

Preparation of high-aspect-ratio TiO₂ nanotube arrays and applications for dye-sensitized solar cells

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High-aspect-ratio TiO₂ nanotube (NT) arrays were successfully fabricated by anodization of Ti foils in an ethylene glycol electrolyte containing 0.25% NH₄F and 1V% H₂O. The structure and morphology of the NT arrays were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The arrays were found to several micrometers in length, with tube diameters of 70–100 nm. The samples calcined at 400–500°C showed only anatase phase. The photovoltaic performance of the TiO₂ NT and nanoparticle (NP) films used in dye-sensitized solar cells (DSSCs) were investigated by I–V characteristics curve. The results indicated that all the NT-based DSSCs have better photovoltaic performance than the NP-based counterparts owing to higher charge collection efficiencies and higher surface area.

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1. Introduction

Dye-sensitized solar cells (DSSCs) based on the photosensitization of a nanocrystalline TiO₂ electrode, as designed by Gratzel in 1991, received considerable attention as a potential, cost-effective alternative to silicon solar cells [1]. The certified efficiency of DSSCs based on the nanoparticle TiO₂ photoelectrode is 11.2% [2]. However, this efficiency is still low for commercialization of DSSCs. To increase the efficiency of DSSCs, an enormous rise in short-circuit current is essential. To accomplish this, breakthroughs in preparation of TiO₂ thin film are expected. Among many possible approaches, TiO₂ nanotube (NT) arrays with a quite high-aspect-ratio is one of the most promising options, because they have higher charge collection efficiencies than a nanoparticle-based structure, as well as better control of the interface makes this morphology desirable for DSSCs [3, 4].

There were many studies about TiO₂ nanotube (NT) arrays. It is well known that electrochemical anodization of Ti metal is a relatively simple approach for preparation of nanotube arrays. However, in most of these studies, the nanotube arrays fabricated by electrochemical anodization of Ti metal in an hydrofluoric (HF) electrolyte or neutral fluoride solutions, were found to only several hundred nanometers in length. It is not beneficial to TiO₂ nanotube (NT) arrays applications for DSSCs. And there are very few papers related on the effects of the length-to-width aspect ratio on the photovoltaic performance of the TiO₂ NT samples used in DSSCs. In the present work, we investigate the high-aspect-ratio TiO₂ nanotube (NT) arrays prepared by anodization of Ti foils in an ethylene glycol electrolyte containing 0.25% NH₄F and 1V% H₂O. The crystal structure and morphology of the NT arrays were characterized. Furthermore, the influence of the length-to-width aspect ratio on the photovoltaic

performance of the TiO₂ NT samples used in DSSCs were investigated. At the same time, the photovoltaic performance of NT- and NP-based DSSCs were compared. This work should be valuable for the practical application of TiO₂ in the field of DSSCs.

2. Experimental

2.1 Experimental detail

2.1.1 Preparation of TiO₂ nanotube arrays

The high-aspect-ratio TiO₂ nanotube arrays were prepared by anodization of Ti foils (99.9%, 0.30 mm, Western Metal Materials co., LTD. China) in a two-electrode cell containing a Pt counterelectrode. The anodization was performed at different anodization potential in an ethylene glycol electrolyte containing 0.25% NH₄F and 1V% H₂O for 10 h that resulted in various nanotube morphology. The as-prepared TiO₂ nanotube samples were rinsed with deionized water and air-dried, then annealed in air for 3 h at the temperature of 500 and 600°C respectively.

2.1.2 Fabrication of DSSCs

TiO₂ nanotube array films were dye-sensitized by immersing for 12 h in an anhydrous ethanol solution of 0.5 mM N719 dye (cis-bis(isothiocyanato) bis (2, 2-bipyridyl 4, 4-dicarboxylato) ruthenium (II) bis-tetrabutylammonium) in ethanol. After dye-sensitization, the samples were rinsed with ethanol to remove nonchemisorbed dye. Then the dye-sensitized TiO₂ nanotube array films used as the working electrode and platinum coated fluorine-doped conductive glass as

counter electrode to assemble sandwich DSSCs. The electrolyte containing 0.3 M lithium iodide (LiI) solution and 0.03 M iodide (I_2) solution in acetonitrile were introduced to the gap between the counter and working electrodes by the capillary force.

2.1.3 Testing and characterization of the samples

The morphology and crystallinity of the TiO_2 nanotube arrays were characterized by field emission scanning electron microscopy ((FESEM; S-4800, Hitachi, Japan). and X-ray diffraction (XRD; DX-2000, Cu-K radiation, 40 kV, and 50 mA in the region of $2\theta = 20-80^\circ$). The current-voltage characteristics were measured with a computer-controlled digital source meter (Keithley, model 2400) under illumination with a Newport solar simulator (AM1.5, $100 \mu W/cm^2$).

