Regular Article

Integration of TiO_2 nanotube arrays into solid-state dye-sensitized solar cells

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Received: 5 October 2010 / Accepted: 16 November 2010 Published online: 28 January 2011 – © EDP Sciences

Abstract. In this investigation, transparent TiO₂ nanotube arrays prepared on a FTO substrate are employed as 1D nanostructures providing elongated direct pathways for electron transport and collection in solid-state dye-sensitized solar cell (SDSC). Donor-antenna (D-A) dyes provide an exciting route for improving the light harvesting efficiency in dye sensitized solar cells owing to their high molar extinction coefficients and the effective spatial separation of charges in the charge-separated state. Hence in this study we fabricated SDSC devices with different thicknesses of transparent TiO₂ nanotube array electrodes sensitized with Ru-(II)-donor-antenna dye and spiro-OMeTAD as a hole conductor. At AM 1.5 G, 100 mW/cm² illumination intensity, a power conversion efficiency of 1.94% was achieved when the TiO₂ nanotubes are initially subjected to TiCl₄ treatment. Furthermore, a linear increase in the cell current without loss in fill factor is observed for increasing length of TiO₂ nanotubes. The structural and morphological characteristics of the transparent TiO₂ nanotube arrays as well as the optimal conditions for the fabrication of SDSCs with transparent TiO₂ nanotubes on FTO glass are reported.

1 Introduction

Dye sensitized solar cells (DSCs) are an attractive alternative for light to electricity conversion applications due to their high efficiency and cost effectiveness [1-3]. The liquid electrolyte based DSC is composed of a dye-adsorbed mesoporous nanocrystalline TiO₂ layer on a transparent conducting glass substrate, electrolyte containing $I^-/I_3^$ redox couples and a Pt coated counter electrode. Photo excited dyes inject electrons into the conduction band (CB) of the TiO_2 , while electron transport to the anode occurs via diffusion of electrons through the disordered TiO_2 nanoparticles [4]. The transport mechanism of electron diffusion plays a decisive role in the mesoporous TiO₂ electrodes due to an absence of an electrical potential gradient in the films as electron transport is limited by grain boundaries of the TiO_2 network and the residence time of electrons in traps [5,6]. To enhance electron transport one can employ 1D nanostructures such as nanowires or nanotubes. In comparison with spherical TiO₂ nanoparticles, tubular TiO₂ of high aspect ratio provides elongated direct pathways for electron travel leading to improved charge collection efficiency [7–9]. To this end, recently much attention has been focused on highly ordered TiO₂

nanotube arrays fabricated by anodization of titanium for DSC which was used due to several attractive characteristics inherent to the nanostructural architecture of these nanotube arrays [10,11]. This is particularly important for SDSCs as they suffer from fast interfacial electron-hole recombination at the hole conductor $(HC)/TiO_2$ interface than in liquid electrolyte containing DSC. Hence, the recombination kinetics of the SDSCs at the HC/TiO_2 interface should be optimized. Furthermore, complete pore filling of the HC in the mesoporous structure is required for the fast regeneration of excited dye molecules. Due to the above mentioned facts, the thickness of the titania electrode in SDSC is limited to about 1.5 μ m, whereas in the electrolyte cells usually it can be of 10–20 $\mu \mathrm{m}$ thick. In a recent publication, TiO₂ nanotube arrays on FTOcoated glass substrate of $>2 \ \mu m$ thickness were successfully applied in the fabrication of solid-state dye sensitized solar cells using an organic dye and ionic liquids [12]. In this contribution, we investigated regularly aligned TiO_2 nanotube arrays within 0.4 to 1.4 μ m thickness range to study the influence of nanotube length on the overall cell performance of the SDSC.

