

Effects of Anodization Growth of TiO₂-Nanotube Array Membrane on Photo-conversion Efficiency of Dye-Sensitized Solar Cell

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Membranes of TiO₂ nanotube(NT) arrays were grown by potentiostatic anodic oxidation in an ethylene glycol electrolyte with small addition of H₂O and NH₄F. Ti metal plate with a thickness of 0.1 mm was completely converted into ~0.2 mm-thick TiO₂ NT membrane for 24 to 96 h of anodization. Stacked NTs in membrane were separated into individual NT from the neighboring NTs as anodization continues up to 96 h. As-fabricated membrane of NTs were mechanically grinded to yield fine NT particles for the photoanode application to dye-sensitized solar cells (DSCs), in replacement of conventional TiO₂ particles. Photo-conversion efficiency of the DSC using TiO₂ crystalline NT particles is varying from 2.22% to 5.03%. Fine TiO₂ NT particles can increase dye attachment due to high surface to volume ratio.

Keywords: TiO₂ nanotube, anodic oxidation, dye-sensitized solar cell, photo-conversion

1. INTRODUCTION

Photoanode of dye-sensitized solar cells (DSCs) is consisted of transparent conducting oxide (TCO) and a layer of TiO₂ particles.^[1] DSC using this structure can reach an efficiency as high as 10%.^[2] 15 to 20 nm-sized TiO₂ particles coated on TCO are interconnected in three dimensions on TCO. The large number of dye molecule injected into the layer of TiO₂ particles are attached to the particle surfaces, which enables efficient light harvesting. Light harvesting efficiency is governed by two major factors in the photoanode of DSC. As the number of dye molecules attached to the surface of TiO₂ particles increases, more electrons are injected to the particles by photoenergy, which results in higher efficiency. The injected electrons to TiO₂ particles diffuse through the particle networks to the collecting TCO substrate. Electron transport is a limiting factor on the performance of the electron collecting layer of TiO₂ particles network. This is due to the structural defects of the particle itself and defects at the contact between the crystalline particles. Both defects lead to enhanced scattering of electron and reducing electron lifetime, thus resulting in slow mobility and less current density.

TiO₂ nanostructure possesses unique properties relevant to application to photovoltaics.^[3] Among many processing route, anodic oxidation becomes a focus of considerable interest as it can produce highly ordered TiO₂ nanotube (NT) arrays

providing unique material architectures of a large internal surface area with very high aspect ratio.^[4-7] Recently, TiO₂ NT arrays membrane over 1.0 mm thick was fabricated by anodic oxidation of 1.0 mm Ti plate.^[4] In the anodic oxidation of titanium, electrolyte composition is a critical determinant with regard to the length and diameter of tube and surface morphology. Paulose *et al.* reported the growth of long TiO₂ NT arrays of aspect ratio ~10,000 by anodic oxidation of titanium using ethylene glycol solution.^[4] Many advantages can manifest themselves in application of the highly ordered TiO₂ NT arrays to the photoanode of DSCs.

In addition to the precisely oriented nature of TiO₂ NTs, high aspect ratio of the NT have advantages for application to DSCs. High aspect ratio tube possesses high surface to volume ratio which enables more dye molecules to be attached to TiO₂, compared to the spherical particle which is the lowest in surface to volume ratio. However, it needs a large number of very fine individual NTs to increase the dye attachment to the outer/inner surface of NTs. TiO₂ NTs grown by anodic oxidation are generally formed in either stacked or bundled NTs, in which the outer surfaces of the NTs are not available for the dye molecule attachment. Membrane of highly ordered TiO₂ NT arrays, as a thick film, was directly applied to photoanode of DSC as reported in the literature, overall efficiency of 6.89% was achieved.^[5] However the membrane of TiO₂ NT arrays is not transparent to light, the direct application of membrane is also very limited.

In this work, we report the fabrication and electrical char-

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acterization of DSC using TiO₂ NT particles. These NT particles were made from the thick membrane of NT arrays grown by simple anodic oxidation of Ti plate, for the replacement of conventional TiO₂ particles.

