

NANO EXPRESS Open Access

Effect of TiO₂ nanotubes with TiCl₄ treatment on the photoelectrode of dye-sensitized solar cells

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Abstract

In this study, we used the electrochemical anodization to prepare TiO_2 nanotube arrays and applied them on the photoelectrode of dye-sensitized solar cells. In the field emission scanning electron microscopy analysis, the lengths of TiO_2 nanotube arrays prepared by electrochemical anodization can be obtained with approximately 10 to 30 μ m. After titanium tetrachloride ($TiCl_4$) treatment, the walls of TiO_2 nanotubes were coated with TiO_2 nanoparticles. XRD patterns showed that the oxygen-annealed TiO_2 nanotubes have a better anatase phase. The conversion efficiency with different lengths of TiO_2 nanotube photoelectrodes is 3.21%, 4.35%, and 4.34% with 10, 20, and 30 μ m, respectively. After $TiCl_4$ treatment, the efficiency of TiO_2 nanotube photoelectrode for dye-sensitized solar cell can be improved up to 6.58%. In the analysis of electrochemical impedance spectroscopy, the value of R_k (charge transfer resistance related to recombination of electrons) decreases from 26.1 to 17.4 Ω when TiO_2 nanotubes were treated with $TiCl_4$. These results indicate that TiO_2 nanotubes treated with $TiCl_4$ can increase the surface area of TiO_2 nanotubes, resulting in the increase of dye adsorption and have great help for the increase of the conversion efficiency of DSSCs.

Keywords: TiO₂ nanotube arrays, dye-sensitized solar cells, TiCl₄ treatment

Background

Dye-sensitized solar cells (DSSCs) have received considerable attention lately because they are cost-effective and environmentally friendly with efficiencies comparable to those of the traditional silicon-based cells [1]. Generally, granular titanium dioxide powder is commonly used in dye-sensitized solar cell light anode structure. The solgel method is used to produce porous film structure, but small pores form between particles of the transmission path of clutter, resulting in a more dye adsorption capacity and low clutter of electron transfer path. The path is too long and will make the leakage current and the probability of electron recombination, thus affecting the overall conversion efficiency of solar cells. The titanium dioxide nano-tubular structure of high surface area and large aspect ratio can be beneficial to the dye adsorption, and more rules of order can be reduced when the electron and hole in the transmission probability of recombination. ${\rm TiO_2}$ nanotubes have been synthesized by various methods including hydrothermal method [2], seeded growth [3], template-assisted deposition [4], and anodization [5]. Especially, anodization is a relatively simple method for synthesizing large-area and self-organized ${\rm TiO_2}$ nanotube arrays [6-8]. In this paper, we used the electrochemical anodization to prepare ${\rm TiO_2}$ nanotubes arrays with different thickness and applied them on the photoelectrode of dye-sensitized solar cells. The ${\rm TiO_2}$ nanotubes and solar cells were investigated by field-emission scanning electron microscopy, X-ray diffraction (XRD), *I-V* characteristic analyses, and electrochemical impedance spectroscopy (EIS) to study the effect of titanium tetrachloride (${\rm TiCl_4}$) treatment on the photoelectrode of ${\rm TiO_2}$ nanotubes for dye sensitized solar cells.

Methods

In this study, the growth of nanotubes was anodized on Ti foils (purity of 99.6%, thickness of 0.2 mm) by constant current at 15 mA in the ethylene glycol solution containing 0.3 wt.% $\rm NH_4F$ and 2 vol.% deionized water kept at 20°C. The anodized $\rm TiO_2$ nanotubes were

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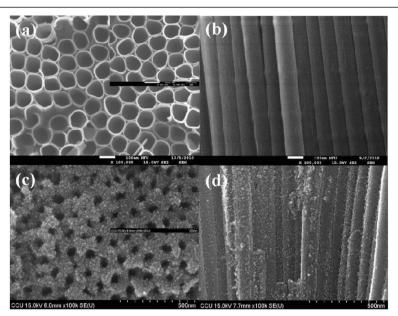
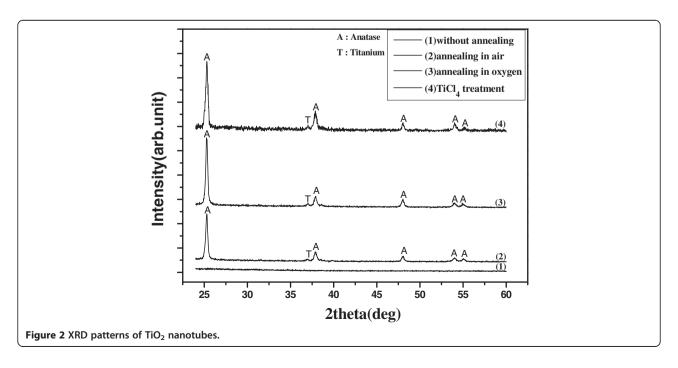


Figure 1 SEM images of TiO₂ nanotubes. (a) Top view and (b) side view before TiCl₄ treatment, and (c) top view and (d) side view after TiCl₄ treatment.

