

Dye-sensitized Solar Cells Using Semiconductor Thin Film Composed of Titania Nanotubes

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Over two times higher short-circuit photocurrent density was attained in the dye-sensitized solar cells by using titania nanotubes as a semiconductor thin film in the thin film thickness region in comparison with that made of P-25. Titania nanotubes were synthesized by a surfactant-assisted templating mechanism using a laurylamine hydrochloride / tetraisopropylorthotitanate with acetylacetone system.¹⁾ Nanotubes have a mono-crystalline structure of anatase and showed the highest photocatalytic activity among the commercially available nano-crystalline titania. The dye-sensitized solar cell system using the mono-crystalline titania nanotubes showed about 5% sunlight-electricity conversion.

Key Words : Titania Nanotubes, Dye-sensitized Solar Cell, Mono-crystalline Structure, High Photocatalytic Activity

1 Introduction

We present an efficient dye-sensitized solar cell, which shows high short-circuit photocurrent density especially in the thin film thickness region, using mono-crystalline titania nanotubes as the semiconductor thin film of dye-sensitized solar cells. Mono-crystalline titania nanotubes with high aspect ratio facile electron transfer through titania thin layer due to extremely decrease in the contact number among nanotubes in comparison with that of nanoparticles. We succeeded in preparation of such a mono-crystalline nanotube of titania.

About three years ago, we succeeded in preparation of silica nanotubes using laurylamine hydrochloride (LAHC) / tetraethoxysilane (TEOS) system^{2, 3)} and extended the method to synthesize titania nanotubes using LAHC / tetraisopropylorthotitanate (TIPT) with acetylacetone (ACA) system last year.¹⁾ Titania nanotubes were synthesized by Hoyer⁴⁾ using anodic porous alumina. Their diameter of titania nanotubes were 100 to 70 nm and had polycrystalline structure, indicating that high electron transfer can not be expected. Kasuga *et al.*⁵⁾ synthesized titania nanotubes with diameter of 8 nm by chemical treatment of fine TiO₂-SiO₂ particles with 10 M NaOH aqueous solution at 383 K. Unfortunately, their formation mechanism is unknown, and the photocatalytic activity of their nanotubes was not high, although their BET specific surface area was 400 m²/g. In comparison with their synthetic method, our method by templating mechanism is applicable to various synthetic conditions, anticipating that it has possibility to make highly active and mono-crystalline structure nanotubes.

In this paper, we present the preparation of titania nanotubes, and a mono-crystalline structure of these nanotubes characterized by transmission electron microscopy (TEM) images, together with electron diffraction, X-ray diffraction and nitrogen adsorption isotherms. We ap-

plied the mono-crystalline titania nanotubes for a semiconductor thin film electrode in dye-sensitized solar cells and attained over two-times higher short-circuit photocurrent densities of the thin film electrode made of titania nanotubes in the thin film region in comparison with those of P-25.

2 Experimental

2.1 Formation of titania nanotubes

We used mainly the LAHC / TIPT with ACA system. In some cases, octadecylamine (ODA) was used as a surfactant. The reaction behavior in the ODA system was almost the same as that in the LAHC system. The experimental procedure was described in the previous paper.¹⁾ Characterization of the produced materials was made by small angle X-ray scattering (SAXS), X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction, scanning electron microscopy (SEM), and isotherm of nitrogen adsorption. The photocatalytic activity of titania nanotubes was measured through the formation rate of I₃⁻ due to the oxidation of I⁻ to I₂. The produced titania materials were ground in a mortar made of agate, and 50 mg of them were suspended by magnetic stirring in 10 ml of 0.2 M KI aqueous solution, after which the solution was irradiated with 365 nm rays (UV-lamp).

2.2 Preparation of titania thin films and solar cells

Thin titania films were made by applying a titania sample on a fluorine doped conducting tin oxide glass plate. We used a gel with white color, which was obtained after reactions at 353 K for three days, as the starting titania sample. Since the titania nanotubes in the gel contained surfactant molecules in the pore, surfactant molecules were removed from mesopores by washing with isopropyl alcohol. We controlled the alcohol content and viscosity of the gel simultaneously by changing the centrifuga-

tion speed, when the sample was separated from the alcohol solution by centrifugation. Next, the conducting glass was covered on two parallel edges with adhesive tape to control the thickness of the TiO_2 film and to provide non-coated area for electrical contact. The titania sample was applied to the free edges of the conducting glass and distributed with a glass rod sliding over the tape covered edges. After drying, the sample was calcined at 723 K for 30 minutes. Dye was introduced to the titania thin films by soaking the film for about 20 h in a 3×10^{-4} M solution of the ruthenium dye in ethanol. Cis-di(thiocyanate)bis(2,2'-bipyridyl-4,4'-di-carboxylate) ruthenium(II) (R535) produced by Grätzel's group^{6,7)} was used as the dye. The solar cell comprised titania thin film electrode on a conducting glass plate, a platinum electrode and electrolyte between the titania thin film and the platinum. We used 0.03 M iodine and 0.3 M lithium iodide in 3-methyl-2-oxazolidinone(NMO)/acetonitrile solution as the electrolyte. The volume ratio of NMO to acetonitrile was 1/9. The photocurrent-voltage characteristics were measured using a potentiostat (Hokuto Denko HA-501G, HB-105) by irradiating with simulated solar light, *i.e.*, AM 1.5 100 mW/cm² (ORIEL 1000 W 91192). The cell size was 1 cm² or 0.25 cm². P-25 was used as reference titania particles for comparison. The preparation of TiO_2 films of P-25 was made after Nazeeruddin *et al.*⁷⁾

