Preparation and Characterization of Dye-Sensitized Solar Cellscontaining TiO₂ Nanotube Clusters/Nanoparticle Hybrid Films

著者	HAYASHI Kazuho, NAKAMURA Takahiro, OGIHARA Takashi
journal or publication title	Key Engineering Materials
volume	485
page range	153-156
year	2011-07
URL	http://hdl.handle.net/10098/6828

Preparation and Characterization of Dye-Sensitized Solar Cells containing TiO₂ Nanotube Clusters/Nanoparticle Hybrid Films

Kazuho Hayashi^{1,a}, Takahiro Nakamura^{1,b}, Takashi Ogihara^{1,c}

¹9-1 Bunkyo 3-chome, Fukui-shi, Fukui, Japan

^ahayashi@sozai.matse.u-fukui.ac.jp

^bnakamura@sozai.matse.u-fukui.ac.jp

^cogihara@matse.u-fukui.ac.jp

Keywords: TiO₂ nanotube, anodic oxidation, dye-sensitized solar cell, ionic transport

Abstract. TiO₂ nanotube array films were synthesized by the anodic oxidation of a Ti plate in an NH₄F electrolyte. The thickness of the films was dependent upon the oxidation time. Nanotube clusters were produced when the films were subjected to sonication. Pastes were subsequently prepared by mixing the nanotube clusters with TiO₂ nanoparticles. The pastes were used to fabricate photoelectrodes of dye-sensitized solar cells. The generation efficiencies of cells with TiO₂ nanotube clusters were lower than those of cells without these clusters. TiO₂ nanotube clusters were very large, and therefore, they might have intercepted the ionic transport.

Introduction

Dye-sensitized solar cells (DSCs) can be used to generate power with an ideal conversion efficiency of more than 30%. They can be fabricated without the need for large-scale and clean facilities as in the case of semiconductor cells [1]. Moreover, cells having high power generation efficiency can potentially be fabricated more cheaply by using organic dyes without Ru, porous electrodes with high surface area, solid electrolytes, and so on.

Generally, DSC photoelectrodes are prepared from TiO₂ nanoparticles. The nanopores of the photoelectrodes are formed from gaps between the nanoparticles. Consequently, the nanopores are complicated shapes for ionic transport through electrolyte solution permeated into TiO₂ photoelectrode. In this study, TiO₂ nanotube clusters were first synthesized as describe in the literature [2]. They were then used in the preparation of the photoelectrodes. The structure of a TiO₂ nanotube is very simple; therefore, they are used as a transport tube for the ion.

Experimental

TiO₂ nanotube arrays were grown by anodic oxidation of a Ti plate (30 mm × 20 mm, thickness: 0.20 mm, Nilaco) at a constant potential of 60 V in a 90 mmol dm⁻³ NH₄F electrolyte (solvent: ethylene glycol:H₂O = 50:1 vol%) at 20°C for 15–60 min. A carbon plate was used as a counter electrode. The distance between the electrodes was 15 mm. Then, the Ti plate was rinsed with distilled water and dried at room temperature. The resulting film was peeled off from the Ti plate (Fig.1). The film was broken into clusters by sonication in distilled water for 6 h. The clouded water was centrifuged and calcined in an electric oven (Yamato, DR-22) at 450°C for 24 h. The calcination temperature was determined by DTA-TGA (differential thermal and thermogravimetric analysis, carried out at a rate of +10°C min⁻¹, SHIMADZU, DTG-60/60) data. The geometries, crystal structures, and specific surface areas of the clusters were evaluated by SEM (scanning electron microscope, JEOL, JSM-6390YH), XRD (X-ray diffractometer, SHIMADZU, XRD-6100), and the BET method (Brunauer-Emmett-Teller method, BEL JAPAN, INC., BELSORP-mini), respectively.