annealed in oxygen at 450°C for 60 min. For the treatment of $TiCl_4$, TiO_2 nanotubes were immersed in 0.2 M $TiCl_4$ solution for 1 h and annealed in air at 350°C for 30 min. Pt counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution and heating at 400°C for 15 min [9]. To adsorb N3 dye, TiO_2 nanotubes were immersed in 3×10^{-4} M solution containing N3 dye and ethyl alcohol at 45°C for 8 h in the oven. The working electrodes were then rinsed with ethanol. Electrolyte

solution is adopted from Everlight Chemical Industrial Corporation (ESE-20). The electrode was assembled into a sandwich-type open cell using platinum plate as a counter electrode. Both electrodes were spaced by a kind of polymer films. The thickness was 60 μm , and the size of TiO $_2$ working electrode was 0.25 cm 2 (0.5 \times 0.5 cm). The surface morphology of the TiO $_2$ nanotubes was observed by scanning field emission electron microscopy. Structural analysis was carried out by powder



X-ray diffraction (XRD). The ultraviolet–visible absorption spectrum of the TiO_2 electrodes was observed by a UV–vis spectrophotometer. The current–voltage characteristics and impedance of samples were measured by Keithley 2400 source meter (Keithley Instruments Inc., Cleveland, OH, USA), and EIS was determined under simulated sunlight with white light intensity, $P_L = 100 \text{ mW/cm}^2$.

Results and discussion

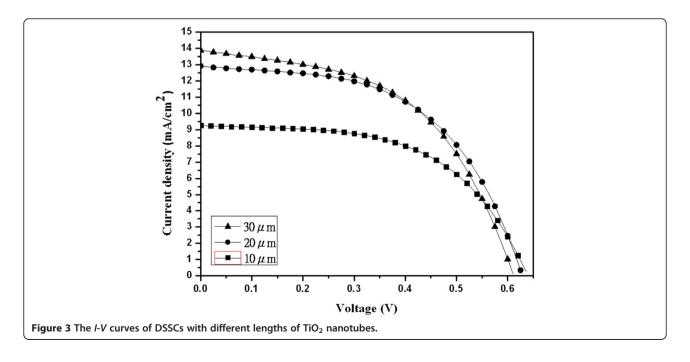
Figure 1 shows the SEM images of the TiO₂ nanotubes before and after TiCl₄ treatment. Clearly, after the samples were treated with TiCl₄, the walls of TiO₂ nanotubes were coated with TiO₂ nanoparticles, which could increase the surface area of TiO₂. In order to explore the impact of annealing gas on the properties of TiO₂ nanotubes, the samples were carried out with XRD characterization. XRD patterns of TiO2 nanotubes are shown in Figure 2. It is found that the as-formed TiO₂ nanotubes are amorphous and are converted to anatase after annealing. The oxygen annealed TiO2 nanotubes have a better anatase phase than that annealed in air. After the treatment of TiCl₄, TiO₂ nanotubes also show a good anatase phase. Figure 3 shows the currentvoltage characteristics of DSSCs with the electrodes of different lengths of TiO2 nanotubes without TiCl4 treatment. The parameters for the short-circuit current density (J_{sc}) , the open circuit potential (V_{oc}) , the fill factor, and the overall conversion efficiency (η) are listed in Table 1. From the results of Figure 3 and Table 1, it is found that the best conversion efficiency of DSSCs is 4.35%, while the length of TiO_2 nanotubes is 20 μ m.

Table 1 The parameters of current-voltage characteristics for DSSCs with different lengths of TiO₂ nanotubes

Sample (µm)	V _{oc} (V)	J _{sc} (mA/cm²)	$V_{\rm m}$ $I_{\rm m}$ (V) (mA/cm ²)		FF (%)	η (%)		
10	0.63	9.56	0.44	7.29	53.63	3.21		
20	0.63	12.92	0.43	10.12	53.61	4.35		
30	0.61	13.89	0.41	10.59	51.11	4.34		

The result of conversion efficiency is quite higher than the previous reports [10-12]. This may be due to the length of ${\rm TiO_2}$ nanotubes in this study, which is quite longer than those of the previous reports. It is advantage to adsorb N3 dye on the ${\rm TiO_2}$ nanotubes. Figure 4 shows the current–voltage characteristics of DSSCs with the electrodes of different lengths of ${\rm TiO_2}$ nanotubes after ${\rm TiCl_4}$ treatment. The parameters for the $J_{\rm sc}$, the $V_{\rm oc}$, the fill factor, and the η are listed in Table 2. From the results of Figure 4 and Table 2, it is found that the best conversion efficiency of DSSCs can be improved up to 6.58%, while the length of ${\rm TiO_2}$ nanotubes is 20 µm.

