

—Communication—

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°C . The morphology of product was 8-10 nm in width and about 100 nm in length with tubular shape. The specific surface area was $270 \text{ m}^2 \text{ g}^{-1}$, much higher than that of starting material titania powder with $50 \text{ m}^2 \text{ g}^{-1}$. Photovoltaic properties of these titania film was also examined. The results were $V_{\text{oc}}=0.704$, $I_{\text{sc}}=1.26 \text{ mA}$, $\eta=2.9\%$, $\text{FF}=0.66$ for titania nano tube, and $V_{\text{oc}}=0.767$, $I_{\text{sc}}=1.20 \text{ mA}$, $\eta=3.0\%$, $\text{FF}=0.72$ 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 ordered 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, 5)} 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 $[\text{Pt}(\text{NH}_3)_4](\text{HCO}_3)_2$ as structure-directing agent. Very small fibers of the salt with sizes in the nano meter range are coated with titanate species forming the tube walls.⁶⁾ 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.⁷⁾ Titania nano tubes with high photocatalytic activity were synthesized in laurylamine hydrochloride/tetraisopropyl orthotitanate modified with acetylacetone system.⁸⁾ 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_4OH solutions over 100°C .^{9, 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 $\text{TiO}_2 \cdot \text{SiO}_2$ gel or nano size TiO_2 fine powders in 5-10 M NaOH solutions for 20 h at 110°C . Synthesized titania nano tubes had a large specific surface area up to $400 \text{ m}^2 \text{ g}^{-1}$.¹¹⁻¹⁵⁾

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 photoelectronic properties.

2 Experimental

Basically titania nano tube was synthesized based on the method developed by Kasuga as mentioned in Introduction.¹¹⁻¹⁵⁾ 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 $50 \text{ m}^2 \text{ g}^{-1}$ and the purity was $>99.5\%$. The chemical analysts of this titania was as follows: Alumina (Al_2O_3) $<0.3\%$, Silica (SiO_2) $<0.2\%$, Iron oxide (Fe_2O_3) $<0.01\%$, Hydrochloric acid (HCl) $<0.3\%$ and that of the sodium hydroxide was: Sodium carbonate (Na_2CO_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[®] cup to from 10 M NaOH solution.

Then 0.2 g of TiO_2 (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 HNO_3 aqueous solution to make pastes. Polyethyleneglycol (PEG #500,000) was added with 40 wt% against the amount of TiO_2 as a thickener. Conductive transparent fluorine doped tin oxide (FTO) coated glass with average sheet resistance about $30 \Omega \text{ cm}^{-1}$, 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 I_2 , 0.4 M 4-t-butylpyridine and 0.5 M *i*-propyl-2, 3 dimethylimidazolium iodide into the 3-methoxy propion nitril as a solvent. Ruthenium dye, bis(isothiocyanato)-ruthenium(II)-2,2'-bipyridine-4,4'-dicarboxylate bis-tetrabutyl ammonium (Ru-535 bisTBA, Solaronix) was used without further purification.

About 0.25 cm^2 active area of the dye sensitized TiO_2 solar cells were constructed fundamentally according to the method by Nogueira and Paoli.¹⁶⁾ At first on the glass substrate, titania pastes in $60 \mu\text{m}$ thickness were applied to fabricate TiO_2 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 TiO_2 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 evaluation the solar cell is as follows. The 300 W Xe lump (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.¹¹⁾ 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

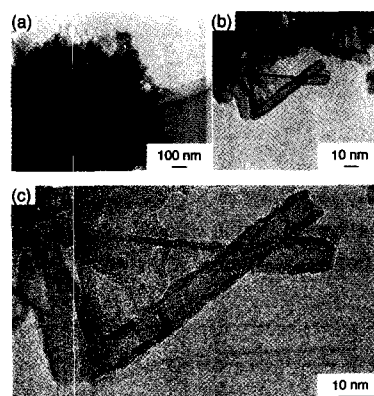


Fig. 1 TEM images of titania nano tube at (a) low magnification, (b) high magnification and (c) ultra high magnification.

