XAS Characterization of Anodic TiO_2-Nanotube Arrays for Dye-sensitized Solar Cells

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Since the breakthrough work conducted by O'Regan and Grätzel in 1991[1], dye-sensitized solar cell (DSSC) has provided an attractive alternative to silicon-based photovoltaics because of its special features, such as low cost and high energy conversion efficiency. A new generation of DSSCs with oriented TiO_2-nanotube arrays directly grown on the Ti substrate (TiNT/Ti) by electrochemical anodic oxidation method has demonstrated favorable electron transport properties and superior light-harvesting efficiency compared to those found for DSSCs incorporating NP-TiO_2 [2]. Such DSSCs require backside illumination (i.e., through the semi-transparent Pt counter-electrode due to the opaque Ti substrate) and their efficiencies are normally much lower than front-side illuminated cells because the incident light is partially absorbed by the counter-electrode and the electrolyte.

Most recently, we introduce a transparent electrode comprising an free-standing TiNT film oriented perpendicular to the fluorine-doped tin oxide (FTO) conductive glass [3]. This electrode is fabricated using a facile process involving flaking the anodic TiNT film off Ti-metal substrate to open its closed bottom and strongly adhering it onto FTO glass by a nanocrystalline TiO_2 (NP-TiO_2) thin underlayer. As compared to the closed-end TiNT film, the used of opened-end TiNT film exhibited an increase in one-sun efficiency from 5.3% to 9.1%.

In the present study, we used X-ray absorption near edge structure (XANES) data to provide the information of local structure in TiO_2 at the bottom part of TiNT arrays. The Ti K-edge XANES data were collected using synchrotron radiations at NSRRC BL17C1 beam lines by total electron-yield method.

Vertically-oriented TiNT arrays was flaked off the underlying Ti foil using H_2O_2 solution. As can be seen in Figs. 1a and 1b, the tube-ends at bottom are covered by a closed bottom barrier with ~100 nm thickness. Figures 1c and 1d show the FESEM image of the nearly fully opened bottom of TiNT film after treatment in the oxalic acid solution for 16 h. As shown in Fig. 2, only the characteristic peaks of anatase TiO_2 can be observed at the opened-end TiNT arrays, while, the presence of broad, additional peaks were detected as in the bottom part of the closed-end TiNT arrays. Accordingly, the bottom barrier might exist an aggregated rutile and anatase TiO_2, which is a known disadvantage for light harvest and charge collection. Therefore, removing the bottom barrier leads to a higher light-convert-electricity efficiency of the opened-end TiNT-based DSSCs relative to the closed-end TiNT-based DSSCs.

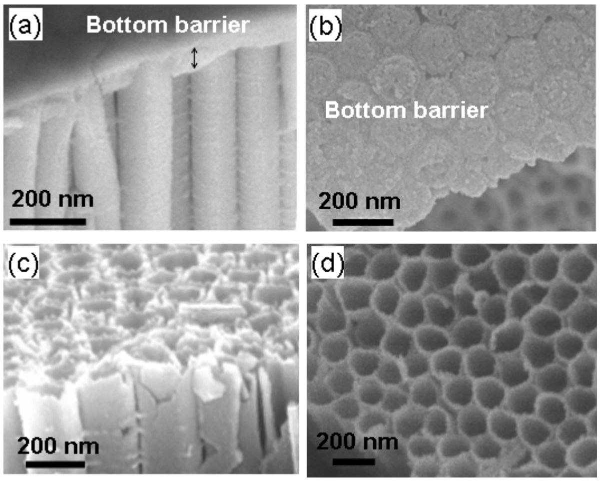

Fig. 1: FESEM images of (a) side view and (b) bottom view of the closed-end TiNT arrays; (c) side view, and (d) bottom view of the opened-end TiNT arrays.

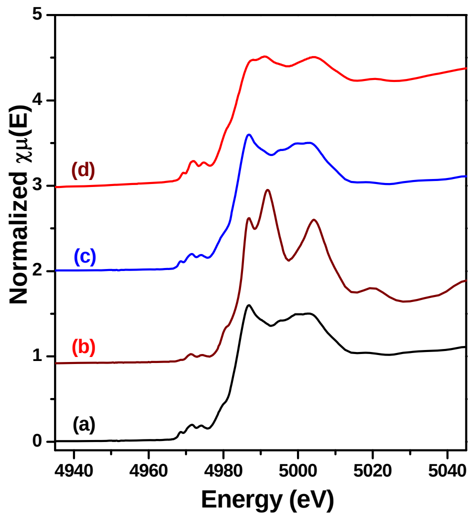

Fig. 2: The Ti K-edge XANES spectra of (a) the standard anatase TiO_2, (b) the standard rutile TiO_2, (c) the opened-end TiNT arrays, and (d) the closed-end TiNT arrays.

References

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