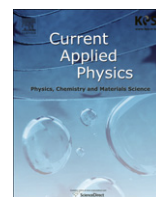




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Improved conversion efficiency of dye-sensitized solar cell based on the porous anodic TiO₂ nanotubes

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ABSTRACT

The porous nanotubes were successfully fabricated by coating a porous layer on the walls of the TiO₂ nanotubes. This method was proved available for effectively increasing the specific surface area of the nanotubes. The DSSCs based on such porous nanotubes has a higher conversion efficiency than that of the DSSCs using common TiO₂ nanotubes. This could be explained by the enhanced loading of dye molecules on porous TiO₂ nanotubes, which resulted in the improvement of short-circuit current. The light to electric energy conversion efficiency of the DSSCs applying porous TiO₂ nanotubes is about 1.79% nearly two times higher than that of the DSSCs based on normal TiO₂ nanotubes.

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1. Introduction

As next-generation solar-to-electric energy conversion facility, dye-sensitized solar cell (DSSC) has been recognized as a viable competitor to the well developed but relatively expensive hetero-junction solar cell technologies [1]. At present, DSSCs based on TiO₂ nanoparticles (NPs) working electrode with an adsorbed ruthenium complex have achieved a conversion efficiency up to 11% [2]. However, despite of its high surface area, the disordered pore structure of the TiO₂ nanoparticles anode inherently induces a short electron diffusion length and ineffective infiltration, and has been a major limited factor for further improvement of DSSCs performance [3]. Therefore, considerable efforts have been devoted

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to the development of more efficient photoanode structures, including ordered meso-structured TiO₂ films [4], one-dimensional nanorod/nanotube arrays [5–8], and etc. Among these structures, although highly ordered TiO₂ nanotubes (NTs) have a smaller surface area compared to the porous TiO₂ films, its several unique advantages make it preponderating over other structures, such as i) a higher charge transport speed, ii) a significantly greater diffusion length, (iii) an order of magnitude smaller charge recombination rate resulting from confining the injected electrons by the surface electrical fields in the central zone of the tubes and (iv) a superior void penetration of the organic hole conductor in preparation of solid-state DSSCs due to a less intricate shape of the nanostructure [9–11]. Furthermore, a thicker photoanode is always preferred because it provides a higher surface area for dye loading. Also a weak absorption of the best dyes in the near-infrared region can then be counteracted with a long path length for photon absorption [12]. The porous TiO₂ films typically have a thickness no more than 10 μm while the best TiO₂ NTs based solar cells reported up to date was fabricated by using nanotubes with lengths ranging from 20 to 35 μm. A conversion efficiency of 2.9% was firstly achieved using a 360-nm-thick transparent TiO₂ NTs to assemble DSSCs in a front

