Application of Titania Nanotubes to a Dye-sensitized Solar Cell

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Titania nano tube was successfully obtained by hydrothermal treatment of nano size TiO$_2$ fine powder in 10 M NaOH solution for 20 h at 110℃. The morphology of product was 8-10 nm in width and about 100 nm in length with tubular shape. The specific surface area was 270 m$^2$ g$^{-1}$, much higher than that of starting material titania powder with 50 m$^2$ g$^{-1}$. Photovoltaic properties of these titania film was also examined. The results were $V_{OC}=0.704$, $I_S=1.26$ mA, $\eta=2.9\%$, FF=0.66 for titania nano tube, and $V_{OC}=0.767$, $I_S=1.20$ mA, $\eta=3.0\%$, FF=0.72 for titania nano powder (P-25).

Key Words : Dye-sensitized Solar Cell, Hydrothermal Synthesis, Titanium Dioxide, Titania Nanotube

1 Introduction

The TiO$_2$ particles have been widely used for various applications such as pigment, photocatalyst, photoelectron conversion device, UV protection shield, Anti-Bacteria material, and so on. In order to improve their specific properties, much effort have been paid for morphology control of the TiO$_2$ particles. Titania nano tube is one of the promising material for above use because of the high specific surface area and specially order structure. It was firstly synthesized by a two-step template process. Starting from the porous aluminum oxide, a polymer mold suitable for the formation of titanium dioxide nano tubes was obtained. Then, the tubular structure was formed by electrochemical deposition in the mold. After dissolution of the polymer, titania nano tubes in 70-100 nm inner diameter were obtained.1-3) Similar replication process has been also reported by using SiO$_2$ sheaths as a mold.4) The formation of titania nano tubes filled with up to 24.5% of Pt metal clusters is reported by sol-gel processing with an inorganic platinum salt [Pt(NH$_3$)$_2$](HCO$_3$)$_3$ as structure-directing agent. Very small fibers of the salt with sizes in the nano meter range are coated with titane species forming the tube walls.5) Mono dispersed hollow nano cylinders consisting of crystallized titania particles have been prepared directly in a porous alumina membrane by a deposition technique using an aqueous solution system of titanium tetrafluoride.6) Titania nano tubes with high photocatalytic activity were synthesized in laurylamine hydrochloride/tetraisopropyl orthotitanate modified with acetylate tone system.7) In contrast to these methods, direct formation process of the titania nano tube without a template were also reported. Nanotube-shaped TiO$_2$ powder was prepared by a digestion of the powder obtained by the reaction of TiOCl$_2$ and NH$_2$OH solutions over 100℃.8-10) Recently a notable simple method has been proposed by Kasuga et al., in which titania nano tubes with 8 nm in diameter and 100 nm in length were obtained by only treating TiO$_2$·SiO$_2$ gel or nano size TiO$_2$ fine powders in 5-10 M NaOH solutions for 20 h at 110℃. Synthesized titania nano tubes had a large specific surface area up to 400 m$^2$ g$^{-1}$.11-13)

In this study, Kasuga’s synthesis method without a template was traced to produce titania nano tubes. Considering future mass production of Dye-Sensitized Solar Cell in low cost, widely used titania nano powder (P-25) was selected as a raw material. Although Kasuga et al.11) have also tried to synthesize the titania nano tubes from P-25, detailed analyses have not yet been reported. And then it was newly examined to apply for the electrode of dye-sensitized solar cell with aiming to improve the photovoltaic properties.

2 Experimental

Basically titania nano tube was synthesized based on the method developed by Kasuga as mentioned in Introduction.14-16) All chemicals were reagent grade and used without any purification. The nano meter sized TiO$_2$ powder (P-25, Nippon Aerosil Co., Ltd.) was used as the starting material. The primary particle size was 30 nm in diameter. The crystal structure was the mixture of anatase form (70%) and rutile. The specific surface area of TiO$_2$ was 50 m$^2$ g$^{-1}$ and the purity was $>$99.5%. The chemical analysts of this titania was as follows: Alumina (Al$_2$O$_3$) < 0.3%, Silica (SiO$_2$) < 0.2%, Iron oxide (Fe$_2$O$_3$) < 0.01%, Hydrochloric acid (HCl) < 0.3% and that of the sodium hydroxide was: Sodium carbonate (Na$_2$CO$_3$) < 1.5%, Chloride (Cl) < 0.005%, Phosphate (PO$_4$) < 0.001%, Sulfate (SO$_4$) < 0.001%. Water used in the experiment was deionized by the ion exchanger after the distillation.

A typical experimental procedure is as follows. Firstly 8 g of NaOH and 20 ml of water were put into a tubular 30 cm$^3$ of Teflon$^8$ cup to from 10 M NaOH solution.
Then 0.2 g of TiO₂ (P-25) powder was added in the solution. These were placed in the pressure resistable glass bottle (100 mL GL-45, Duran). After sealing the bottle, it was set into a dry oven at 110°C for 20 h. After the reaction was completed, the product was separated from the solution by centrifuge then rinsed with hydrochloric acid and pure water to remove the residual alkaline, and finally dried by freeze drier. The TEM (JEM-20EXII, JEOL) was employed to carry out electron diffraction and morphology observation.

