidal NTs, with expected significant improvements in PE performance.

High temperature calcination (Fig. 3) resulted in a NT structure composed mostly of hematite and magnetite. A study is currently underway to increase the percentage of hematite, the crystalline phase more favorable for PE water splitting. The LSV indicated that larger outer NT diameters result in improved PE performance at 0.5V (Fig. 4).

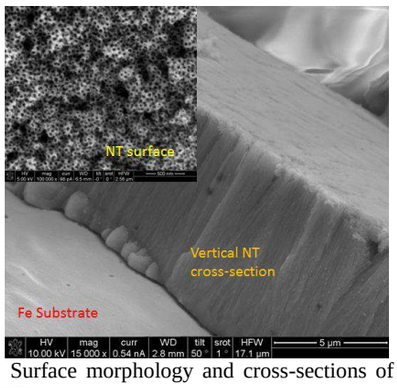

Figure 1: Surface morphology and cross-sections of Fe oxide NTs.

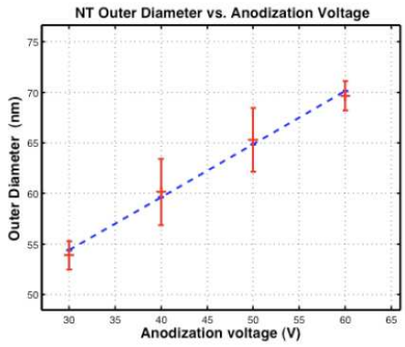

Figure 2: Nanotube diameters as a function of final applied voltage.

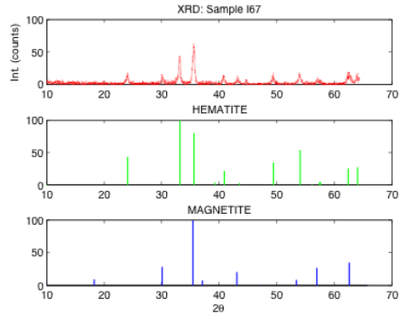

Figure 3: Diffraction patterns for the Fe oxide NTs: the dominant crystalline phases after 1 hour calcination at 450 C were hematite and magnetite.

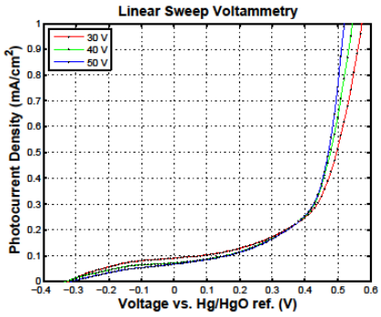

Figure 4: Linear sweep voltammetry for the Fe oxide NTs: larger diameters resulted in better PE performance at 0.5 V.

References

[1] Aurora, P., Rhee, P., Thompson, L. T., Journal of Electrochemical Society, 157 (**2010**) K152-K155.
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[3] La Tempa, T. J., J. Phys. Chem. C. 113 **(2009)** 16293-16298.