

## Nanostructures for photoelectrochemical water splitting

Peter H. Aurora, Leon Webster and Levi T. Thompson\*  
University of Michigan, Ann Arbor, MI 48109 (U.S.A)  
\*lth@umich.edu

### Introduction

Photo-electrochemical (PEC) cells are used to produce hydrogen from renewable resources, namely solar energy and water. A PEC cell typically consists of photo-anode where water is oxidized, a cathode where hydrogen is evolved and an electrolyte. A major obstacle to their use is the poor efficiency of the photo-anode. By some accounts, the rate of hydrogen oxidation will need to be increased by more than an order of magnitude to keep pace with the production of electrons and holes [1]. Results presented in this paper explore two strategies for improving the performance of the photo-anode: incorporating nanostructured gold and producing the oxides in the form of nanotubes or nanowires. Gold particles smaller than 5 nm have been reported to possess extraordinary activities for reactions including CO oxidation [3], water gas shift [4] and photocatalytic reactions [5], and hold promise for significantly enhancing the hydrogen oxidation rates. Structures of the nanotubes and nanowires should enhance the transport of electrons before recombination with holes. In addition, these materials possess high surface areas, which should result in increased absorption of solar light and higher efficiency of PEC cells.

### Materials and Methods

Ordered and disordered TiO<sub>2</sub> nanotubes were produced using hydrothermal synthesis (NaOH based bath) [6] and anodization (using HF solution as electrolyte) [2] techniques, respectively. Gold nanoparticles were supported onto the TiO<sub>2</sub> surfaces using the deposition precipitation method [4]. The metal loading was varied from 2-5 wt%. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize microstructural properties of the catalysts, and optical absorption measurements were used to determine their bandgaps ( $E_g$ ). X-ray diffraction and BET surface area experiments were used to characterize these materials. Electrochemical impedance spectroscopy was used to determine the current-voltage characteristics and over-all efficiencies of devices produced using these materials.

### Results and Discussion

The addition of Au nanoparticles to a TiO<sub>2</sub> powder caused a modest reduction in the bandgap. This would allow the TiO<sub>2</sub> to absorb more light in the visible portion of the spectrum. Changes in the electrochemical properties were more modest. The incorporation of nanoparticles has also been reported to enhance the charge separation within the nanostructured TiO<sub>2</sub> network thereby decreasing recombination losses [5] during photocatalysis. Figure 1 illustrates SEM micrographs of the TiO<sub>2</sub> nanotubes prepared by hydrothermal (A) and anodization (B) processes. The addition of gold nanoparticles to the TiO<sub>2</sub> nanotubes resulted in an improvement in the hydrogen oxidation activities. Gold incorporation also produced a shift in the bandgap. Figure 2 shows a Kubelka-Munk curve for the TiO<sub>2</sub> nanotubes (disordered tubes, average internal diameter ~6nm) that is consistent with a bandgap for these nanotubes of 3.34eV.

### Significance

Gold nanoparticles enhanced the water oxidation reaction and reduced bandgap of TiO<sub>2</sub>. Besides utilization in PEC cells, nanostructured TiO<sub>2</sub> can be used in solar cell, batteries, and gas sensors.

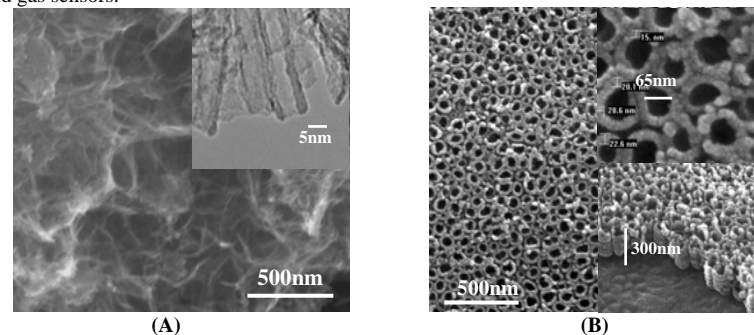


Figure 1. SEM of TiO<sub>2</sub> nanotubes prepared by (A) hydrothermal process and (B) anodization

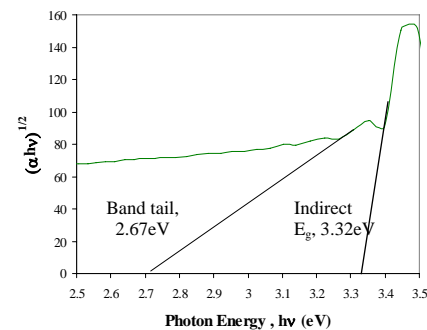


Figure 2. Kubelka-Munk curves for TiO<sub>2</sub> nanotubes calcined at 500°C; bandgap and band tail are observed.

### References

1. Basic Research Needs for Solar Energy Utilization, [http://www.sc.doe.gov/bes/reports/files/SEU\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf) (2005).
2. Mor G.K., Varghese O.K, Paulose M., Shankar K, Grimes C.A, *Sol. Ener. Mater. & Sol. Cells* 90, 2011 (2006)
3. Haruta M. and Date M., *Appl. Catal. A: General* 222, 427 (2001).
4. Kim C. H. and Thompson L.T., *J. Catal* 230, 66 (2005).
5. Subramanian, V., Wolf E. and Kamat P.V., *J. Amer. Chem. Soc.* 126, 4943 (2004).
6. Kasuga T, Hiramatsu M, Hoson A, Sekino T, and Niihara K., *Adv. Mater.* 11, 1307 (1999)