Characterization of Metal Oxides Serving as Photocatalyic Electrodes for Water Splitting under Light Illumination

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Fujishima and Honda in 1972 first showed that n-TiO_2 can be used as a photoanode for the photoelectrolysis of H_2O in a photoelectrochemical cell (PEC). Since then, a large number of semiconductor materials have been investigated for photoelectrocatalytic electrodes for H_2 production and photovoltaic cells for electrical energy conversion. However, the PEC cell suffers from the instability of semiconductor in aqueous media. Metal oxide semiconductors with wide bandgap (2.5-3.5 eV) such as TiO_2, ZnO, Fe_2O_3, $SrTiO_3$, WO_3 and Cu_2O are typically more stable compared to those narrow band gap materials (0.8-2 eV) in aqueous media.

Thermodynamically, the energy requirement for the water splitting reaction is 1.23 eV. However, considering the loss mechanisms such as series resistance and the electrocatalytic overpotential, the optically produced electron hole pairs need an energy difference of approximately 2 eV for efficient photoelectrolysis. Most metal oxide semiconductors are semiconductors having a band gap bigger than 2 eV and have been studied previously for application in water splitting. A major attraction of metal oxide is that it is inexpensive, non-toxic, and readily available.

In the our research, deposition of amorphous iron(III)-oxide films on a conducting glass substrate was achieved via a cathodic bias in a 0.1 M hydrated ammonium iron(II) sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) solution at −1.6 V vs. Ag/AgCl. Analysis by X-ray absorption near edge structure confirmed the iron(III) feature of the amorphous films (Figure 1). The deposited

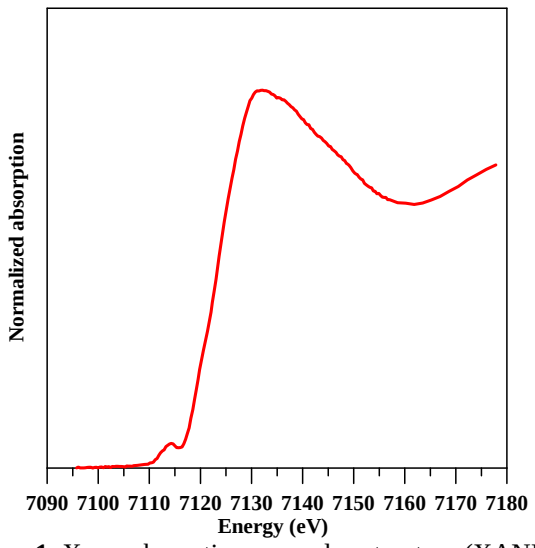

Figure 1. X-ray absorption near edge structure (XANES) spectrum of the iron(III)-oxide film.

films exhibited n-type semiconducting characteristics by showing photoresponses under an anodic bias. The Mott-Schottky method and cyclic voltammetry were employed to characterize the semiconducting properties of the deposited films, which included the band gap (2.2 eV), the potentials of the conduction and valence band edges and flat band (−0.6, +1.6 and −0.58 V vs. Ag/AgCl at pH7, respectively), and the donor density (1×10^{22} cm^{-3}). The deposited iron(III)-oxide films were suitable to serve as an anode for water splitting under illumination.

In addition to water splitting, we also study the dye-sensitized solar cells which is one type of photovoltaic cells. The preparation of the TiO_2 nanoparticles is vitally important to further enhance the efficiency of the dye-sensitized solar cells. In the our work, TiO_2 anatase nanoparticles were synthesized from a titanate for application in dye-sensitized solar cells. This TiO_2 is designated as H240. In contrast to H240, the TiO_2 colloid from the sol-gel synthesis is designated as S240. Structural analysis with x-ray absorption fine structure spectroscopy (Fugure 2) showed that H240 had a low density of oxygen-vacancy defects that would serve as the trap sites to impede electron transport. The transit time of the photogenerated electrons, measured by intensity modulated photocurrent spectroscopy, was significantly shorter in the H240 films than in the S240 films. This structure-intact feature of the titanate-derived TiO_2 has led to a high photocurrent for the dye-sensitized solar cells.

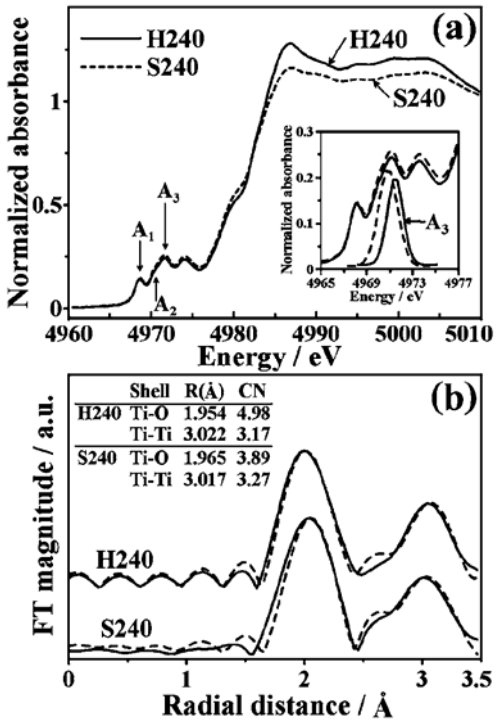

Figure 2. X-ray absorption fine structure spectroscopy analysis of the H240 and S240 TiO_2 nanoparticles: (a) XANES spectra. (b) Fourier transformed $k^3\chi(k)$ EXAFS spectra.