#### ORIGINAL ARTICLE

# Significance of TiCl<sub>4</sub> post-treatment on the performance of hydrothermally synthesized titania nanotubes-based dye-sensitized solar cells

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**Abstract** In this investigation, the effect of concentration of TiCl<sub>4</sub> for the post-treatment of hydrothermally synthesized titania nanotubes-based working electrode for dyesensitized solar cells has been studied. Hydrothermally synthesized TiO<sub>2</sub> nanotubes were treated with different concentrations of TiCl<sub>4</sub> to investigate the effect of TiCl<sub>4</sub> concentration. The solar cell performance increased with the increase in TiCl<sub>4</sub> concentration up to 0.5 M and leveled off. The best solar cell showed a short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and efficiency ( $\eta$ ) of 12.75 mA/cm<sup>2</sup>, 795 mV, 69.2 % and 7.04 %, respectively, while untreated TiO<sub>2</sub> nanotube showed  $J_{sc}$ ,  $V_{oc}$ , FF and  $\eta$  of 2.4 mA/cm<sup>2</sup>, 899 mV, 78.9 % and 1.7 %, respectively.

**Keywords** TiCl<sub>4</sub> treatment · Titania nanotubes · Dye-sensitized solar cells

## Introduction

Dye-sensitized solar cells (DSSCs) have been identified as the best and promising alternative device for the conventional silicon-based devices with economically viable cost (Bisquert et al. 2004; Regan and Gratzel 1991). Highest efficiency of 11.2 % has been reported for mesoporous titania nanoparticles (TNPs)-based DSSCs (Chiba et al.

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2006; Gao et al. 2008). However, due to high charge carrier recombination in TNP-based electrode, further enhancement of efficiency is a great challenge (Kim et al. 2006; Roy et al. 2011). To overcome the charge recombination problem in nanoparticles (NP), 1-D structures such as nanotubes (Lei et al. 2010; Park et al. 2008), nanorods (Liu and Aydil 2009; De Marco et al. 2010) and nanobelt (Dong et al. 2011; Pan et al. 2009) have been proposed and successfully implemented in DSSC. These 1-D structures are found to be promising substitute materials for the TNPs in DSSCs as they provide direct electron pathways and fast electron transport reducing charge carrier recombination (Enache et al. 2007; Lee et al. 2009). TNTs with different morphological structures have been successfully fabricated by anodization of Ti metal both on conducting glass and on Ti substrate (Chang et al. 2011; Yun et al. 2011). Despite superior beneficial factors such as fast electron transport and reduced charge recombination properties of 1-D TiO<sub>2</sub> structures, the reported efficiency for TNT-based DSSC is in the range of 6-7%which is inferior to that of TNPs-based DSSC (Liao et al. 2011; Ye et al. 2011). Solar cell performance of DSSC has been improved significantly by post-treatment methods such as coating of an insulating layer on oxide-semiconductor (Wang et al. 2012) or by treatment of  $TiO_2$ -based electrode by TiCl<sub>4</sub> solution (Xin et al. 2011). Commonly applied posttreatment method involves immersion of TiO2-based electrode in 0.04 M TiCl<sub>4</sub> solution followed by sintering at 500 °C. In this investigation, hydrothermally synthesized TiO<sub>2</sub> nanotube films were treated with different concentrations of TiCl<sub>4</sub> solutions for optimization of TiCl<sub>4</sub> posttreatment method for hydrothermally synthesized TiO<sub>2</sub> nanotube films. Solar cell performances of DSSC fabricated with hydrothermally synthesized TiO<sub>2</sub> nanotube films treated with different TiCl<sub>4</sub> concentrations were investigated and reported in this investigation.



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# Experimental

TNTs were synthesized via hydrothermal method (Kim et al. 2006). In hydrothermal method, 2 g of titania nanoparticles (P25 Degussa) were dispersed in 10 M NaOH<sub>(aq)</sub> solution by stirring for 30 min followed by transferring into a Teflon lined autoclave and kept at 150 °C for 48 h. The resultant product was washed with 0.1 M HCl and distilled water until the pH becomes 8.5. Once the pH of the TNT nanotube was reached 8.5, the nanotube paste was ultrasonicated for 10 min to make TNT suspension. Electrophoretic deposition (EPD) technique was employed to deposit TNT on the conducting substrate (FTO: F-doped  $SnO_2$ ) using two electrode system with Pt wire as a counter while FTO as working electrodes. The electrolyte for EPD was prepared by mixing the TNT suspension and methanol in 2:1 (v/v) ratio and EPD was carried out at an optimized voltage of  $\sim 40$  V for 6 min. The electrodeposited film was heated at 130 °C for 15 min and sintered at 450 °C for 30 min. For TiCl<sub>4</sub> treatment, 0.04, 0.1, 0.5 and 1.0 M concentrations of TiCl<sub>4</sub> (aq) were prepared from 99.9 % TiCl<sub>4</sub> (Sigma Aldrich). 30  $\mu$ l of TiCl<sub>4</sub> of each concentration was placed on the pre-sintered TNT-coated FTO substrate for 30 min followed by removing excess TiCl<sub>4</sub> and finally sintered at 450 °C for 30 min. The TiCl<sub>4</sub>-treated TNT films were immersed into 3 mM of N719 dye (Dyesol) solution for 3 h. Finally, the DSSC was assembled combining the working electrode and Pt counter electrode. Iodide/triiodide-based redox couple was utilized to complete the DSSC. The current-voltage measurements of test DSSCs were performed under one sun condition using a solar light simulator (New Port AAA solar simulator, AM 1.5 global, 100 mW/cm<sup>2</sup>) with an active area of 0.25 cm<sup>2</sup>. The intensity of the light was calibrated with a standard Si-reference cell. UV-vis absorbance spectra are measured by a Shimadzu 2450 UV-vis spectrophotometer. The external quantum efficiency (EOE) experiments were performed on Bentham PVE300 unit with a TMc 300 monochromator-based IPCE with a xenon arc lamp. A calibrated type DH Si photodetector was used as reference.

