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Fabrication of dye-sensitized solar cells with electrolyzed TiO₂ nanotube array films

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Abstract. A TiO₂ nanotube array film was synthesized by the anodic oxidation of a Ti plate in an NH₄F electrolyte. The film was broken into nanotubes by carrying out ultrasonication. The nanotube powder was mixed with TiO₂ nanoparticle powder to form a paste. The paste was used in the fabrication of ceramic porous electrodes of dye-sensitized solar cells.

Introduction

Dye-sensitized solar cells (DSCs) fabricated using TiO₂ have attracted much attention as an alternative device to Si-based solar cells after it was first developed by Prof. Grätzel [1]; this is because the fabrication of such DSCs does not require large-scale plants. The nanopores in the ceramic porous electrodes of the DSC fabricated from ceramic nanopowder paste are very complex and narrow, because their sizes depend on the gaps between the particles. Generally, the particle size is 2 ~ 30 nm, and the thickness of the ceramic porous electrode is 3 ~ 50 μm. Therefore, it is difficult to pass sufficient electric charge to the regions located deep inside the pores. The aim of this study is to first synthesize ceramic nanotubes [2] separately and then use them in the fabrication of ceramic porous electrodes.

Experimental

A Ti plate (50 mm x 15 mm, thickness: 0.20 mm, Nilaco) was used in this study. A direct current of 60 V vs. a carbon plate (same geometry as the Ti plate) was applied to the Ti plate in a 90 mmol dm⁻³ NH₄F electrolyte (solvent; ethylene glycol:H₂O = 50:1 in vol. ratio) for 1 h. The distance between the electrodes was 15 mm. The Ti plate was covered with a light brown film. The plate was then rinsed with distilled water and dried at room temperature. Consequently, the film peeled off from the Ti plate (Fig.1). Subsequently, the film was calcined in an electric oven (Yamato, DR-22) at 450 °C for 24 h. Then, a crystallized anatase TiO₂ nanotube array film was obtained. The geometry and crystal structure of the film were identified using a SEM (scanning electron microscope, JEOL, JSM-6390YH) and an XRD (X-ray diffractometer, Shimadzu, XRD-6100), respectively. The TiO₂ film was ultrasonicated in ethanol for 10 min after which the ethanol became clouded. The clouded ethanol was centrifuged. Then, TiO₂ nanotube powder (represented as NTD) was obtained. There was



Fig.1 Photograph showing TiO₂ nanotube array film peeling off from Ti plate.

TiO₂ nanotube powder (represented as NTR) that was remaining without diffusion by the ultrasonication, too. The geometries of these powders were identified using the SEM.

TiO₂ nanoparticle powder (ST-21, Ishihara Sangyo), TiO₂ nanotube powder, 0.10 g of polyethylene glycol (Nacalai Tesque, M.W. 20000), 400 mm³ of 1.0 mol dm⁻³ diluted nitric acid (pH 2.0), 500 mm³ of 5.0 vol.% Triton X-100 aqueous solution, and 3.0 g of zirconia balls were introduced into a Teflon tube. The ratio of TiO₂ nanoparticle and TiO₂ nanotube powders ($R_{NT} = W_{NT} / (W_{NT} + W_{NP})$, where W_{NT} and W_{NP} are the weights of TiO₂ nanotube powder and TiO₂ nanoparticle powder, respectively) were 0 %, 2.0 %, 5.7 %, and 9.2 %; then, $W_{NT} + W_{NP} = 0.5$ g for all cases. The tube was rocked using a mill machine (RM-01, Seiwa Giken) at a rate of 800 rpm for 24 h. The obtained paste was coated with a thickness of 40 μm on fluorine-doped tin oxide (FTO)-coated glasses (AGC Fabritech) in an area of 1.0 cm². These glasses were dried at room temperature and normal pressure for 1 h and then sintered in an electric oven at 450 °C for 30 min. During the sintering procedure, polyethylene glycol in the TiO₂ nanoparticle / nanotube paste was burned off, and thereby, TiO₂ nanoparticle / nanotube nanotunnels were formed. The FTO-coated glasses on which the porous TiO₂ nanoparticle / nanotube film were coated were dipped into a 0.3 mol dm⁻³ ruthenium organic complex (N₃, Kojima Chemicals) ethanol solution and left for 3 days to be dyed. The dye strongly chemisorbed onto the TiO₂ surface. Thus, a N₃-dyed TiO₂ nanoparticle / nanotube porous thin film was obtained.