490 mg of TiO₂ nanoparticles (ST-21, Ishihara Sangyo), 10 mg of the obtained TiO₂ nanotube

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

clusters, 100 mg of polyethylene glycol (Nacalai Tesque, M.W. 20000), 400 mm³ of 1.0 mmol dm⁻³ dilute 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 bottle. The bottle was rocked by a mill machine (RM-01, Seiwa Giken) for 24 h. The obtained paste was coated at a thickness of 40 µm on FTO-glasses (AGC Fabritech) over an area of 1.0 cm². After drying at room temperature, these glasses were sintered in an electric oven at 450°C for 30 min. The fabricated TiO₂ nanotube clusters/nanoparticle hybrid photoelectrodes were immersed in 0.3 mmol dm⁻³ ruthenium organic complex (N₃, KISCO) ethanol solution and left for 3 days. The dye-adsorbed photoelectrodes were rinsed with ethanol and dried at room temperature.

A dye-sensitized solar cell was assembled from a 10 mm² black opaque paper punched at a diameter of 6 mm (douser), the fabricated dye-sensitized photoelectrode (anode), a 10 mm² cellophane film punched at a diameter of 6 mm (spacer), a 10 mm × 20 mm × 0.2 mm Pt plate (cathode), and an electrolyte (Fig. 2). The electrolyte consisted of 0.3 mol dm⁻³ LiI (Wako) and 0.03 mol dm⁻³ I₂ (Nacalai Tesque) in blended solvent; acetonitrile (Nacalai Tesque) and 3-methyl-2-oxazolidinone (Wako), 1:1 vol%.

The cell was evaluated using a homemade system consisting of a Xe lamp (100 mW cm⁻², 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, potential and current logger, and electronic resistance, respectively. The data from the electrometer and the potentiostat were recorded using a homemade program on a personal computer via an A/D converter (Adtek System Science, aPCI-A57).

Fig.2 Illustration of side view of assembled dye-sensitized solar cell.

Results and discussion

Fig. 3 shows the DTA-TGA curve of the TiO₂ nanotube clusters following sonication. Two exothermic peaks were observed at 230 and 270°C. One of them may be attributed to the burning peak of ethylene glycol remaining in the sample and the other, to the crystallizing peak of TiO₂ anatase phase. Fig. 4 shows XRD curves of the TiO₂ nanotube clusters before (bottom) and after (top) calcination; *I* and 2θ represent the X-ray intensity and the angle between the X-ray source and detector, respectively. No peaks were observed in the bottom curve, implying that the sample before calcination did not crystallize. In the top curve, TiO₂ anatase phase peaks were observed. Calcination at 450°C for 24 h removed any remaining ethylene glycol and facilitated crystallization.

Fig. 5 shows SEM images of the (a) top view of the TiO₂ nanotube clusters after calcination at 450°C for 24 h and a (b) bird's eye view of one of these clusters.

Tube lengths varied from 3.5 µm to 25.5 µm with anodic oxidation time. The outer and inner diameters of the nanotube (130 nm and 85 nm, respectively) remained constant. Fig. 6 shows the relationship between the nanotube length and the anodic oxidation time. The nanotube length increased with the anodic oxidation time. Table 1 lists the specific surface areas of TiO₂ nanotube clusters and nanoparticles, 4.45 and 6.60 m² g⁻¹, respectively, as observed by the BET method.

Fig. 3 DTA-TGA curves of TiO₂ nanotube clusters. The rate of temperature increase was +10°C min⁻¹.

Fig. 4 XRD peaks of obtained TiO₂ nanotube clusters before (bottom) and after (top) calcination at 450 °C for 24 h. The triangle marks indicate the TiO₂ anatase phase peaks.

Table 1 Specific surface areas of TiO₂ nanotube clusters and nanoparticles.

Sample name	Specific surface area [m ² g ⁻¹]
TiO ₂ nanotube clusters	4.45
TiO ₂ nanoparticles	6.60

The difference between the specific surface areas of TiO₂ nanotube clusters and nanoparticles was 32.6%. The amount of TiO₂ nanotube clusters was 2.0% of the amount of TiO₂ included in the paste. The decrease in the specific surface area can be calculated according to the following equation: $32.6\% \times 2.0\% = 0.65\%$.