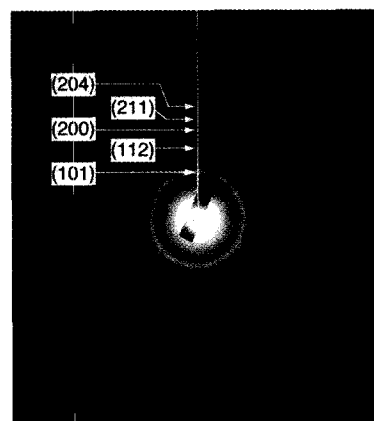


Fig. 2 Electron diffraction pattern of titania nano tube from selected area.

measured by BET was $270 \text{ m}^2 \text{ g}^{-1}$. This is much higher than that of $50 \text{ m}^2 \text{ g}^{-1}$ 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 proceeded by dissolution-precipitation mechanism. Differed with the previous Kasuga's report,¹¹⁾ more tight coagulation is observed in Fig. 1(a). This is possibly due to the difference of reactivity of starting materials between $\text{TiO}_2\text{-SiO}_2$ gel and TiO_2 powder. Moreover some titania nano tubes show incomplete and open tubular representation 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 polycrystalline of anatase phase. The starting material TiO_2 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

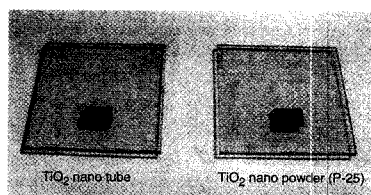


Fig. 3 Observation of titania coated electrodes after soaked in the dye solution.

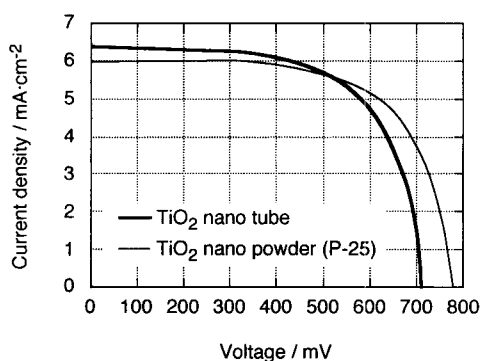


Fig. 4 Photovoltaic properties of solar cells with titania nano tube and titania nano powder electrodes.

min. One is titania nano tube with hydrothermal treatment and the other is titania nano powder (P-25) without any treatment. These electrodes after soaked in the dye solution are compared in Fig. 3.

Evidently, titania film derived from titania nano tube are well colored than that of titania powder(P-25). This phenomenon qualitatively corresponds to the difference of specific surface area of $270 \text{ m}^2 \text{ g}^{-1}$ for titania nano tube and that of $50 \text{ m}^2 \text{ g}^{-1}$ for titania nano powder(P-25).

Photovoltaic properties of the solar cells composed with these electrodes are measured. The obtained I (photo current) vs V(voltage) results are shown in Fig. 4.

The titania film derived from titania nano tube showed $V_{oc} = 704 \text{ mV}$, $I_{sc} = 1.26 \text{ mA}$, $\eta = 2.9\%$, $FF = 0.66$ as open-circuit voltage, short-circuit current density, energy conversion efficiency and fill factor, respectively. These results were nearly equal to those of titania nano powder (P-25); $V_{oc} = 767 \text{ mV}$, $I_{sc} = 1.20 \text{ mA}$, $\eta = 3.0\%$, $FF = 0.72$. Here, the photovoltaic property of titania nano powder (P-25) corresponds to the maximum value of preliminary repeated experiments in the limitation of experimental setup. Therefore the slight difference of higher short-circuit current density of titania nano tube is considered as meaningful. This slight increase of short-circuit current density of titania nano tube is due to the increase of the amount of dye adsorbed. Relatively lower open-circuit voltage of titania nano tube is possibly the result of lower inter connectivity of the tubes. Though specific surface area of TiO_2 nano tube is much larger than that of nano particle, the photovoltaic properties of the cell are not improved as expected. This is possibly because of the aggregation of titania nano tubes to prevent well electrical connectivity as seen in Fig. 1(a). One more possible reason is the restriction of the diffusion of electrolyte, I^-/I_3^- inside the nano tube wall. The aggregation of polyiodide ions such as I_3^- or I_5^- in several complex materials of

channel inclusion compounds to form the long polymerized chains is also proposed.¹⁷⁾

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 $270 \text{ m}^2 \text{ g}^{-1}$, much higher than that of starting material titania powder($50 \text{ m}^2 \text{ g}^{-1}$). Nevertheless, significant difference on photovoltaic properties of the solar cells with these titania films could not be observed. They were:

- (1) Titania nano tube; $V_{oc} = 0.704$, $I_{sc} = 1.26 \text{ mA}$, $\eta = 2.9\%$, $FF = 0.66$
- (2) Titania nano powder(P-25): $V_{oc} = 0.767$, $I_{sc} = 1.20 \text{ mA}$, $\eta = 3.0\%$, $FF = 0.72$

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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