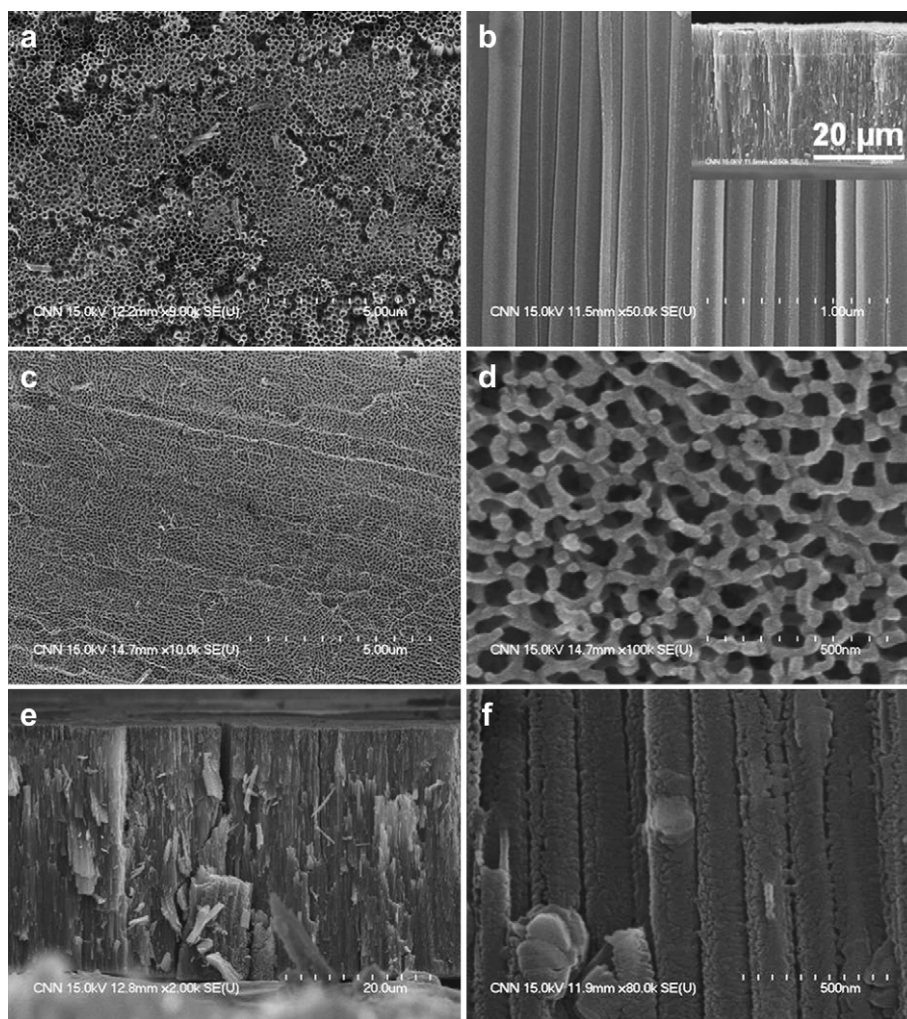


Fig. 1. SEM images of original TiO_2 nanotubes (a), (b), porous TiO_2 nanotubes (c), (d), (e) and (f).

side illumination mode by Grimes and co-workers in 2006 [13], and the performance was further improved to 6.9% with the capability of growing thicker TiO_2 nanotube arrays on transparent substrates [14]. A conversion efficiency of 6.89% was also obtained using 20- μm -thick TiO_2 NTs that were grown on Ti foil in a backside illumination mode [15].

The reported efficiency of DSSC based on TiO_2 NTs is still lower than that of DSSCs based on TiO_2 NP. A possible reason is that the internal surface area of TiO_2 NTs based photoanode is much smaller than that of NPs, with a lower dye loading and sunlight absorption. In this work, we report the fabrication of DSSC based on TiO_2 nanotubes with porous walls by utilizing the high surface area of porous TiO_2 layer and the previously mentioned unique advantages of TiO_2 nanotubes. The results indicate that DSSCs based on such a porous nanotube structure shows a possibility of an improved performance with increased efficiency.

2. Experimental

The TiO_2 nanotubes were fabricated by anodizing a Ti sheet in the solution containing 0.3 wt% NH_4F (98% purity, Sigma–Aldrich) and 2 wt% water in ethylene glycol (99.8% purity, Sigma–Aldrich). Before the anodization Ti sheets were sonicated in acetone, deionized (DI) water and methanol followed by drying in a nitrogen stream. The Ti sheet was fixed by contacting with a Cu

plate as the anode and a graphite plate was used as the counter electrode. Anodizations were performed under a constant potential of 60 V at 20 °C and the growth time was 8 h. Then the obtained TiO_2 nanotubes were dip-coated with a porous TiO_2 precursor. The synthesis of the porous TiO_2 precursor was carried out by using PEG (MW = 2000) as the template and $\text{Ti}(\text{O}i\text{Bu})_4$ as the inorganic source. The detailed methodology of synthesis has been published elsewhere [16]. After dip-coating, samples were heat-treated at 550 °C with a heating rate of 1°/min for crystallization of the TiO_2 and removal of the template PEG. The morphology of the samples was examined by using the scanning electron microscopy (SEM, Hitachi-S4700) and the porous structure of the nanotubes was verified by the nitrogen adsorption–desorption isotherms.

