

Improved Anatase Phase Stability in Small Diameter TiO₂ Nanotube Arrays for High Performance Dye-Sensitized Solar Cells

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Abstract

Anatase is the preferred phase of TiO₂ in dye-sensitized solar cells (DSSCs) because of its lower charge recombination than other phases. However, for small diameter nanotubes before detached from the Ti foil, rutile rather than anatase appears upon a pre-treatment annealing at 400 °C or above. Here we have fabricated highly ordered free-standing small diameter (50 nm) TiO₂ nanotube membranes which were pre-treated at 300 °C to maintain pure anatase phase. **The free-standing nanotube membranes were used to fabricate the photoanodes and were further calcined at 500 °C to achieve full crystallization of the nanotubes.** It was shown that the electron lifetime is much longer in the **300 °C-pre-treated** nanotubes than those **pre-treated** at 400 or 500 °C, leading to a significantly improved power conversion efficiency of 4.59% (enhanced by ~50%).

Keywords

TiO₂ nanotubes; Dye-sensitized solar cells; Small diameter nanotube; Phase transitions; Electron recombination

Introduction

TiO₂ nanotube arrays have received considerable attention for its good oriented charge-transport property, excellent chemical stability, and environment-friendly feature for applications in dye-sensitized solar cells (DSSCs) [1-3]. However, the efficiency of TiO₂ nanotube-based DSSCs is, in general, substantially lower due to the much lower surface area of nanotubes than nanoparticles. Therefore, TiO₂ nanotubes with large surface area have been the pursuit of a large amount of studies, among which the minimization of the nanotube diameter has become one of the important methods to enlarge the aspect ratio. A lot of attempts have been carried out to fabricate small diameters tubes [4-5] and our previous results showed that improved efficiency can be obtained by using small tubes at an anodization voltage of 20 V [6].

The specific crystal structure strongly influences the electronic properties of TiO₂, and the anatase phase is preferred in DSSCs because of its lower charge recombination resulting from steeper band bending [7-8]. Generally, crystallization by thermal annealing is an effective way to obtain the anatase phase. However, previous work showed a tube diameter dependent phase stabilization where rutile rather than anatase occurs upon annealing at the typical annealing temperatures for small tubes [9]. Liu *et al.* applied small diameter (15 nm) TiO₂ nanotubes to DSSCs and obtained an efficiency of only 1.59%, due to the appearance of rutile phase when the nanotubes were annealed at 450 °C [10].

Considering that the interface between rutile and anatase crystallites creates charge trapping sites with high electron recombination reactivity [8,11], in this work, we used low temperature **pre-treatment** (300 °C) to achieve small diameter tubes in pure anatase phase. The crystallized free-standing TiO₂ nanotube membranes were utilized as the photoanodes in DSSCs, showing less recombination losses and the power conversion efficiency η reached 4.59%, showing 50% improvement as compared with the samples annealed at 500 °C.

Experimental Section

Highly ordered TiO₂ nanotube arrays (TNAs) with small diameter were fabricated according

to the reported method [12]. TNAs were synthesized through potentiostatic anodization in a conventional two-electrode electrochemical cell. Ti foil (0.125 mm in thickness, Strem Chemicals, Newburyport, MA, USA) as the working electrode was first processed under 60 V for 0.5 h in an electrolyte with a nominal composition of ethylene glycol, 0.5 wt% ammonium fluoride (NH₄F), and 3 vol% deionized water. The resulting oxide film was annealed at 400 °C for 2 h and was then subjected to a second anodization at 10 V for 48 h to obtain small diameter nanotubes. The film formed during the first anodization was automatically peeled off during the second anodization process. Throughout the anodization, the electrolyte was stirred by a magnetic stirrer. The as-anodized oxide films (with small tubes) obtained during the second anodization were subjected to an intense ultra-sonication for 30 s, followed by a **pre-treatment** at 300, 400 and 500 °C, respectively, for 2 h in air with a heating and/or cooling rate of 3 °C min⁻¹.