## **Results and discussion**

Figure 1 shows the SEM image of the thin films of TiO<sub>2</sub> nanotube on FTO after annealing at 500 °C for 1 h. Randomly oriented TiO<sub>2</sub> nanotubes are clearly visible in The SEM image and the estimated size of the hydrothermally synthesised titania nanotubes are found to be ~250 nm in length and diameter of ~10 nm. The crystal structure of the product was also characterized by powder XRD method (figure not shown). The characteristic diffraction peak at  $2\theta$ of 25.3° for titania anatase (101) crystal face is observed





Fig. 1 SEM image of the hydrothermally synthesized  $TiO_2$  nanotube films deposited on FTO glass by EPD method

and all the other peaks correspond to anatase  $TiO_2$  that agree well with the standard reported values (JCPDS 21-1272) are also observed and absence of any other characteristic diffraction patterns indicating high purity of the prepared  $TiO_2$  nanotube structures.

The current–voltage (I-V) characteristics of the DSSCs based on pristine and TiCl<sub>4</sub>-treated TNT electrodes under the AM 1.5 G illumination at 100 mW/cm<sup>2</sup> are shown in Fig. 2 and the solar cell parameters are summarized in Table 1. Device fabricated with pristine TNT showed an  $V_{\rm oc}$  of 899 mV, a short circuit current density  $(J_{\rm sc})$  of 2.4 mA/cm<sup>2</sup> and a FF of 78.9 %, resulting in a power conversion efficiency of 1.7 %.  $J_{\rm sc}$  was increased to 8.1 mA/cm<sup>2</sup> after treatment of TNT films by 0.04 M TiCl<sub>4</sub>



**Fig. 2** *I*–V characteristics of **a** pristine  $TiO_2$  nanotubes and **b** 0.04 M, **c** 0.10 M, **d** 0.50 M TiCl<sub>4</sub>-treated TNT under the AM 1.5 illumination at 100 mW/cm<sup>2</sup> condition

**Table 1** I-V characteristics of pristine TiO<sub>2</sub> nanotubes and TiCl<sub>4</sub>treated TNT under the AM 1.5 illumination at 100 mW/cm<sup>2</sup> condition

Electrode	$J_{\rm sc}~({\rm mA/cm}^2)$	$V_{\rm oc}~({\rm mV})$	FF (%)	η (%)
Bare-TNT	2.4	899.2	78.94	1.70
0.04 M TiCl <sub>4</sub>	8.15	801.1	71.55	4.68
0.10 M TiCl <sub>4</sub>	8.85	791.5	71.12	4.98
0.50 M TiCl <sub>4</sub>	12.75	795.4	69.25	7.04

solution and the  $J_{sc}$  increases with the increase of TiCl<sub>4</sub> concentration and a remarkable  $J_{sc}$  (12.7 mA/cm<sup>2</sup>) was observed for the 0.5 M TiCl<sub>4</sub>-treated TNT films. As shown in Fig. 2 and Table 1, a modest decrease in  $V_{oc}$  and FF is noticeable for the TiCl<sub>4</sub>-treated TNT photoelectrode and also the decrease in both  $V_{oc}$  and FF with the increase in TiCl<sub>4</sub> concentration is noticeable.