A dye-sensitized solar cell was assembled using a 10 mm square black opaque paper punctured at a diameter of 6 mm (douser), the TiO₂ thin film (anode), a 10 mm square cellophane film punctured at a diameter of 6 mm (spacer), and a 10 mm × 20 mm × 0.2 mm Pt plate (cathode) (Fig. 2). A few drops of 0.3 mol dm⁻³ LiI (Wako) + 0.03 mol dm⁻³ I₂ (Nacalai Tesque) solution (solvent; acetonitrile (Nacalai Tesque) + 3-methyl-2-oxazolidinone (Wako), 1:1 vol.%), which acted as an electrolyte, was added through the hole in the cellophane film. The cell was evaluated using a home-made system consisting of a Xe lamp (Ushio, SX-UI501XQ), a filter (Edmund Optics, 54517), an electrometer (Advantest, R8240), and a potentiostat (Hokuto Denko, HA301), which acted as the light source, IR-cut filter, generated potential and current logger, and electronic resistance, respectively. The data from the electrometer and the potentiostat were recorded using a home-made program on a personal computer via an A/D converter (Adek System Science, aPCI-A57).

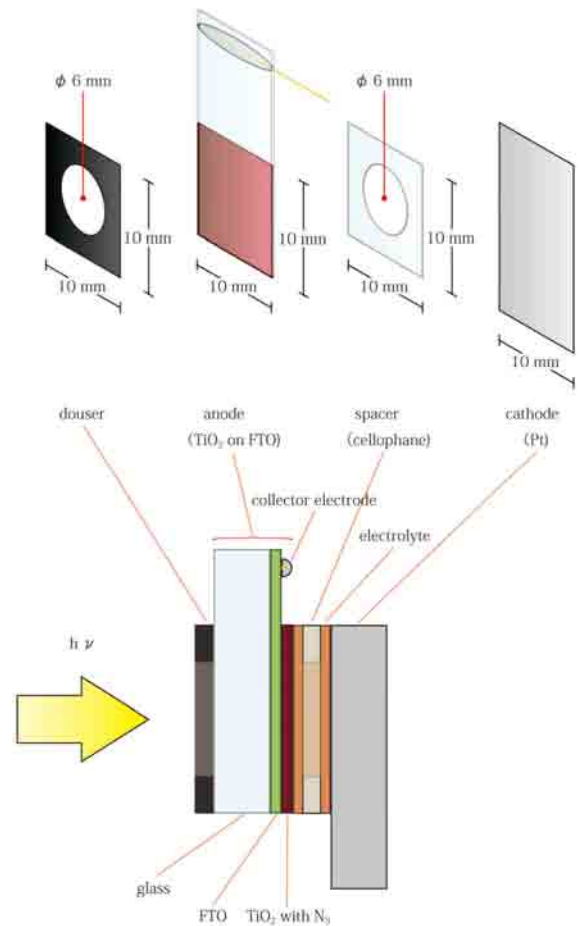


Fig.2 Illustrations of (top) individual parts of dye-sensitized solar cell and (bottom) side view of assembled cell.

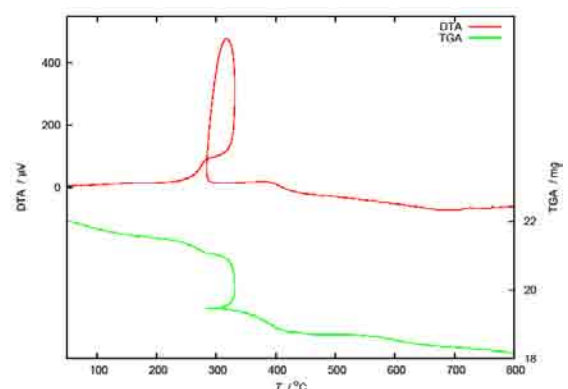


Fig.3 (top) DTA and (bottom) TGA curves of TiO₂ nanotube array film. The rate of temperature increase was +10°C min⁻¹.