In order to study the effect of $\mathrm{TiCl_4}$ treatment on the transport properties of $\mathrm{TiO_2}$ nanotubes, the analysis of EIS for $\mathrm{TiO_2}$ nanotubes has been investigated. Figure 5 shows the spectra of EIS for the dye-sensitized solar cells with and without $\mathrm{TiCl_4}$ treatment. The simulation of equivalent circuit is referred to the previous reports [13-15]. The parameter $R_{\rm k}$, which is represented by charge transfer resistance related to recombination of electrons, is also listed in Table 3. The value of $R_{\rm k}$ decreases from 26.1 to 17.4 Ω after $\mathrm{TiCl_4}$ treatment. These results indicate that the effect of $\mathrm{TiCl_4}$ treatment



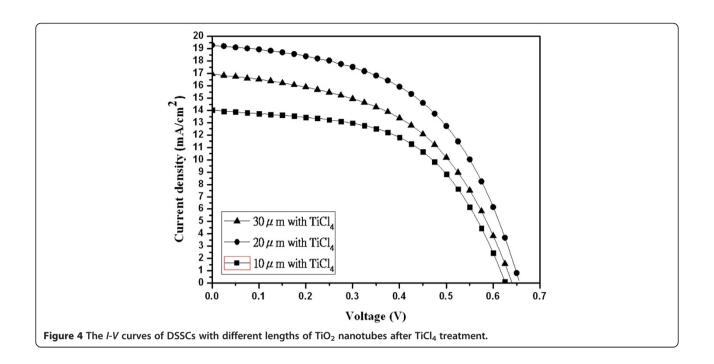


Table 2 The parameters of current-voltage characteristics for DSSCs with different lengths of TiO_2 nanotubes after $TiCl_4$ treatment

Sample (µm) with TiCl ₄	<i>V</i> _{oc} (V)	J _{sc} (mA/cm ²)	V _m (V)	I _m (mA/cm²)	FF (%)	η (%)
10	0.63	14.03	0.44	11.06	54.77	4.81
20	0.66	19.27	0.46	14.30	52.00	6.58
30	0.64	16.97	0.43	12.67	50.15	5.45

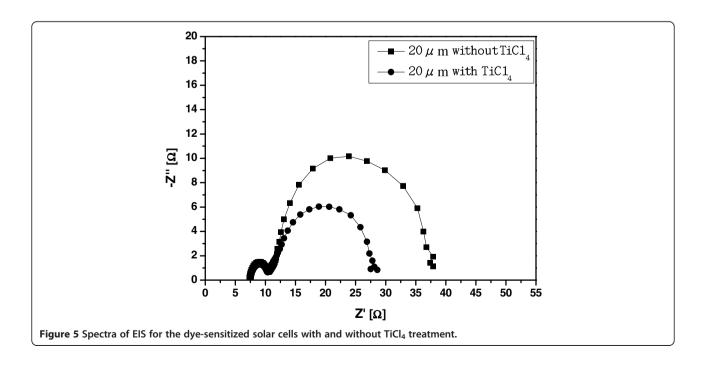


Table 3 The parameters of EIS calculated from Figure 5 for dye-sensitized solar cells with and without TiCl₄ treatment

Sample	$K_{\rm eff}~({\rm s}^{-1})$	τ _{eff} (s)	R _s (Ω)	R _{pt} (Ω)	R _k (Ω)	η (%)
20 μm without TiCl ₄	0.97	1.03	7.35	3.35	26.1	4.35
20 μm with TiCl ₄	1.44	0.69	7.54	2.86	17.4	6.58

on TiO_2 nanotubes can increase the surface area of TiO_2 and the adsorption of N3 dye, resulting in better transport properties of TiO_2 nanotubes and the improvement of conversion efficiency for DSSCs.

Conclusions

In summary, we prepared ${\rm TiO_2}$ nanotube arrays by electrochemical anodization to apply on the electrode of dye-sensitized solar cell. After ${\rm TiCl_4}$ treatment, the walls of ${\rm TiO_2}$ nanotubes were coated with ${\rm TiO_2}$ nanoparticles. It can increase the surface area of ${\rm TiO_2}$ and the adsorption of N3 dye, resulting in better transport properties of ${\rm TiO_2}$ nanotubes and the improvement of conversion efficiency of DSSCs.

Abbreviations

DSSCs: Dye-sensitized solar cells; EIS: Electrochemical impedance spectroscopy; IV characteristics: Current–voltage characteristics; J_{sc} : Short-circuit current density; η : Overall conversion efficiency; TiCl₄: Titanium tetrachloride; V_{oc} : Open circuit potential; XRD: X-ray diffraction.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

THM wrote this manuscript. YTJ and NYL carried out the preparation of samples. SMC and LWJ carried out the XRD measurements. JKT and TCW carried out the *I-V* measurements. WRC, WW, and CJH carried out the EIS measurements. All authors read and approved the final manuscript.

Acknowledgment

This research is supported by the National Science Council, R.O.C., under contract nos. NSC 100-2622-E-150-014-CC3 and NSC 100-2221-E-150-058.

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Received: 16 July 2012 Accepted: 9 October 2012 Published: 23 October 2012

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doi:10.1186/1556-276X-7-579

Cite this article as: Meen et~al: Effect of TiO_2 nanotubes with $TiCl_4$ treatment on the photoelectrode of dye-sensitized solar cells. Nanoscale Research Letters 2012 7:579.

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