3 Results and discussion

3.1 Titania nanotubes

The reaction in the mixed solution of LAHC aqueous solution and TIPT modified with ACA proceeded as follows. When the two solutions were mixed, precipitates were formed. The solution was stirred further to dissolve the precipitates completely at 313 K, and the solution became transparent. When the temperature of the transparent solution was increased to 353 K, the reaction started. After 3 h from the start of reaction, the solution became a gel with yellow color. After 5 h, the hard gel became weak, and a liquid phase appeared. After 25 h, the solution became a gel with white color again with a transparent yellow liquid thin layer on the gel, and this state was maintained for three days.

Figure 1a shows a TEM image of nanotubes in a gel sample. We can see long nanotubes (diameter 10 nm, length 200 nm) as well as short ones (diameter 10 nm, length 30 nm). SAXS results indicate that these short nanotubes are predominant. Electron diffraction patterns of these nanotubes show the Debye-Scherrer rings of anatase. A TEM image of the calcined sample in the ODA / TIPT with ACA system is shown in Fig. 1b. We can see lattice image of the nanotubes, which clearly shows that nanotubes are mono-crystals of anatase. The electron diffraction pattern exhibited in Fig. 1c also shows that nanotubes are crystals of anatase. These TEM images and electron diffractions clearly show that titania nanotubes are mono-crystals of anatase. This is remarkable feature of titania nanotubes.

Figure 2a shows the nitrogen adsorption isotherm of a calcined sample at 673 K. The isotherm shows a typical

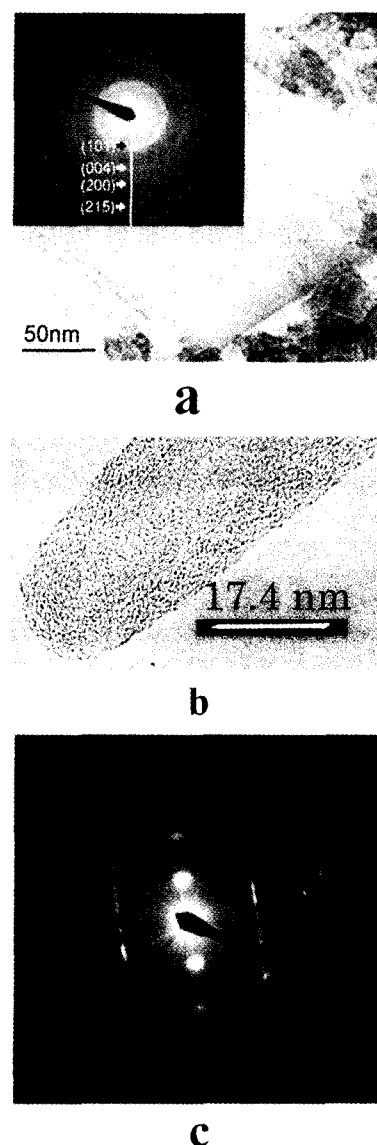


Fig. 1 a) TEM image of titania nanotubes in gel sample. Inset: Electron diffraction of titania nanotubes; b) TEM image of calcined titania nanotubes at 773 K for 4 h in ODA / TIPT with ACA system; c) Electron diffraction pattern of the calcined titania nanotubes.

IUPAC type IV pattern, indicating that an open mesosize tubular shape was formed. The peak pore diameter obtained was as 4.6 nm as shown in Fig. 2b.

The photocatalytic activity of titania nanotubes was very high as described in the previous paper.¹⁾ The best activity at present was obtained for the sample calcined at 573 K for 24 h. The best activity was 7 times higher than that of standard photocatalytic particle JRC-3, 2.8 times higher than that of JRC-4, which corresponds to P-25, and even higher than ST-01, which is known as the highest photocatalytic active commercially available particle. Thus, we can conclude that very photocatalytic active titania nanotubes can be made by the present method.