2. EXPERIMENTAL PROCEDURE

Ti metal plates (99.9% purity) with a thickness of 0.1 mm were anodized into membranes of self-aligned highly ordered TiO₂ NT arrays. The potentiostatic anodic oxidation was performed in a two-electrode configuration with Ti plate as the working electrode under constant potential of 60 V at ~22°C for up to 96 h. Platinum mesh was used as a counter electrode (2 cm separation). Complete conversion of a Ti plate into a membrane of TiO₂ NT arrays was completed after 24 h anodization. TiO₂ NT arrays having lengths of ~200 μm were grown in vertical direction from the both side of Ti plate.

Electrolyte used was an ethylene glycol solution with an addition of H₂O (2.0 vol. %) and NH₄F (0.5 wt. %). As-fabricated TiO₂ NT membrane was thoroughly washed with alcohol, and then immersed in a dilute HCl (0.1M) solution for 20 min followed by washing with deionized water and drying in oven at 80°C. It is to remove any unwanted deposits and surface impurities introduced during anodization. As-anodized membrane of TiO₂ NT arrays is amorphous phase. As-grown brittle TiO₂ NT membrane was produced into fine powders by mechanical grinding in a ceramic dish. The powders were then immersed in ethyl alcohol and sonicated for 1 h to yield non-clustered NT particles. The length of the resulting fine NT particles was less than ~2.0 μm. As-processed fine NT particles in amorphous phase were crystallized into anatase phase by annealing at 580°C for 3 h in oxygen atmosphere. Morphology and structure of TiO₂ NT arrays and particle were investigated by scanning electron microscope (SEM) and X-ray diffraction technique.

5 g of TiO₂ NT particles was produced into a paste form. NT particles were mixed with 120 ml of ethanol (99.9%), 1.6 g ethyl cellulose, and 20 ml of α-terpineol. The paste was coated in a thickness of 20 to 25 μm on to fluorine-doped tin oxide (FTO) (Pilkington TEC 8) by Doctor Blade method, followed by annealing at 450°C for 30 min. As-coated paste on FTO was immersed for 8 h into N3 (Ruthenium 535) dye solution, cis-bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) 0.027 g mixed with 100 ml ethanol (99.95%). Pt counter electrode were prepared by coating a solution of H₂PtCl₆·6H₂O and 2-propanol dehydrate (v/v = 1:1) followed by drying at 450°C for 30 min. Electrode spacing was ensured by the use of Surlyn-film spacers, 60 μm in thickness. Electrolyte was made using a solute of 5 ml acetonitrile and 0.392 g 4-tert-butylpyridine mixed with 0.0635 g Iodine and 0.335 g Lithium Iodide. The electrolyte was introduced into the

clamped electrode by capillary action. Photocurrent (I) and photovoltage (V) characteristic of the as-fabricated DSC was measured under the 100% AM 1.5 illumination.

3. RESULTS AND DISCUSSION

TiO₂ NT arrays membrane was produced by complete conversion of Ti plate (0.1 mm in thickness) using anodic oxidation. The thickness of membrane is ~200 μm. Figure 1 shows the plane-view of TiO₂ NT membrane (1.5 × 1.5 cm²) completely converted from Ti plate. The as-anodized membranes for 24, 48, and 96 h are shown in Figs. 1(a), (b), and (c), respectively. SEM micrographs of TiO₂ NT arrays grown for 24 h are shown in Fig. 2. Figure 2(a) shows the surface morphology of the NT arrays. Average inner diameter of the tube is ~100 nm. Figures 2(b) and (c) are the cross-section view of NT membrane showing parallel alignment of the NT arrays. The NT arrays are all stacked as it is seen in Figs. 2(b) and (c), thus the outer surface of each NT does not exist. It is therefore impossible to attach dye molecules onto the outer surface of NTs, dyes can only be attached to the inner surface of the tubes. It indicates that direct application of the NT membrane to the DSC photoanode is difficult due to the limited dye attachment onto NTs.