For the measurement of photovoltaic properties, following procedures were taken. Above synthesized titania nano tube or titania powder (P-25) with 30 wt% were put into HNO₃ aqueous solution to make pastes. Polyethylene-neglycol (PEG #500,000) was added with 40 wt% against the amount of TiO₂ as a thickener. Conductive transparent fluorine doped tin oxide (FTO) coated glass with average sheet resistance about 30 Ω cm⁻¹, was used as a substrate. The counter electrode was Pt coated FTO glass. The electrolyte solution was prepared by mixing 0.5 M LiI, 0.05 M I₂, 0.4 M 4-butylypyridine and 0.5 M isopropyl-2, 3 dimethylimidazolium iodide into the 3-metoxi propion nitrit as a solvent. Ruthenium dye, bis(isothiocyanato)-ruthenium(II)-2,2′-bipyrindine-4,4′-dicalboxylate bitetrabutyl ammonium (Ru-535 bisTBA, Solaronix) was used without further purification.

About 0.25 cm² active area of the dye sensitized TiO₂ solar cells were constructed fundamentally according to the method by Nogueira and Paoli. At first on the glass substrate, titania pastes in 60 μm thickness were applied to fabricate TiO₂ electrode then heated at 450°C for 50 min in air. After, that the electrode was soaked in 0.5 mM ruthenium dye ethanol solution for 20 h at room temperature. Finally, dye sensitized TiO₂ electrode and counter electrode were faced each other, and electrolyte were infiltrated into the space between these electrodes to form the solar cell. The apparatus for evaluating the solar cell is as follows. The 300 W Xe lamp (Hyper Xenon Exciter, Bunkoh Keiki Co., Ltd.) was used as the light source. A glass filter (HA-50, HOYA) was equipped to cut the IR (over 700 nm) and UV (under 400 nm) spectral regions. Intensity of the illumination was maintained 100 mW cm⁻², using a pyranometer (LI-200SB, LICOR). The experimental data of photocurrent and voltage was automatically transmitted to PC via 12-bit A-D converter and relayed set of variable resistors.

3 Results and Discussion

Hydrothermal synthesis was carried out to form the titania nano tube. After the treatment, the product was dispersed in ethanol in an ultrasonic bath, and the suspension was dropped onto a perforated copper mesh. The product was observed by transmission electron microscopy at an accelerating voltage of 200 kV. TEM images of the product are shown in Fig. 1.

The morphology of products was quite similar as already reported. Numerous needle-shaped products about 100 nm in length are seen. The width of products is about 8 nm and the lattice fringes with 1.5 nm thickness are present on both side. The specific surface area measured by BET was 270 m² g⁻¹. This is much higher than that of 50 m² g⁻¹ before the hydrothermal treatment, and no spherical particle of starting material about 30 nm in diameter can be seen. Therefore the formation of these needle-shaped products is considered to be proceed by dissolution-recrystallization mechanism. Diffened with the previous Kasuga’s report, more tight coagulation is observed in Fig. 1(a). This is possibly due to the difference of reactivity of starting materials between TiO₂-SiO₂ gel and TiO₂ powder. Moreover some titania nano tubes show incomplete and open tubular representaiton in Fig. 1(b) and (c). It may give a clue of the elucidation toward the formation mechanism of titania nano tube.

The selected-area electron diffraction pattern from agglomerated tube products in TEM observation showed (101), (112), (200), (211) and (204) diffractions of the anatase phase (Fig. 2).

From Fig. 2 it can be said that the products are poly crystalline of anatase phase. The starting material TiO₂ powder (P-25) consists of the mixed phase of anatase (70%) and rutile. Nevertheless, no diffraction of rutile was observed. This gives a support of the formation mechanism described above.

Finally the application of this titania nano tube for dye-sensitized solar cell was examined. Two titania coated electrodes were prepared by sintering at 450°C for 50
ions such as I₃⁻ or I₅⁻ in several complex materials of aggregation of titania nano tubes to prevent well electrical conductivity as seen in Fig. 1(a). One more possible reason is the restriction of the diffusion of electrolyte, I⁻ / I₃⁻ inside the nano tube wall. The aggregation of polypiodide ions such as I⁻ or I₅⁻ in several complex materials of channel inclusion compounds to form the long polymerized chains is also proposed.

4 Conclusion

From the results of tests described above, the following conclusions may be drawn.

Hydrothermal synthesis was carried out to form the titania nano tube. The morphology of product was about 8-10 nm in width and 100 nm in length with tubular shape. The specific surface area was 270 m² g⁻¹, much higher than that of starting material titania powder (50 m² g⁻¹). Nevertheless, significant difference on photovoltaic properties of the solar cells with these titania films could not be observed. They were:

1. Titania nano tube: $V_{oc} = 0.704$, $I_{sc} = 1.26$ mA, $\eta = 2.9\%$, $FF = 0.66$

2. Titania nano powder (P-25): $V_{oc} = 0.767$, $I_{sc} = 1.20$ mA, $\eta = 3.0\%$, $FF = 0.72$

For further improvement of the solar cell performance, optimum condition should be found out to avoid the aggregation of titania nano tubes.

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References