Nanostructures for photoelectrochemical water splitting

Peter H. Aurora, Leon Webster and Levi T. Thompson* University of Michigan, Department of Chemical Engineering Ann Arbor, MI 48109 (U.S.A) *ltt@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 a 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 photocalytical reactions [5], and they 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_2 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_2 surfaces using the deposition precipitation method [4]. The metal loading was varied from 2-5 wt%. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction and BET surface area analysis were used to characterize microstructural properties of the materials, and optical absorption measurements were used to determine their bandgaps (E_g).

Results and Discussion

The addition of Au nanoparticles to a TiO₂ powder caused a slight reduction in the bandgap. This would allow the TiO₂ to absorb more light in the visible portion of the spectrum. There was also a modest improvement in the electrocatalytic properties. It has been reported that the incorporation of nanoparticles can enhance charge separation within the TiO₂ network thereby decreasing recombination losses and increasing photocatalytic activity [5]. Figure 1 illustrates SEM micrographs of the TiO₂ nanotubes prepared by hydrothermal (A) and anodization (B) processes. The addition of gold nanoparticles to the TiO₂ nanotubes is expected to result in a significant improvement in the water oxidation activities [5]. Gold incorporation also produced a reduction in the bandgap from 3.17 to 3.06 eV (5 wt% Au loading). Figure 2 shows a Kubelka-Munk curve for the TiO₂ nanotubes (disordered tubes with average internal diameters of ~6 nm) that is consistent with a bandgap for these nanotubes of 3.34 eV.

Significance

Gold nanoparticles enhanced the water oxidation reaction and reduced the bandgap of TiO_2 . In addition to utilization in PEC cells, nanostructured TiO_2 can be used in solar cells and batteries.



Figure 1. SEM of TiO_2 tubes prepared by (A) the hydrothermal process and (B) anodization.



Figure 2. Kubelka-Munk curves for TiO₂ nanotubes calcined at 500°C; bandgap and band tail are observed.

References

- Basic Research Needs for Solar Energy Utilization, 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)