The resulted porous TiO_2 nanotubes were immersed overnight in a dye solution of 0.0005 M cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bistetrabutylammonium (N719) (Solaronix S. A.) in ethanol. The sensitized photoanode was sandwiched together with a Pt coated ITO counter electrode using a 60 μm hot-melt polypropylene spacer. The electrolyte containing 0.5 M tetrabutylammonium iodide, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile was injected into the space between electrodes. For comparison, the DSSC, based on original TiO_2 nanotubes without coating of porous TiO_2 layer, was also fabricated in the same way. The current-voltage curves of DSSCs were

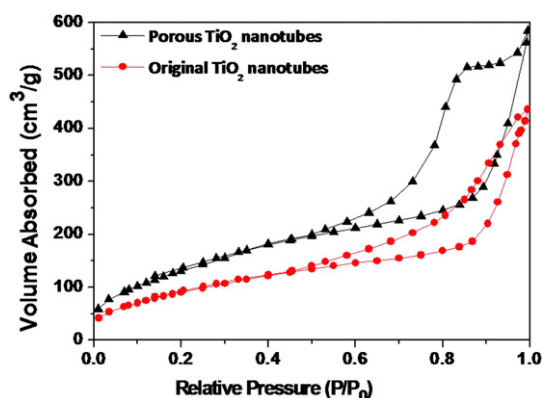


Fig. 2. N_2 adsorption–desorption isotherms of porous and original TiO_2 nanotubes. P_0 here is the saturation vapor pressure of liquid nitrogen.

measured under a simulated AM 1.5 G illumination and the irradiated area was kept as 0.3 cm^2 .

3. Results & discussion

After anodization, well-aligned TiO_2 nanotubes were formed on the top of the Ti sheet. Figure 1 (a) and (b) show the surface topologies of the original TiO_2 nanotubes. The size of the nanotubes is very uniform and the tube walls are quite smooth, which is not effective enough for loading of dye molecules. The outer and inner diameters of the nanotubes are 175 nm and 134 nm, respectively. The inset in Fig. 1(b) displays that the length of the TiO_2 nanotubes is about $32 \mu\text{m}$. Through coating a porous layer on the walls of TiO_2 nanotubes, we could get a porous TiO_2 nanotube structure and could further increase the specific surface area of the nanotubes. As shown in Fig. 1(f), the outer diameter of the nanotubes changed from 175 nm to 200 nm indicating the successful coating of porous TiO_2 layer and the thickness of the porous layer on outer walls is about 25 nm. Such a thin layer is attributed to narrow spaces between nanotubes. By contrast, from the top images of porous layer coated TiO_2 nanotubes (Fig. 1(c) and (d)), it was found that the inner diameter decreased from 134 nm to 81 nm and hence the thickness of the porous layer on inner walls is about 53 nm. Although the formation of nanoparticles could be observed on the top, the nanotubes keep open-ended and are not full-filled by the porous TiO_2 . In other words, the coating of additional TiO_2 layer did not change the original 1-D tubal structure. The length of the porous nanotubes remains constant compared with that of the original TiO_2 nanotubes as shown in Fig. 1(e).

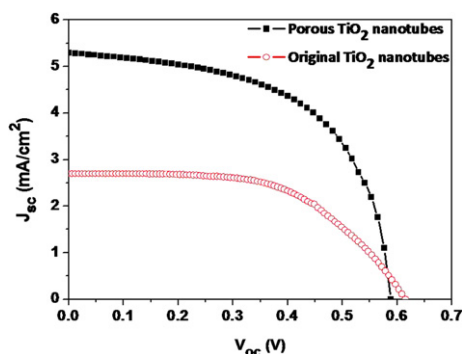


Fig. 3. Current-voltage curves of DSSCs based on porous TiO_2 nanotubes and original TiO_2 nanotubes under AM 1.5 G solar illumination.

Table 1

Performances data of DSSCs based on porous and original TiO_2 nanotubes.

Sample name	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
P-Cell	0.59	5.29	0.57	1.79
O-Cell	0.62	2.69	0.56	0.93

Figure 2 shows the nitrogen adsorption–desorption isotherms of porous and original TiO_2 nanotubes. The plots exhibit obvious hysteresis behavior. By comparing with the four classifications of hysteresis loops established by IUPAC [17] in 1994, the relative steep branches in isotherms of original TiO_2 nanotubes has close resemblance to H1 hysteresis loops representing the cylindrical pore shape. In contrast, the isotherms of porous TiO_2 nanotubes is a intermixture of H1 and H2 loops, which indicates the ink-bottle shaped pores concomitant with the cylindrical pores. The estimated BET surface areas of original and porous TiO_2 nanotubes are 179 and $278 \text{ m}^2/\text{g}$, respectively. The considerable increase of specific surface area proves the availability of coating porous layer on the wall of TiO_2 nanotubes.