3. Results and discussion

3.1 XRD analysis

Fig. 1 (a, b and c) shows XRD patterns of unannealed TiO_2 nanotube arrays and annealed TiO_2 nanotube arrays on Ti foil at $500^\circ C$ and $600^\circ C$, respectively. As the unannealed TiO_2 nanotube arrays have an amorphous structure, Only Ti peaks were shown in Fig. 1(a). After annealing process at $500^\circ C$ for 3 h, two broad peaks at $2\theta = 25.23^\circ$ and 47.88° which correspond to (101) and (200) plane diffraction of anatase TiO_2 (JPCDS 21-1272) appeared, suggesting that the phase structures of the samples was anatase, which is recommended for the preparation of an optimum dye-sensitized film electrode [5]. However, after annealed at $600^\circ C$ for 3 h, the intensity of the (101) diffraction peaks of the anatase become weaker, whereas, an additional peak at $2\theta = 27.5^\circ$ corresponding to (110) plane diffraction of rutile (IPCDs 87-920) appeared and had stronger peak intensity, indicating that the samples were composed of mixed-phase crystal structure of anatase and rutile.

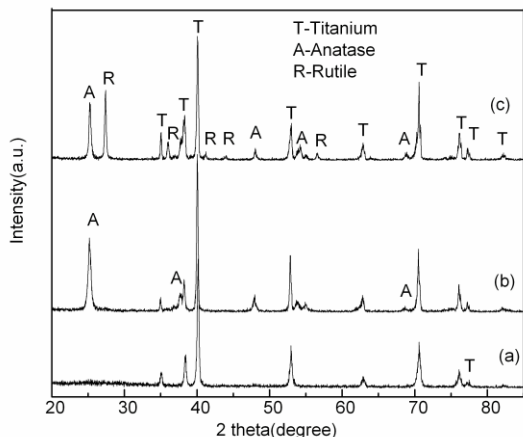


Fig. 1. XRD pattern of TiO_2 nanotube arrays: unannealed TiO_2 nanotube arrays (a), and annealed TiO_2 nanotube arrays at $500^\circ C$ (b) and $600^\circ C$ (c).

3.2 SEM analysis

Fig. 2 shows the SEM images of TiO_2 nanotube arrays prepared by the electrochemical anodization in an ethylene glycol electrolyte containing 0.25% NH_4F and 1V% H_2O . Anodization is carried out under various applied potentials ranging from 15 to 45 V for 10 h. It could be seen from Fig. 2 (a) that, the nanoporous structure appeared and some parts of them started to be damaged, the shapes were not very regular on the top. When the anodization potential was 25 V (Fig. 2b), TiO_2 nanotube arrays could be formed, but the pore diameter was about 70 nm and the nanotube length was about $2.9 \mu m$, respectively. When further increased the potential to 35 V (Fig. 2c), the TiO_2 nanotube arrays with a regular, well-aligned architecture could be obtained, and the resulting nanotube length increased to $6.5 \mu m$, and the average diameter was about 85 nm. When the anodization potential reached 45 V, the nanotube array sample with an average diameter of 100 nm have a length of about $8.7 \mu m$. It could be indicated that the length-to-width aspect ratio of nanotube samples were 41.2, 76.5 and 87.0 as the anodization potential increased from 25 V, 35 V, and 45 V, respectively. This was due to the fact that with anodization potential increasing, the electrochemical etching rate at the bottom of the tubes (field assisted oxidation of Ti and electrical dissolution of TiO_2) and the rate of chemical dissolution also increased, resulting in longer nanotube arrays of greater diameter [6, 7]. For a given the tube diameter, the increased anodization potential enabled substantial increases in the nanotube length, which was attributed to that the larger anodization potential increased driving force for ionic transport through the barrier layer at the bottom of the pore resulting in faster movement of the Ti/ TiO_2 interface into the Ti metal. Therefore, within certain range for anodization potential, increasing anodization potential could enhance the length-to-width aspect ratio of nanotube arrays.