3.2 Characteristics of the thin film electrode made of titania nanotubes

Surfactant molecules in titania nanotubes can be removed from mesopores by washing with alcohol. We

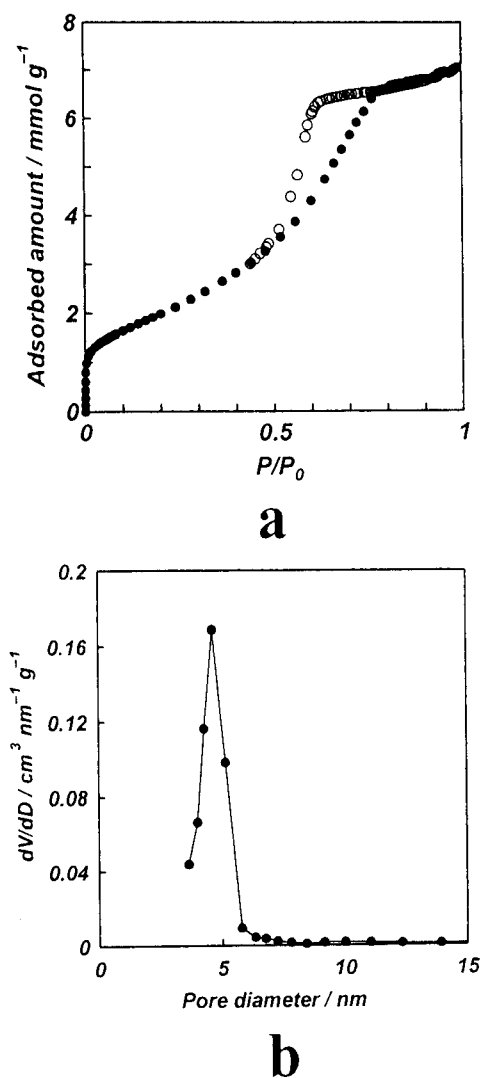


Fig. 2 a) Nitrogen adsorption isotherm of the calcined sample at 673 K. b) Pore size distribution of the calcined sample shown in Fig. 2a.

controlled the alcohol content by the centrifugation speed, when the sample was separated from the alcohol solution by centrifugation. We chose the best alcohol content, which gave the highest short-circuit photocurrent density because the open-circuit voltage was almost constant around 0.6 V.

Figure 3 shows an example of photocurrent-voltage characteristics of a cell made of the titania nanotubes. The film thickness was 4 μm , and the cell size was 0.5 cm $\times$ 0.5 cm. The obtained short-circuit photocurrent density was 15.3 mA/cm², and the open-circuit voltage was 0.58 V. The light-to-electric energy conversion yield was 4.88%, and the fill factor was 0.54.

In order to compare the cell composed of titania nanotubes with a cell composed of the standard titania particles P-25, we measured the photocurrent-voltage characteristics of the cell made of P-25. The open-circuit voltage was about 0.6 V, which was the same as the cell made of titania nanotubes. Thus, we can evaluate the efficiency of the cell by comparing the values of the photocurrent density.

Figure 4 shows the short-circuit photocurrent density

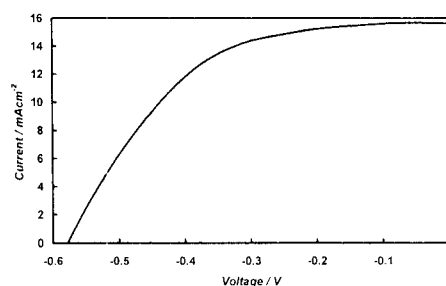


Fig. 3 An example of photocurrent-voltage characteristics of a cell made of titania nanotubes. The obtained short-circuit photocurrent density, open-circuit voltage, fill factor and light-to-electric energy conversion yield were 15.3 mA/cm², 0.58 V, 0.54, and 4.88%, respectively. The film thickness was 4 μm , and the cell size was 0.5 cm $\times$ 0.5 cm.

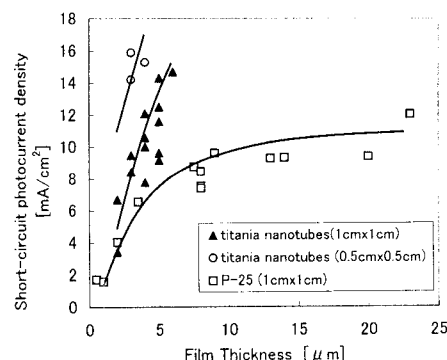


Fig. 4 Relationship between the short-circuit photocurrent density and the film thickness.

obtained from the cells made of titania nanotubes, together with those of P-25, against the film thickness. In the thin film region, the photocurrent density of the cell made of titania nanotubes was 2 times to 3 times higher than that of P-25. The high photocurrent density in the thin film region might be attributed to the significant decrease in the inter-crystalline contact of titania by using mono-crystalline titania nanotubes with a high aspect ratio instead of the nanoparticles.

4 Conclusion

Titania nanotubes were synthesized by the surfactant-assisted templating mechanism in laurylamine hydrochloride / tetraisopropylorthotitanate with an acetylacetone system. Titania nanotubes had a mono-crystal anatase structure and showed very high photocatalytic activity. The thin film electrode made of titania nanotubes in dye-sensitized solar cells showed much higher short-circuit photocurrent densities than those of P-25 in the thin film region.

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