Preparation of Nanocrystalline Titania from Titania Nanotube: X-ray Absorption Spectroscopic Studies and Application to Dye-Sensitized Solar Cells

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Dye-sensitized solar cell (DSSC) based on nano-crystalline TiO_2 film has received considerable attention for the conversion of sunlight into electricity.[1] DSSC generally involves the use of dye-sensitized TiO_2 film on transparent conductive oxide (TCO) layers as photoanode, a platinized TCO as counter electrode, and the I^-/I_3^- redox couples as electrolyte. In this system, TiO_2 film not only provides high surface area for dye adsorption, but also function as semiconductor for electron transport. Thus, to prepare TiO_2 electrode with high surface area and favorable electron transport properties is the requisite to fabricate a high-efficiency DSSC.

Since the pioneering works conducted by Kasuga *et al.*[1], titania nanotube prepared by alkaline hydrothermal method has stimulated substantial interests for its unique tubular morphology and high surface area. However, DSSC based on such nanotube as electrode exhibits poor photovoltaic performance likely due to the structure is neither anatase nor rutile. Recently titania nanotube is found to be highly reactive in aqueous acid solution to proceed phase-transformations to anatase or rutile. In this report, the effect of acid concentration on the phase-transformations of titania nanotube was systematically studied, and the resulted nanocrystalline titania were applied to DSSC photoanode.

Titania nanotube (Tnt) was prepared by alkaline hydrothermal method modifying our previous procedures [2]. TiO_2 powders (Degussa P25) were mixed with 10 M $NaOH_{(aq)}$ and then autoclaved at 130 ^oC for 24 hours. After the hydrothermal treatment, the white solid was retrieved by centrifugation, washed with deionized water and dilute HNO_3, and followed by drying. The acid treatment for nanotube to proceed phase transformation was carried out by dispersing nanotubes in $HNO_{3(aq)}$ of designated molar concentration at 80 ^oC for 24 h. The products were recovered by centrifugation and then dried.

As evidenced by x-ray diffraction, the ratio of anatase/rutile within the resulted nanocrystalline titania decreases gradually as increasing in acid concentration. When $HNO_{3(aq)}$ was at 0.05 M, apparent phase-trans-formation from nanotubes to anatase can be observed. As acid concentration increased, rutile also appeared and resulted in the progressive decrease of anatase/rutile ratio. The decrease was more pronounced when $HNO_{3(aq)}$ concentration was less than 0.5 M. Pure rutile titania was eventually obtained at 2.5 M $HNO_{3(aq)}$ concentration. Upon increasing in acid concentration, the crystal size of anatase decreases and rutile increases progressively, accompanied by the gradual reduction of surface areas.

Fig. 1 shows the Ti K-edge XANES spectra, obtained at BL17C1, of Tnt and its acid-treated products. These pre-edges features were attributed to the forbidden transitions from the core 1s level to unoccupied 3d states of Ti^{4+}. The Ti atoms in P25 TiO_2 locate in a symmetric octahedral coordination. After hydrothermal treatment, the obtained Tnt shows a distinguishing pre-edge peak around 4.97 eV indicating the coordination of Ti atoms has been remarkably chang-ed. With treating with H_2O, there was no observable change in structure. Upon increasing in acid concentra-tion, the structures of the resulted samples returned to the symmetric octahedral coordination. All XANES spectra were consistent with the XRD results.

The photoanodes made of the prepared pure anatase titania were found to exhibit higher conversion efficiency of 8.01%, which is much higher than those of P25 (5.76%) and sol-gel TiO_2 (7.44%) in dye-sensitized solar cells application.

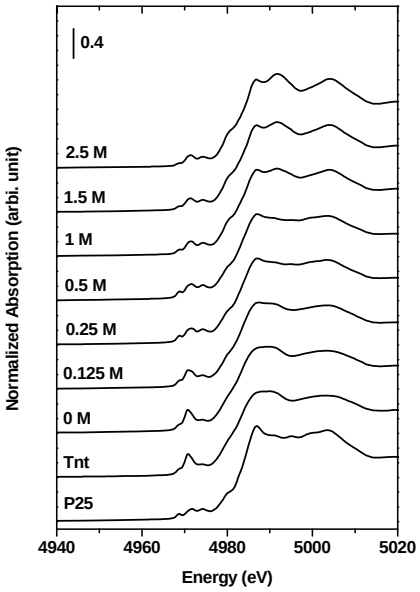

Figure 1. Ti K-edge XANES spectra of Tnt and its acid-treated products.

References

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