Results and discussion

Light brown films were obtained by the anodic oxidation of the Ti plate. Differential thermal and thermogravimetric analyses of the films were carried out at a rate of $+10\text{ }^{\circ}\text{C min}^{-1}$. An exothermic peak and a decrease in weight were observed at $300\text{ }^{\circ}\text{C}$. The rate of temperature increase was reversed at $300\text{ }^{\circ}\text{C}$. It is considered that ethylene glycol remaining in the TiO_2 nanotube array films was burned. The bottom curve in Fig. 4 shows the XRD pattern of the films before calcinations; in this figure, I and 2θ represent the X-ray intensity and the angle between the X-ray source and detector, respectively. No peaks were observed in this curve, which implies that the films were not crystallized. The films were calcined in an electric oven at $450\text{ }^{\circ}\text{C}$ for 24 h to remove ethylene glycol and were

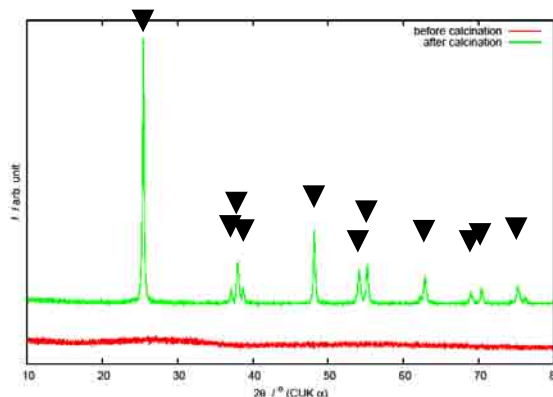


Fig.4 X-ray diffraction peaks of synthesized TiO_2 nanotube film (bottom) before calcination and (top) after calcination at $450\text{ }^{\circ}\text{C}$ for 24 h. The triangle marks indicate the TiO_2 peaks.

allowed to crystallize. The top curve in Fig. 4 shows the XRD pattern of the films after calcination. Characteristic peaks of TiO_2 anatase crystals are observed in the pattern. Fig. 5 (left) shows a SEM image of the TiO_2 films. It is observed that the films consist of an array of tubes. The outer diameter, inner diameter, and length of the tubes are observed to be ca. 100 nm, ca. 80 nm, and 10 ~ 15 μm , respectively. The terminals (parts that are connected to the Ti plate) of the tubes are closed.

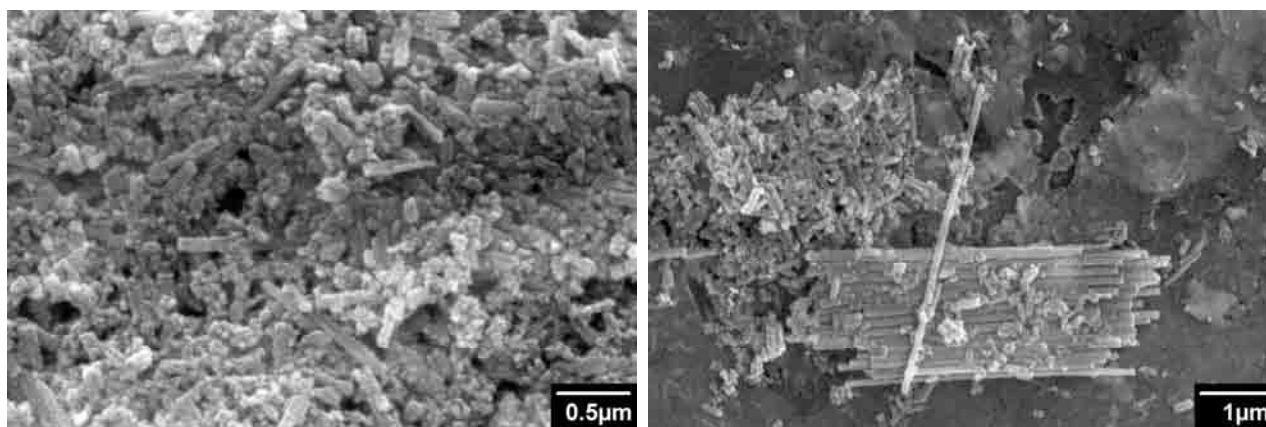


Fig.5 SEM images of TiO_2 nanotubes (left) dispersed and (right) not dispersed by ultrasonication in ethanol.

The TiO_2 nanotube array films were ultrasonicated in ethanol. Then, two powders – NTD and NTR – were obtained. Their XRD peaks indicate that they contain TiO_2 anatase crystals. Fig. 5 (right) shows the SEM image of these powders. It is observed that NTD and NTR consist of long tubes, tubes that were broken short, and clusters of tubes.