Efficient solid state solar cells have been constructed with mesoporous [13,14] TiO₂ using donor-antenna (D-A) dye, cis-di(thiocyanato)(2, 2'-bipyridyl-4, 4'-dicarboxylic

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acid)-(2, 2'-bipyridyl-4, 4'-bis(vinyltriphenylamine) ruthenium(II) (from here on referred to as Ru-TPA-NCS) in combination with Spiro OMeTAD as hole conductor. Recently we also reported the use of a such dye in TiO_2 nanotube arrays in order to obtain highly efficient electrolyte cells [15]. For the liquid electrolyte solar cell constructed with transparent TiO_2 nanotubes and D-A dye, comparatively a higher efficiency has been obtained than with the N-719 dye and the higher efficiency was assigned to lower interfacial recombination losses as a result of increased spatial separation of the final charge separate states. The extended π -electron delocalization in the bpy ligand enables the donor-antenna dye molecules to have very high molar extinction coefficients [16]. The extended separation of electron and holes realized in Ru-TPA-NCS has been shown to retard the recombination process at the TiO_2 dye interface and at the TiO₂-hole conductor interface in solid state solar cells [16,17]. This is of particular interest in solid-state DSSC's employing organic hole-conductors (HC), as it suffers from fast interfacial charge recombination losses relative to liquid electrolyte based devices. Herein we demonstrate how the combined effects of better charge transport/collection inherent in nanotubes and enhanced pore-filling of Spiro OMeTAD in nanotubes and extended charge separation of D-A dye result in enhanced performance in solid state solar cells. Furthermore SDSCs are promising due to their large potential to convert solar energy to electrical energy at low cost and their capability to solve the leakage or sealing problems that exist in liquid electrolyte dye-sensitized solar cells. In this paper, the optimal conditions for the fabrication of DSSCs with transparent TiO₂ nanotubes on FTO glass and D-A dye are investigated and discussed.

2 Experimental section

A detailed methodology of fabricating optically transparent nanotube arrays has been published elsewhere [18]. Titanium films, approximately 1500 nm-thick, are rf sputtered onto fluorine-doped tin oxide (FTO)-coated glass substrates held at 500 °C. The resulting films are then anodized at a constant potential of 12 V. The anodization process results in the formation of 1.2 μ m-thick titania nanotube arrays. The samples are annealed at 450 °C in oxygen for 3 h with heating and cooling rates of 2.5 °C/min to induce crystallinity. These transparent nanotube array samples were subjected to a TiCl₄ treatment by placing them in a 0.04 M TiCl₄ solution for 30 min in airtight bottles followed by dip in 0.1 M HCl solution for 30 min. Subsequently these samples were rinsed with water and annealed at 500 °C for 30 min using a heat gun.

Titanium films, of different thicknesses are rf sputtered onto FTO-coated glass substrates held at 500 °C for the fabrication of the different lengths of TiO₂ nanotube arrays. For the fabrication of solar cell, bare and TiCl₄ treated TiO₂ nanotube array substrates were coated with dye by leaving them overnight in a 0.5 mM solution of the Ru-TPA-NCS dye in Dimethylformamide (DMF); the synthesis of which has been detailed elsewhere [14]. After the physisorbed dye molecules were rinsed away by dipping the samples in DMF, the samples were subsequently dried in vacuum at 45 °C for at least 1 h. The hole-conductor (HC) was deposited on dye/TiO₂ layer by spin-coating. HC solution comprises of spiro-OMeTAD (0.16 M), and tert-butylpyridine (0.16 mM) dissolved in water-free chlorobenzene. N-lithiofluoromethane sulfonamide (Li-salt solution, 30 mM) in cyclohexanone was added as additive. For each substrate, 70 μ l of the hole conductor solution was used for the spin-coating. As a final step, 40 nm thick Au-layer was vapor-deposited by electron beam deposition in a vacuum chamber of BA 510 type from Balzers (Liechtenstein) under vacuum with the help of a mask and the active surface is 0.12 cm².