Figures 3(a) and (b) are the SEM micrographs of as-anodized TiO₂ NT arrays for 48 h, and Figs. 3(c) and (d) are the micrographs of NT arrays grown for 96 h. Figures 3(a) and

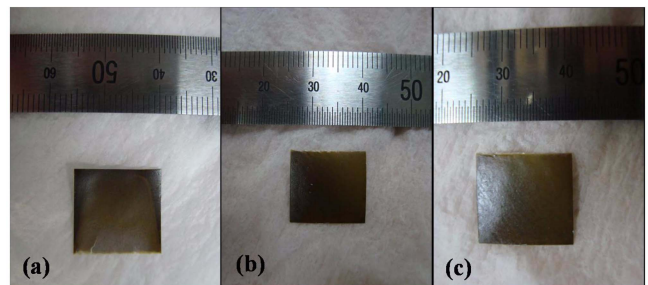


Fig. 1. As-fabricated membrane (~200 μm in thickness) of TiO₂ NT arrays converted from 0.1 mm thick Ti-plate: anodized for (a) 24 h, (b) 48 h, and (c) 96 h.

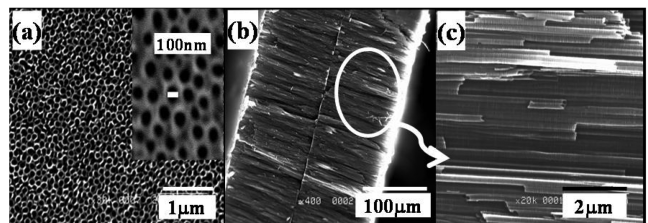
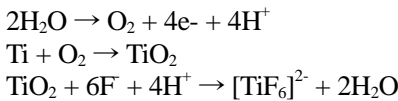


Fig. 2. SEM micrographs of the as-anodized TiO₂ NT arrays for 24 h. (a) Surface morphology showing open end of the NTs in ~100 nm diameter, (b) cross-sectional view of the NT membrane, and (c) cross-section view shown at higher magnification.

(c) show the cross-section structure of NT membranes grown for 48 and 96 h, which reveals the similar stacked structure as it is seen in Figs. 2(b) and (c) for 24 h anodization. However, the stacked NTs become separated from the neighboring NTs into many individual NTs, as shown in Figs. 3(b) and (d). These individual NTs are not straight but curved. Thus, it is highly probable that the dye attachment onto these NTs can be increased significantly since the both inner and outer surface of NTs are available for the dye attachment. It is not clearly understood at present why the stacked NTs are separated from the others. Zhu *et al.* argue that capillary stress, created during evaporation of liquids from the mesopores of dense TiO₂ NT arrays, may promote the separation of NTs.^[8] However, it is not understood why it only occurs in NTs anodized for 48 and 96 h in this experiment.

Anodic oxidation of 0.1 mm-thick Ti-plate for 24 h results in complete conversion into TiO₂ NT arrays as it is seen in Fig. 2. As the NT arrays are further under potentiostatic anodization for up to 96 h, TiO₂ is consumed into the electrolyte and the tube wall thickness is decreasing. The formation of TiO₂ NTs in an electrolyte containing H₂O and NH₄F is described via the following reactions.^[9]



TiO₂ NTs are chemically dissolved by F⁻ as explained above equation. This leads to the continuous decrease of tube wall thickness as it is under potentiostatic anodization. As the tube wall thickness continues to decrease, the stacked NTs may become separated into individual NTs under the

influence of capillary stress.

The membranes of NT arrays shown in Fig. 3 are processed into fine particles by sonication and mechanical grinding. Morphologies of the as-prepared NT particles are shown in Fig. 4 after mechanical grinding and sonication. The NT particles are less than ~2.0 μm in tube length. They are in amorphous phase, which is transformed into anatase phase by annealing at 580°C for 3 h in oxygen atmosphere. Figure 5 is the X-ray diffraction patterns obtained from the as-annealed NT particles showing the patterns of anatase phase.