Fig. 6 shows the SEM image of the surface of the porous TiO_2 nanoparticle / nanotube film fabricated on the FTO-coated glass. It is observed that the TiO_2 nanotubes were well dispersed in the TiO_2 nanoparticles. The parameters related to the power generation efficiency of DSCs are listed in Table 1. In this table, E_{OC} , J_{SC} , W_{Max} , E_{Max} , and J_{Max} represent the open-circuit potential, short-circuit current, maximum power, potential at W_{Max} , and current at W_{Max} , respectively. It is observed that the fill factor increases with the addition of TiO_2 nanotube powder when $R_{NT} = 0 \sim 5$. The fill factor is calculated using the expression $(E_{Max} \times J_{Max}) / (E_{OC} \times J_{SC})$. Usually, the cell has an internal resistance r . When the cell generates a current J , the cell voltage becomes $E_{OC} - Jr$. When the fill factor is 1, r becomes 0. An increase in the fill factor results in a decrease in the internal resistance. This decrease is attributed to the improvement in the charge transfer rate in the TiO_2 porous film owing to the addition

of TiO₂ nanotube powder (Fig.7 (c)). The fill factor decreases as the amount of TiO₂ nanotube powder added increases. This decrease may be attributed to the interception of charge transfer by the walls of the TiO₂ nanotubes. The value of the fill factor after the addition of NTD is larger than that after the addition of NTR. This can be attributed to two reasons. (1) The charge transfer is intercepted by the walls of the TiO₂ nanotube clusters (Fig.7 (a)). (2) TiO₂ nanoparticles cannot use the charges in the long TiO₂ nanotubes (Fig.7 (b)).

Table 1 Parameters related to power generation efficiency of dye-sensitized solar cells

R_{NT} / %	E_{OC} / mV	J_{SC} / mA cm ⁻²	Fill factor	Generation efficiency / %	W_{Max} / mW cm ⁻²	E_{Max} / mV	J_{Max} / mA cm ⁻²
0	592	11.8	0.463	3.24	3.24	354	9.06
2.0 (NTD)	644	11.4	0.531	3.88	3.88	411	9.44
2.0 (NTR)	625	10.5	0.522	3.42	3.42	406	8.42
5.7 (NTD)	644	9.71	0.556	3.48	3.48	434	8.00
5.7 (NTR)	614	10.8	0.494	3.27	3.27	392	8.34
9.2 (NTD)	585	13.4	0.486	3.82	3.82	358	10.7
9.2 (NTR)	590	14.7	0.475	4.14	4.14	359	11.5



Fig.6 SEM image of hybrid TiO₂ nanoparticle / nanotube film.

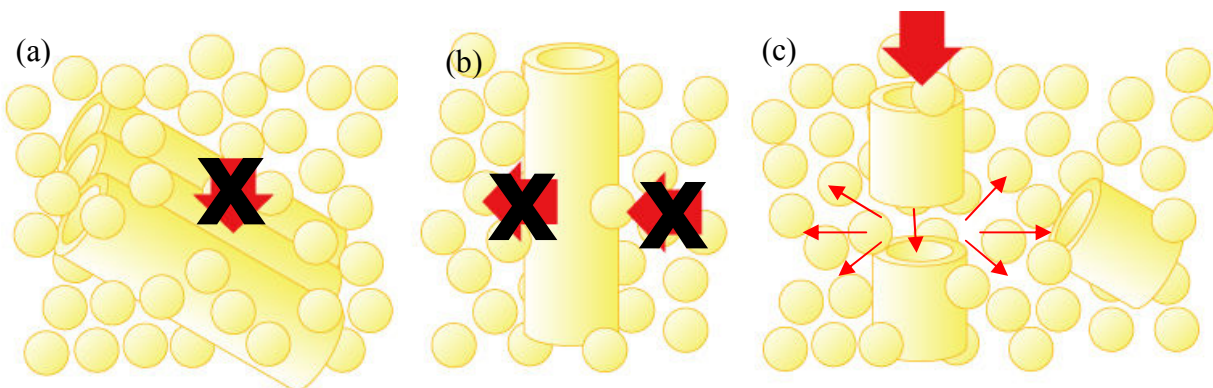


Fig.7 Schematic illustration of path of electric charges in porous electrode. (a) Large TiO₂ nanotube clusters intercept the charges. (b) Charges cannot enter in or pass through long TiO₂ nanotubes. Charges inside can only exit out of the tube. (c) Charges can pass through TiO₂ nanotubes and diffuse from the exit when TiO₂ nanotubes have reasonable length.

Summary

The charge transfer rate in TiO₂ porous electrodes was improved by the addition of TiO₂ nanotubes. The TiO₂ nanotubes should be short and should not form clusters. The optimal ratio of TiO₂ nanoparticle and TiO₂ nanotube powders is $R_{NT} = 3 \sim 5 \%$.

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