The best solar cell showed a  $J_{\rm sc}$ ,  $V_{\rm oc}$ , FF and  $\eta$  of 12.75 mA/cm<sup>2</sup>, 795 mV, 69.2 % and 7.04 %, respectively, for the 0.5 M TiCl<sub>4</sub>-treated TNT electrode. We have obtained even better solar cell performance for 1.0 M TiCl<sub>4</sub>-treated TNT films than 0.5 M-treated films, but at such a high TiCl<sub>4</sub> concentration, we noticed the detachment of the electrodeposited TNT films from the FTO substrate and 0.5 M was taken as the best value. The significance of TiCl<sub>4</sub> post-treatment of hydrothermally synthesized TNT electrode is evident by more than fivefold enhancement in  $J_{\rm sc}$  and four-fold enhancement in  $\eta$  compared to  $J_{\rm sc}$  and  $\eta$ values of the pristine TNT films. Figure 3 shows the corresponding external quantum efficiency (EQE) results for the solar cell performance presented in Fig. 2 for DSSCs fabricated with TNT nanotube that are subjected to different  $TiCl_4$  concentration. It can be seen from Fig. 3 that measured EQE spectra match the adsorbed dye spectra on  $TiO_2$  (inset in Fig. 3), although the EQE at longer wavelengths is somewhat broader which may indicate a blue shift of the absorption spectrum of the adsorbed dye. The EQE measurements show that the TiCl<sub>4</sub> treatment affects the shape of EQE curves. Furthermore, the increase in the EQE spectral response in the 600-800 nm wavelength region with the increase of TiCl<sub>4</sub> concentration which could be attributed to the light scattering effect, that in turn enhances the light harvesting properties can be clearly noticeable.

As explained previously, the increase in  $J_{sc}$  and overall efficiency of DSSC fabricated with hydrothermally synthesized TNT nanotube with increasing TiCl<sub>4</sub> concentration compared to the solar cell fabricated with pristine TNT electrode is clearly noticeable. There could be several reasons for the observed TiCl<sub>4</sub> concentration effect on enhancing the solar cell performance. To investigate the reason for observed higher  $J_{sc}$  for TNT with increasing TiCl<sub>4</sub> concentration, we compared the dye adsorption



Fig. 3 External quantum efficiency of **a** pristine  $TiO_2$  nanotubes and **b** 0.04 M, **c** 0.10 M, **d** 0.50 M TiCl<sub>4</sub>-treated TNT under the AM 1.5 illumination at 100 mW/cm<sup>2</sup> condition

Table 2 Adsorbed dye amounts on pristine  $TiO_2$  nanotubes and  $TiCl_4$ -treated TNT at different  $TiCl_4$  treatment concentrations

Electrode	Dye loading (molecule/cm <sup>2</sup> ) $\times 10^{16}$		
Bare-TNT	2,048		
0.04 M TiCl <sub>4</sub>	2,409		
0.10 M TiCl <sub>4</sub>	2,770		
0.50 M TiCl <sub>4</sub>	3,492		

amounts of both pristine TNT, TiCl<sub>4</sub>-treated TNT with the variation of TiCl<sub>4</sub> concentration, and the results are given in Table 2. As given in Table 2, dye loading amounts increases after TiCl4 treatment of TNT which could be due to formation of a thin film of titania particles around the TNT increasing surface roughness. Hence, observed increase in  $J_{sc}$  with the pre-treatment TiCl<sub>4</sub> concentration could be assigned to increase in dye loading amounts with the increase of TiCl<sub>4</sub> concentration. It has been reported that for both TiO<sub>2</sub> nanotube arrays fabricated by anodization and TiO<sub>2</sub> nanoparticle-based photoelectrodes, posttreatment with 0.04 M TiCl<sub>4</sub> resulted in enchancing the  $J_{sc}$ (Bandara et al. 2011; Sommeling et al. 2006). Compared to post-treatment method in the literature, in this investigation we used higher concentration of TiCl<sub>4</sub> solution. As shown in Tables 1 and 2, treatment of hydrothermally synthesized TiO<sub>2</sub> nanotube by 0.04 M TiCl<sub>4</sub> solution, enhances the dye loading and hence  $J_{sc}$  significantly. However, for hydrothermally synthesized TiO2 nanotube photoelectrode, further increase in concentration of TICl<sub>4</sub> solution to 0.5 M



resulted in enhance in  $J_{sc}$  which could be due to availability of more void space in electrodeposited TiO<sub>2</sub> nanotube photoelectrode compared to ordered arrays of TiO<sub>2</sub> nanotube photoelectrode. Even though the system described in this report needed much higher TiCl<sub>4</sub> concentration, it will not adversely affect the cost as the nanotube fabrication is much simpler and economical than the arrayed  $TiO_2$ nanotube. We further investigated the series  $(R_s)$  and shunt  $(R_{\rm sh})$  resistances of TiCl4-treated TNT and bare TNT which can be obtained from the slopes of the I-V curves. With the increase in the concentration of pre-treatment TiCl<sub>4</sub> solution, decrease in the calculated  $R_s (dV/dI)_{I=0}$ for TNT is noticeable while  $R_{\rm sh}$  remains the same. Reduced  $R_{\rm s}$  yielding faster charge transport and an optimum device operation and hence enhanced device performance for 0.5 M TiCl<sub>4</sub>-treated TNT-based devices can be justified based on  $R_s$  values as well.

# Conclusions

The investigation showed that the efficiency of the DSSC based on hydrothermally synthesized TNT can be improved significantly by the TiCl<sub>4</sub> treatment and the best solar cell was fabricated with 0.5 M TiCl<sub>4</sub>-treated TNT electrode. Enhanced in dye loading and electron transport with the increase in TiCl<sub>4</sub> treatment was found to be the main reasons for enhanced solar cell performance.

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