Annealing-free Electrochemical Preparation of Mesoporous Anatase Films for Application to Dye-sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have attracted great interest owing to the potential low cost alternative to the silicon solar cells. DSSC typically consists of nanocrystalline TiO_2 film with monolayer adsorption of dye molecules, redox electrolyte and counter electrode. The nanocrystalline TiO_2 films are often prepared on transparent conductive oxide (TCO) substrates by spin-coating and doctor-blading. The post annealing is usually necessary for sintering of TiO_2 nanoparticles. If we can develop a process to form the TiO_2 films without annealing at elevated temperatures, wider heat-labile substrates, including ITO/glass and plastic substrates, can be used readily for DSSCs.

We report here the formation of mesoporous anatase films by anodizing of titanium without post-annealing [1]. Anodizing has been recently used to form unique TiO_2 nanotubular films. Fluoride-containing aqueous and organic electrolytes are usually needed to grow the nanotubular films, but the film obtained is amorphous. Post-annealing at ~450°C of the anodized specimens is indispensable for the formation of crystalline anatase films. In contrast, we have found a new electrolyte, i.e., phosphate-containing glycerol electrolytes, in which mesoporous anatase films are formed directly without post-annealing. Another interesting fact is that the pore size of the cylindrical pores is as small as 10 nm. Thus, the higher surface area can be achieved, compared with the nanotube films with pore sizes usually larger than 50 nm.

Transparent electrode was also prepared by anodizing of titanium film magnetron-sputtered on to ITO-coated glass substrate [2]. At an optimized anodizing time, we could get a transparent electrode with relatively high photoelectrochemical properties for water splitting under UV light irradiation. However, prolonged anodizing resulted in the marked reduction of the conductivity of ITO layer, probably as a consequence of the incorporation of phosphate species into the ITO layer. Using the transparent electrode, we have successfully prepared DSSCs.



Fig. 1 SEM image of the cross-section of a mesoporous anatase film with cylindrical pores of ~ 10 nm diameter.

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[2] E. Tsuji, N. Hirata, Y. Aoki, H. Habazaki, Mater. Lett., 91 (2013) 39-41.