The photovoltaic current-voltage measurements were carried out by a Keithley 6517 Source-Measure unit under AM 1.5 G conditions (Xenon arc lamp, Air Mass Filters from Oriel). The intensity of the light was calibrated with a standard Si-reference cell from the Fraunhofer Institut für Solarenergie (ISE), Freiburg as 100 mW/cm². All efficiency values reported in this work were not corrected by the spectral mismatch factor. The IPCE values were measured using a lock-in amplifier (SR830, Stanford Research Systems) with a current preamplifier (SR570, Stanford Research Systems) under short-circuit conditions after illuminating the devices with monochromatic light from a Xenon lamp passing through a monochromator (Spectra-model). UV-Vis spectra were recorded with a Perkin Elmer Lambda 900 spectrometer. Surface morphology of TiO₂ nanotubes were examined using LEO 1530 Gemini field emission scanning electron microscope (FE-SEM).

3 Results and discussion

SEM images of surface and cross section of bare TiO_2 nanotube arrays is depicted in Figures 1a and 1b respectively while in Figures 1c and 1d, surface and cross section of TiCl₄ treated TiO₂ nanotube arrays are depicted respectively. As shown in Figure 1, the anodization process resulted in the formation of titania nanotube arrays with extremely smooth surfaces without any individual tube protrusions with approximately dimensions of: pore diameters of 80 nm (standard deviation SD 8 nm), wall thicknesses of 17 nm (SD 2 nm), and lengths of 1.2 μ m. From the top-view of the SEM images of $TiCl_4$ treated TiO_2 nanotube arrays, it appears the TiCl₄ treatment resulted in a slight increase in wall thickness of the TiO_2 nanotubes. By comparing the cross-sectional images of TiCl₄ treated and non-treated TiO₂ nanotubes arrays, it can be observed that outside of NT appears hazy after TiCl₄ treatment and we believe inside of the NT to have the same haziness which is not clearly distinguishable from cross sectional SEM image. It can be assumed that the haziness and surface roughness arise as a result of a deposition of a very thin TiO_2 layer on these nanotubes which could not be distinguished by SEM images very clearly.

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Fig. 1. Scanning electron microscope images of 1.2 μ m TiO₂ nanotube-array: (a) top-view and (b) cross-section before TiCl₄ treatment; (c) top-view and (d) cross-section after TiCl₄ treatment.

Table 1. IV characteristics of the D-A dye sensitized TiO₂ nanotube arrays under 1.5 AM (global) illumination.

	$V_{oc} (mV)$	$J_{sc} (\mathrm{mA/cm}^2)$	FF (%)	$\eta~(\%)$
TiO_2 nanotube	622	3.75	45	1.04
${ m TiCl_4}$ treated ${ m TiO_2}$ nanotube	547	7.40	47	1.94

The I-V characteristics of solar cells fabricated using 1.2 μ m long transparent TiO₂ nanotubes and TiCl₄ treated 1.2 μ m long transparent TiO₂ nanotubes sensitized with Ru-TPA-NCS are shown in Figure 2 and Table 1. The 1.2 μ m long transparent TiO₂ nanotubes cell showed a short circuit photocurrent density (J_{sc}) of 3.75 mA cm^{-2} , an open circuit potential (V_{oc}) of 622 mV and a fill-factor (FF) of 0.45 resulting in an overall conversion efficiency of $\sim 1.04\%$. However, TiCl₄ treated TiO₂ nanotube solar cell sensitized with Ru-TPA-NCS showed higher J_{sc} and efficiency; J_{sc} of 7.4 mA cm⁻², V_{oc} of 547 mV and a FF of 0.47 resulting in an overall conversion efficiency of 1.94%. i.e. an improvement of efficiency by ${\sim}90\%$ compared to pristine ${\rm TiO}_2$ nanotube cells. It has been shown that the TiCl₄ treatment of mesoporous TiO₂ layer enhances the overall solar cell performance of DSSC due to increase in dye uptake and change in surface properties of mesoporous TiO_2 layer [18,19]. Dye adsorption analysis and surface morphology study of pristine TiO_2 nanotube arrays and $TiCl_4$ treated TiO_2 nanotube