Fig. 7 shows an SEM image of a hybrid TiO₂ nanotube clusters/nanoparticle photoelectrode. It is found that the surface was flat despite the addition of TiO₂ nanotube clusters.

Parameters related to the power generation efficiency of DSCs are listed in Table 2. 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. The fill factor is calculated using the expression $(E_{MAX} \times J_{MAX}) / (E_{OC} \times J_{SC})$. The addition of TiO₂ nanotube clusters led to a decrease in J_{SC} and the power generation efficiency with an increase in the nanotube length. The difference in J_{SC} between the cells containing and not containing 13.2 μm nanotube clusters is approximately 30%. A measurement of the alternating-current impedance and a fitting with an equivalent described in Fig. 8 indicated that the resistances of the related TiO₂ photoelectrodes were 150 Ω and 113 Ω, respectively. Sums of the other resistances were 70 Ω in both of the cells. These differences may be attributable to an electrolyte resistance inside the TiO₂ photoelectrodes. Therefore, the decrease in J_{SC} may be caused by the

Fig. 5 SEM images of (a) top view of the TiO₂ nanotube clusters after calcination at 450 °C for 24 h, (b) bird's eye view of one of the clusters.

Fig. 6 Relationship between TiO₂ nanotube length and anodic oxidation time.

Fig. 7 SEM image of hybrid TiO₂ nanotube / nanoparticle photoelectrode.

electrolyte resistance. Another explanation for the decrease in J_{SC} could be the decrease in the amount of dye-adsorption related to the decrease in the surface area of the TiO_2 photoelectrode.

The electrolyte resistance can be attributed to the interception of ionic transport through electrolyte solution permeated into TiO_2 photoelectrode by the walls of the large TiO_2 nanotubes. In addition, the entrances of the nanotubes were much smaller than the side wall surfaces of the nanotube clusters. Thus, ion could not enter the nanotubes (Fig.9 (a)). The size of the TiO_2 nanotube clusters may have to be decreased by employing stronger sonication to solve the abovementioned problems (Fig. 9 (b)).

Table 2 Parameters related to power generation efficiency of dye-sensitized solar cells.

Tube length [μm]	E_{OC} [mV]	J_{SC} [mA cm ⁻²]	W_{MAX} [mW cm ⁻²]	E_{MAX} [mV]	J_{MAX} [mA cm ⁻²]	Fill factor	Generation efficiency [%]
No tube	603	10.5	3.26	386	8.45	0.514	3.26
4.45	603	8.60	2.67	391	6.84	0.515	2.67
9.62	613	7.55	2.40	391	6.14	0.518	2.40
13.20	603	7.17	2.21	383	5.78	0.511	2.21
20.20	603	6.44	2.14	405	5.28	0.550	2.14

Fig 8. An equivalent circuit of dye-sensitized solar cells.

Fig. 9 Schematic illustrations inside TiO_2 nanotube clusters/nanoparticle hybrid photoelectrodes; (a) ionic transport through electrolyte solution was intercepted by large TiO_2 clusters, (b) ion can pass small TiO_2 nanotube clusters.

Summary

The generation efficiencies of dye-sensitized solar cells with TiO_2 nanotube clusters were lower than those of cells without these clusters. TiO_2 nanotube clusters were very large, and therefore, they intercepted the ionic transport. To improve their performance, the TiO_2 nanotube clusters may have to be decreased in size using stronger sonication.

References

- [1] M. Gratzel: J. Photochem. Photobiol. C: Photochemistry Reviews, Vol. 4 (2003), p. 145.
- [2] H. Park, D. J. Yang, J. S. Yoo, K. S. Mum, W. R. Kim, H. G. Kim, and W. Y. Choi: J. Ceram. Soc. Jpn., Vol. 117 (2009), p. 596.

Electroceramics in Japan XIV

doi:10.4028/www.scientific.net/KEM.485

Preparation and Characterization of Dye-Sensitized Solar Cells Containing TiO₂ Nanotube Clusters/Nanoparticle Hybrid Films

doi:10.4028/www.scientific.net/KEM.485.153