The J-V characteristics of DSSCs based on porous and original TiO_2 nanotubes are shown in Fig. 3 and the key parameters are summarized in Table 1. For convenience, the DSSCs based on porous and original TiO_2 nanotubes are marked as P-cell and O-cell, respectively. It is found that the efficiency of P-cell, i.e. 1.79%, is nearly twice of that of O-cell whose efficiency is about 0.93%. The short-circuit current densities for P-cell and O-cell are 5.29 and $2.69 \text{ mA}/\text{cm}^2$, respectively. The increase of current could account for the improved efficiency. The enlarged surface area of the porous TiO_2 nanotubes leads to enhanced loading of dye molecules and the retained tubal structure after coating porous TiO_2 keeps its superior electron transport ability. The open-circuit voltage slightly decreased when using porous TiO_2 nanotubes for DSSC and it gives minor influence to the efficiency compared to the larger increase in current. All these effects contribute to the improvement of DSSC performance.

4. Conclusion

We successfully fabricated TiO_2 nanotubes with porous walls and applied it into dye-sensitized solar cells. The coating of TiO_2 layers on nanotube walls effectively improved the specific surface area while maintaining the 1-D tubal structure, which provides a better charge transport channel than the porous films. The advanced amount of absorbed dye molecules on the porous walls of TiO_2 nanotubes resulted in great increase of short-circuit current and hence the promotion in DSSCs performances in spite of the slight decrease in open-circuit voltage.

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References

- [1] B. O'Regan, M. Gratzel, *Nature* 353 (1991) 737.
- [2] M.K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, *J. Am. Chem. Soc.* 127 (2005) 16835.
- [3] C. Xu, P.H. Shin, L. Cao, J. Wu, D. Gao, *Chem. Mater.* 22 (2010) 143.
- [4] M. Zukulova, A. Zukal, L. Kavan, M.K. Nazeeruddin, P. Liska, M. Gratzel, *Nano Lett.* 5 (2005) 1789.
- [5] M. Adachi, Y. Murata, J. Takao, J. Jiu, M. Sakamoto, F. Wang, *J. Am. Chem. Soc.* 126 (2004) 14943.
- [6] K. Zhu, N.R. Neale, A. Miedaner, A. Frank, *J. Nano Lett.* 7 (2007) 69.

- [7] K. Shankar, J. Bandara, M. Paulose, H. Wietasch, O.K. Varghese, G.K. Mor, T.J. LaTempa, M. Thelakkat, C.A. Grimes, *Nano Lett.* 8 (2008) 1654.
- [8] G.K. Mor, O.K. Varghese, M. Paulose, K. Shankar, C.A. Grimes, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2011.
- [9] I. Mora-Seró, F. Fabregat-Santiago, B. Denier, J. Bisquert, R. Tena-Zaera, J. Elias, C. Lévy-Clement, *Appl. Phys. Lett.* 89 (2006) 203117.
- [10] H.J. Snaith, L. Schmidt Mende, *Adv. Mater.* 19 (2007) 3187.
- [11] F. Fabregat Santiago, E.M. Barea, J. Bisquert, G.K. Mor, K. Shankar, C.A. Grimes, *J. Am. Chem. Soc.* 130 (2008) 11312.
- [12] O.K. Varghese, M. Paulose, C.A. Grimes, *Nat. Nanotechnol.* 4 (2009) 592.
- [13] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, *Nano Lett.* 6 (2006) 215.
- [14] O.K. Varghese, M. Paulose, C.A. Grimes, *Nat. Nanotechnol.* 4 (2009) 592.
- [15] K. Shankar, G.K. Mor, H.E. Prakasam, S. Yoriya, M. Paulose, O.K. Varghese, C.A. Grimes, *Nanotechnology* (2007) 18 065707.
- [16] W.Z. He, J.J. Qiu, S.J. Park, J.H. Lee, Y.D. Kim, H.K. Kim, Y.H. Hwang, *J. Nanosci. Nanotechnol.* 9 (2009) 7145.
- [17] IUPAC Recommendations, *Pure Appl. Chem.* 66 (1994) 1739.