arrays revealed the same trend. Figure 3 shows the dye absorption spectra of $TiCl_4$ treated and untreated TiO_2 nanotube arrays. As shown in Figure 3, the optical absorption of Ru-TPA-NCS dye coated TiCl₄ treated TiO₂ nanotube electrode is higher than that of the TiO_2 nanotube electrode indicating that enhanced dye uptake by $TiCl_4$ treated TiO_2 nanotubes resulted in higher J_{sc} than untreated TiO_2 nanotube electrode. Furthermore, it has been reported that the $TiCl_4$ treatment of TiO_2 results in increased charge injection efficiency as a result of a positive shift in the flat-band potential of TiO_2 [19,20]. Also it has been suggested that the thin TiO_2 layer formed on mesoporous particles may act as a charge recombination barrier preventing electron access to the surface. Therefore, we believe that a combination of effects of enhanced dye adsorption, efficient charge injection and reduced charge recombination, resulted in higher solar cell efficiency in $TiCl_4$ treated TiO_2 nanotube arrays.

Rectification study of the $TiCl_4$ treated and pristine TiO_2 nanotube arrays confirmed increased rectification



Fig. 2. (Color online) Current-voltage characteristics of a 1.2 μ m long transparent nanotube arrays sensitized with Ru-TPA-NCS under AM 1.5 G illumination: TiCl₄-treated 1.2 μ m TiO₂ nanotube arrays (\circ) and untreated TiO₂ nanotube arrays (\Box).



Fig. 3. (Color online) UV-Vis absorption spectra of 1.2 μ m long transparent pristine TiO₂ nanotube arrays (compact), untreated 1.2 μ m long transparent TiO₂ nanotubes treated with Ru-TPA-NCS dye (doted) and TiCl₄ treated 1.2 μ m long transparent TiO₂ nanotubes treated with Ru-TPA-NCS dye (dashed).

for TiCl₄ treated TiO₂ nanotube arrays than for untreated TiO₂ nanotube arrays. Rectification characteristics of TiCl₄ treated and non-treated 1.2 μ m long nanotube arrays are shown in Figure 4. As shown in Figure 4, the non-treated TiO₂ nanotube arrays has least rectification ratio and coating of a thin TiO₂ layer on those nanotubes by TiCl₄ treatment resulted in increase in rectification behaviour. These observations suggest the existence of some recombination sites on as prepared 1.2 μ m pristine TiO₂ nanotube arrays and some of these sites can be repaired by coating a thin compact TiO₂ layer indicating that the efficiency of DSSC of TiO₂ nanotube arrays



Fig. 4. (Color online) Dark current-voltage characteristics of $1.2 \ \mu m$ long transparent nanotube arrays coated with Ru-TPA-NCS, before TiCl₄ treatment (dashed) and after TiCl₄ treatment (solid).



Fig. 5. Cross-sectional SEM image of spiro-OMeTAD filled $1.2 \ \mu m$ transparent TiO₂ nanotube-arrays.

can be increased by fabrication of TiO_2 nanotube arrays on a good TiO_2 blocking layer.

One of the significant constraints which limit the solar cell efficiency of a solid state solar cell is the pore filling of the hole-conductor in mesoporous TiO₂ layer [21]. Poor hole-conductor filling in the dye coated TiO₂ electrode results in inefficient regeneration of the dye ground state resulting in a decrease of both J_{sc} and FF. It has been proposed that the difficulty of pore filling of HC can be surmount by constructing aligned mesoporous oxide channels perpendicular to the current collector [22,23]. As such, our 1.2 μ m long transparent TiO₂ nanotube arrays on FTO glass should provide best opportunity to fill the HC efficiently. By comparing SEM images of empty nanotubes (Fig. 1b) and HC conductor filled nanotube (Fig. 5), we could observe a homogeneous penetration of hole conductor in the entire inter-tube spacing (from top of TiO_2 nanotubes to the bottom of the substrate) and formation of an overlayer of hole conductor on top of TiO_2 nanotube arrays. We presume that the capillary action of the TiO_2 nanotubes may facilitate homogeneous and efficient pore-filling of hole conductors inside TiO_2 nanotubes leading to enhanced solar cell performance.