The synthesized small tubes were peeled off completely during a third anodization under 60V at 30°C for 1h, using a method reported in [13]. After that, the free-standing membranes were exploited to fabricate front-side illuminated DSSCs. Briefly, they were attached to fluorine doped tin oxide (FTO) glasses with a thin layer (thickness ~ 1.5µm) of doctor-blade coated anatase TiO₂ nanoparticles (average size ~ 20nm, from Wuhan Geao Instruments Science and Technology Co. Ltd., China). **Next, the samples were calcined again at 500 °C for 2 h to fully crystallize the TNAs since some samples were annealed at a lower temperature before detaching, and also to ensure good electrical connection between TNA membranes and FTO substrates.** The as-formed photoanodes were immersed in a 1:1 (v/v) acetonitrile and tert-butylalcohol solution containing 3×10⁻⁴ M N719 dye for 48 h. A 25-µm-thick hot-melt spacer separated the sensitized electrode and the counter electrode which was prepared by thermal decomposition of H₂PtCl₆ isopropanol solution on FTO glass at 380 °C for 30 min. The interspace was filled with a liquid electrolyte of DMPII/LiI/I₂/TBP/GuSCN in 3-methoxypropionitrile.

Morphological and structural variations of the TNAs were observed by field-emission scanning electron microscope (FESEM, FEI Sirion 200) **and a transmission electron microscope (TEM, JEOL JEM-2100F).** X-ray diffraction (XRD, Rigaku 9KW SmartLab,

Japan) analysis was performed for crystalline phase identification. The $J-V$ characteristics were measured by a sourcemeter (Model 2420, Keithley, USA) under AM 1.5G illumination (100 mW cm^{-2}) which was provided by a 300 W solar simulator (Model 91160, Newport-Oriel Instruments, USA). Electrochemical impedance spectroscopy (EIS) was performed in the dark at various bias voltages with the CHI 660C electrochemical workstation (CH Instruments, USA). The amplitude of the alternative signal was 10 mV and the frequency ranged from 10^{-1} to 10^5 Hz.

Result and Discussion

FESEM images of small diameter TNAs are shown in Fig. 1a-1c. It is well known that the nanotube diameter decreases with decreasing anodization voltage [14]. In the present work, an anodization voltage of 10 V was used (in the second anodization step) to limit the diameter of TiO_2 nanotubes to 50 nm, as seen from Fig. 1a-1c. **The TEM image in Fig. S1 also shows the formation of small diameter nanotubes.**

For comparison, large diameter TNAs (of the same thickness, but with a larger diameter of about 120 nm, Fig. 1d), which were anodized at 60 V, were also fabricated. Fig. 2a and 2b show XRD patterns for different diameter TNAs on the Ti foil after annealing in air at different temperatures. For small diameter TNAs (Fig. 2a), no rutile phase can be found when annealed at 300 °C, while a phase transition from anatase to rutile can be observed when annealed at 400 and 500 °C. For large diameter TNAs (Fig. 2b), this phase transition occurs at 500 °C. The percentage of the rutile phase can be estimated by the equation, $\text{Rutile\%} = A_{\text{rutile}} / [0.884A_{\text{anatase}} + A_{\text{rutile}}]$, where A_{anatase} and A_{rutile} refer to the integrated intensities of the strongest diffraction peak of the anatase and rutile phases, respectively [15]. The results (Fig. 2c) suggested that the rutile content at 300 °C was 0 and it increased to 9.1 and 15.9% after calcination at 400 and 500 °C, respectively. This is due to the “substrate effect”, that is, when the metallic Ti substrate was oxidized, a thin compact rutile layer was directly formed at the interface, which initiate the observed phase transition in TNAs [8, 16, 17]. As estimated from the Scherrer’s equation [18], the average crystallite size of the small diameter NTAs (**~22 nm**) is smaller than the large ones (**~30 nm**). The small crystallites are

unstable and inclined to coalesce together [19], resulting in a much more severe "substrate effect" observed in small diameter TNAs. Indeed, for large diameter TNAs which were anodized at 60 V, the anatase to rutile phase transition temperature is retarded to 500 °C (Fig. 2c).