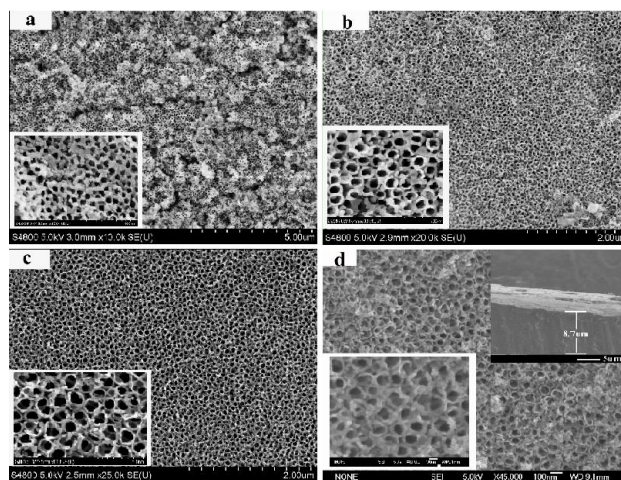


Fig. 2. SEM images of TiO_2 nanotube arrays made with different anodization potential: (a) 15 V; (b) 25 V; (c) 35 V and (d) 45 V. The insets are the magnified views of the surfaces.

3.3 Photoelectric performance of DSSCs based on TiO₂ NT- and NP samples

Fig. 4 shows Current–voltage characteristics of DSSCs based on TiO₂ NT samples fabricated at different anodization voltage and TiO₂ NP sample under simulated AM 1.5 light. Detailed photovoltaic performance parameters of DSSCs for films with different anodization voltage were presented in Table 1. When compared with the DSSC based on TiO₂ NP sample, the photoelectrochemical characteristics of TiO₂ NT samples increased and the enhancement of η was attributed to the strong effects of the increases of J_{sc} as the the V_{oc} increased. It demonstrates that the increased surface area provided by high-aspect-ratio TiO₂ nanotube (NT) arrays enhanced the total amount of dye, thus TiO₂ nanotube (NT) arrays had advantages over TiO₂ nanoparticle film in the light-harvesting efficiencies and the surface area. However, the V_{oc} decreased slightly with increasing anodization voltage. This might be attributes to the fact increasing the surface area of nanotube arrays could obtained more injected electrons, which could make the recombination possibility of injected electron on TiO₂ nanotube arrays and electron acceptor ion in the electrolyte increased [8], resulting in the dark current (i_o) increased. According to the formula:

$$V_{oc} = \left(\frac{nRT}{F} \right) \ln \left(\frac{i_{sc}}{i_o} - 1 \right) \quad (1)$$

Hence, it could be found that the open circuit voltage (V_{oc}) decreased.

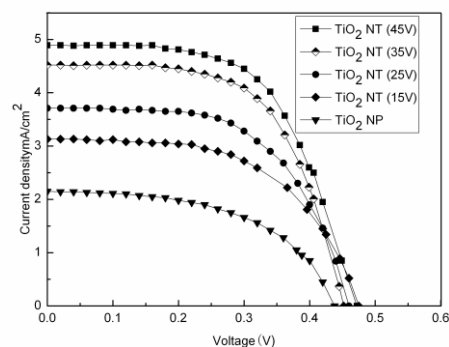


Fig. 4. Current–voltage characteristics of DSSCs based on TiO₂ NT samples fabricated at different anodization voltage and TiO₂ NP sample under simulated AM 1.5 light.

Table 1. Current–voltage characteristics of DSSCs based on different TiO₂ NT samples and TiO₂ NP sample under simulated AM 1.5 light.

Sample	Anodization Voltage (V)	L/W	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
1 (NT)	45	87.0	4.9	0.47	0.59	1.36
2 (NT)	35	76.5	4.5	0.45	0.61	1.24
3 (NT)	25	41.2	3.7	0.46	0.58	0.99
4 (NT)	15	—	3.1	0.48	0.56	0.83
5 (NP)	—	—	2.2	0.44	0.53	0.51

4. Conclusions

In conclusion, we investigated the morphology and crystallinity and photovoltaic performance of DSSCs based TiO₂ NT samples prepared from electrochemically anodizing Ti foils in an viscous aqueous electrolytes. High-aspect-ratio TiO₂ nanotube arrays with tube diameters ranging from 70–100 nm and and several micrometers in length were successfully obtained. The pore diameter and the length of the TiO₂ NT samples increased when the anodization voltage changed from 15 V to 45 V. The nanotube arrays were fully crystalline with the anatase under calcined at 500°C for 3 h. It was observed that increasing the anodization voltage led to increasing the J_{sc} and decreasing slightly the V_{oc} of DSSCs based TiO₂ NT samples. Finally, varying the electrochemical fabrication conditions was known to affect

the geometry and surface properties of the nanotube arrays. Investigations of the consequences of these morphological changes on the photoconversion processes are likely to improve significantly the photovoltaic performance of DSSCs based TiO₂ NT samples.

Acknowledgements

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