Figure 6 shows the as-fabricated DSC using NT particles with N3 dye attachment. Photocurrent (I) and the photovoltage (V) of the cell were measured with an active area of 0.2 cm² using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator. I-V characteristics of the devices are shown in Fig. 7. It is possible there may be some error in comparing photo-conversion efficiency in three different samples, due to the differences in exact active layer thickness and area. However, the highest photo-conversion efficiency

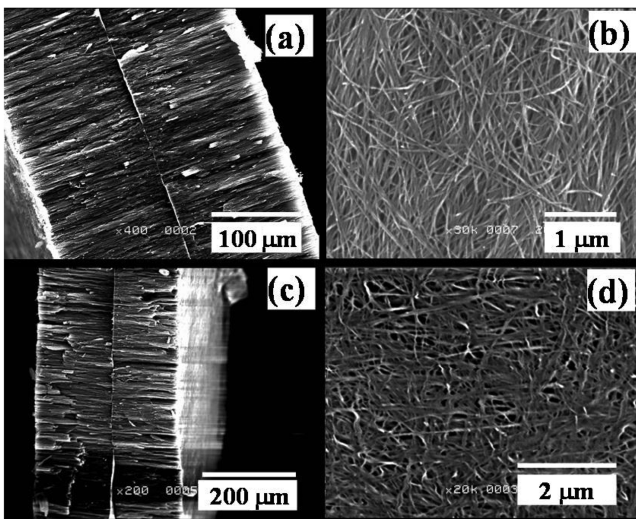


Fig. 3. SEM micrographs of the as-anodized TiO₂ NT arrays. (a) Cross-sectional view and (b) surface NT morphology of the membrane grown for 48 h. (c) Cross-sectional view and (d) surface NT morphology of the membrane grown for 96 h.

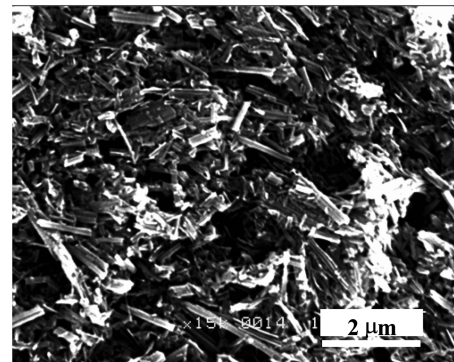


Fig. 4. SEM micrograph showing the NT particles after mechanical grinding and sonication.

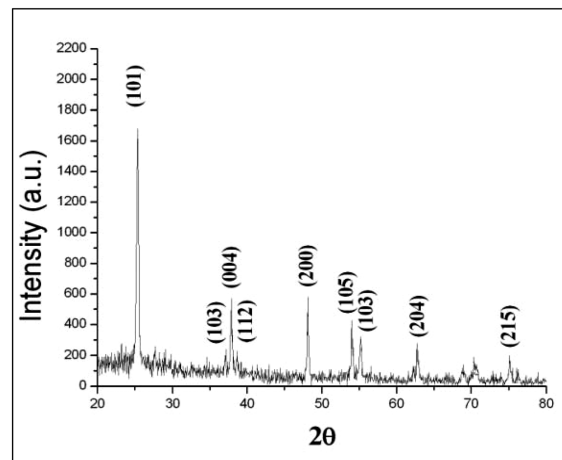


Fig. 5. X-ray diffraction patterns obtained from TiO₂ NT particles, annealed at 580°C for 3 h. All the indexed diffraction patterns are from the anatase phase.

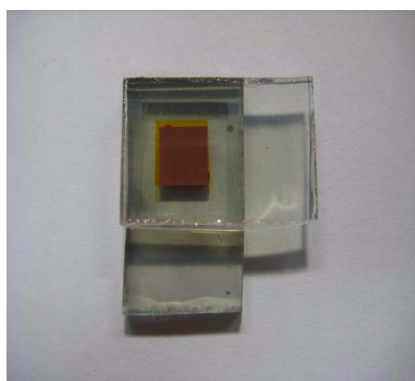


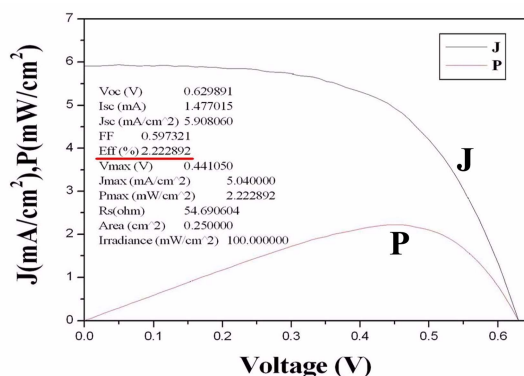
Fig. 6. As-fabricated DSC using NT particles grinded from the TiO₂ membrane grown for 96 h.