Fig. S2 shows the XRD patterns of the top and bottom of the 500 °C-annealed free-standing small diameter TNA membranes that were pre-treated at different temperatures (300, 400 and 500 °C). It can be seen that this pre-treatment does affect the phase even though the final annealing temperature is the same (500 °C) for all the samples. No rutile phase can be detected in TNAs pre-treated at 300°C. Due to the absence of the influence of the "substrate" for the free-standing membrane, the TNAs can maintain in anatase phase up to 500 °C [15]. While for TNAs pre-treated at 400 and 500 °C, tiny amount of rutile phase has already been developed at the bottom of nanotubes which acts as nucleation sites for the growth of rutile phase in the final annealing at 500°C. The HRTEM image of the small diameter nanotubes pre-treated at 500 °C (Fig. S1) shows the coexistence of the anatase (d -spacing of 0.355 nm, (101) plane) and the rutile (d -spacing of 0.228 nm, (200) plane) phases. Also, as seen from Fig. S2, the rutile peak was more pronounced at the bottom than at the top of the nanotube membrane, indicating the "substrate effect" on the formation of rutile phase. It should be noted that, during the pre-treatment annealing, the rutile crystals predominantly exist at the nanotube-Ti metal interface region, which results in less rutile being detected from the bottom of the free-standing TNAs when they were peeled off from the Ti substrate (Fig. S2b as compared to Fig. 2a).

These small diameter TNA membranes pre-treated at different annealing temperatures were exploited as photoanodes of DSSCs. The photocurrent density vs. voltage (J - V) and the characteristic photovoltaic parameters were shown in Fig. 3. It can be seen that the short-circuit current density (J_{sc}) decreases with increasing pre-treatment annealing temperatures due to the more trap densities and hence more electron recombination associated with the rutile phase in TNAs pre-treated at higher temperatures [19]. The higher trap densities and larger electron recombination probability also result in decreased open-circuit voltages (V_{oc}) in samples with more rutile phases, i.e., pre-treated at higher temperatures.

Consequently, due to the maintenance of pure anatase phase in the sample pre-treated at a low temperature (300 °C), a significant increase in power conversion efficiency (η) of ~50% can be achieved, as compared with the sample pre-treated at 500 °C (η increased from 3.10% to 4.59%). The η of DSSC equipped with large diameter TNAs is also compared in Fig. 3.

To analyze the electron recombination behaviors in DSSCs based on the small diameter TNAs, electrical impedance spectroscopy (EIS) was performed in dark under various biased voltages. The electron lifetime (τ_n) was calculated from the Bode phase plots by $\tau_n = 1/(2\pi f_{\text{peak}})$, where f_{peak} is the characteristic peak frequency in the mid frequency (1-100 Hz) region [20]. As shown in Fig. 3b, the lifetime for TNAs pre-treated at low annealing temperature (300 °C) is the highest, due to reduced surface traps and lower probability of electron recombination in pure anatase phase. The electron lifetime in TNAs pre-treated at 300 °C is about 4 times the value in TNAs pre-treated at 500 °C, which is the dominant factor for the significantly increased photocurrent observed (Fig. 3a).

Conclusion

Overall, by lowering the pre-treatment annealing temperature, we have successfully peeled off the small diameter TNAs from the Ti substrate and applied them as the photoanode in DSSCs. **Pure anatase phase was maintained (for samples pre-treated at 300 °C) in the subsequent annealing at 500 °C due to the removal of “substrate effect”.** It is found that the electron lifetime in TNAs pre-treated at 300 °C is about four times the value in the sample pre-treated at a higher temperature of 500 °C, mainly due to the pure anatase phase with reduced electron trap density as compared with rutile phase. The resultant conversion efficiency of the small diameter TNAs-based DSSCs with pure anatase phase is significantly enhanced by ~50%, as compared with the TNAs pre-treated at a higher temperature of 500 °C. Pure anatase phase with good crystallinity is of crucial importance to the improvement of photovoltaic performance of DSSCs.

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Figure captions

Fig. 1. FESEM images of (a) the top and the cross-sections of (b, c) small and (d) large diameter TNAs.

Fig. 2. XRD patterns of the top of (a) small diameter, (b) large diameter TNAs before detached from Ti foils. (c) Summary of the phase composition of the TNAs membranes.

Fig. 3. (a) J - V characteristics of DSSCs based on different diameter TNAs pre-treated at different temperatures. (b) Electron lifetime of DSSCs as a function of bias voltages. (c) The photovoltaic parameters of DSSCs based on different diameter TNAs.