of 5.03%, which is still relatively low in general (Fig. 7(c)), is obtained with DSC using TiO₂ NT anodized for 96 h. This can be attributed to two major factors. The first is the photocurrent magnitude (J_{sc}) of 14.04 mA/cm² under 1.5 AM illumination, as shown in Fig. 7(c). The length (< 2.0 μm) of NT particle (not spherical) is very long, which may affect significantly on the photocurrent. Electrons are injected from the dye molecules to TiO₂ NT by photoenergy. Then, the electrons diffuse through the networks of TiO₂ NT particles. However, electron pathway through the networks may become very long due to the network shape formed by long individual NTs. The NT network can be very similar to mesh type network. Electron life time may be not long enough to avoid hole-capture during long diffusion, the current density will decrease. The longer the distance for electron diffusion, less electrons can reach to FTO.

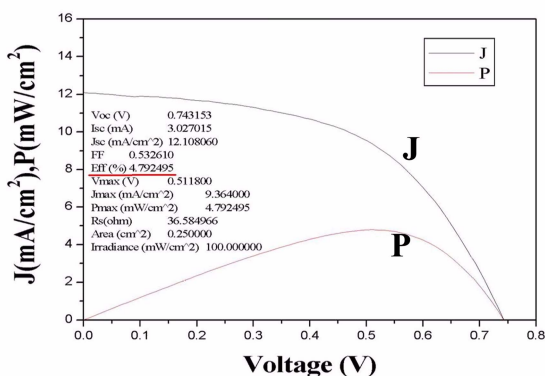
Second factor for improvement is the fill factor (0.59 to 0.53) in this work as shown in Fig. 7. The fill factor is generally reduced with increasing series resistance. The series resistance can be also increased due to the mesh type network of NTs, hence fill factor is reduced. Poor contact between the TiO₂ NT particles and FTO may also increase resistance. As mentioned above, both the photocurrent and fill factor can be improved by controlling of NT particle size and distribution. It is further required to process shorter and finer NT particles by anodizing and mechanical grinding. In spite of the relatively poor quality of NT particle size and distribution, the photo-conversion efficiency of 5.03% is stimulating motivation for the improvement of TiO₂ NT particles processing and DSC fabrication.

4. CONCLUSIONS

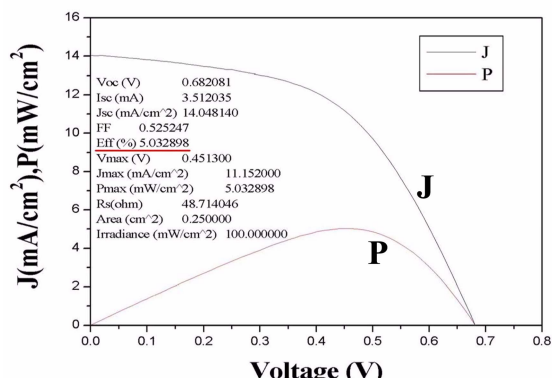
Ti metal was anodized in an ethylene glycol electrolyte with small addition of H₂O and NH₄F at a constant potential of 60 V. Ti plate (0.1 mm in thickness) was completely converted into TiO₂ NT arrays membrane, which results in around 200% increase in thickness of the membrane for 24 h of anodization.



(a)



(b)



(c)

Fig. 7. Photocurrent (I) and photovoltage (V) characteristic of DSCs under 100% AM 1.5 illumination. DSC using TiO₂ NT arrays grown for (a) 24 h, (b) 48 h, and (c) 96 h.

As the NT arrays are further under potentiostatic anodization for upto 96 h, the stacked NTs become separated from the neighboring NTs as many individual NTs in a less than ~100 nm of diameter.

As-fabricated NT membranes were processed into fine individual NT particles for the photoanode application to DSCs in replacement of conventional TiO₂ particles. Photoconversion efficiency of the DSC using TiO₂ NT particles is improved from 2.22 to 5.03%. Both the photocurrent and fill factor can be improved by controlling the NT particle size and distribution.

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