It has been reported that the charge collection of TiO_2 nanotube arrays is more efficient than that of TiO_2 nanoparticles [24,25]. A recent study of DSC with an I^{-}/I_{3}^{-} redox couple indicated that the electron transport time of dye sensitized solar cells made from a given film thicknesses of TiO_2 nanoparticles and TiO_2 nanotubes is similar [26-28]. However, nanotube arrays have slower recombination rate compared to nanoparticles owing to fewer surface recombination sites existing in the nanotube arrays than in nanoparticles [26]. Similarly, it has also been shown that the electron diffusion length (which depends on the diffusion coefficient and lifetime of the photoinjected electrons) of the titania nanotubes is of the order of 100 μ m [27]. Given the facts that the recombination in the nanotube film is slower than that in the nanoparticles films and the similar transport times for both films, an enhanced charge collection efficiency (η) for nanotube arrays could be expected according to the relationship $\eta = 1 - (\tau_c / \tau_r)$, where τ_c and τ_r are charge transport and recombination time constants respectively [28]. Hence, the enhanced charge collection and slower charge recombination properties of TiO₂ nanotube arrays are beneficial factors for fabrication of SDSC devices as it is well known that the charge recombination rate is higher in SDSC than DSC. However these properties have yet to be studied in a SDSC configuration.

Usually the SDSC performance heavily depends on the titania thickness and for obtaining optimum efficiency, a compromise between absorption and charge collection is sought in any dye-titania combination. Therefore, we wanted to know the effect of thickness of the titania nano arrays on the SDSC performance. Thus one of the most interesting observations of this investigation is the dependence of solar cell performance on the length of the TiO_2 nanotubes. We prepared three different nanotube array samples with different lengths of 0.55, 1.05 and 1.4 $\mu m.$ The experimental conditions for the preparation of these tubes were slightly different from that for 1.2 μ m long tubes. SDSCs were fabricated as described above except that nanotube arrays were not treated with TiCl₄. The I-V characteristics of the solar cells fabricated using 0.55, 1.05 and 1.4 μ m long transparent nanotube arrays sensitized with Ru-TPA-NCS are shown in Figure 6a and the dependence of solar cell efficiency with the tube length is given in Figure 6b. As shown in Figure 6, it is clearly evident that there is a linear increase in the cell current with length of tubes without loss in FF up to a length of 1.4 μ m. This results in an increase in efficiency for the longer tubes. A saturation of efficiency or current is not yet reached up to 1.4 μ m long tubes and it is obvious that solar cells using TiO₂ nanotube arrays can profit from longer tubes. Currently we are concentrating our work



Fig. 6. (Color online) (a) Current-voltage characteristics of a 0.55 μ m (\triangle), 1.05 μ m (\circ) and 1.4 μ m (\Box) long transparent nanotube arrays sensitized with Ru-TPA-NCS and (b) dependence of the efficiency vs. length of nanotube for solar cells under AM 1.5 G illumination.

in preparation and optimization of titania nanotubes of longer lengths on FTO substrates.

4 Conclusion

In conclusion, we fabricated solid-state solar cells exhibiting power conversion efficiency of 1.04% using 1.2 μ m long transparent TiO₂ nanotube arrays sensitized with donor antenna dye Ru-TPA-NCS and Spiro-OMeTAD as hole conductor. By TiCl₄ treatment of these nanotube arrays the photoconversion efficiency could be improved to 1.94%. The hole-conductor spiro-OMeTAD can be filled in TiO₂ nanotubes having a pore diameter of 60 nm reasonably well which could be due to both capillary effect of nanotubes and better wetting of the Ru-TPA-NCS dye by the spiro-OMeTAD. We demonstrated for the first time that an efficient solid state solar cell can be fabricated using transparent TiO₂ nanotube arrays on FTO, Ru-TPA-NCS as dye and Spiro-OMeTAD as hole conductor. A linear increase in J_{sc} and efficiency could be achieved with the increasing length of nanotube arrays up to 1.4 μ m. Increase in dye uptake using longer tubes and improvement of the electronic properties of TiO₂ nanotube arrays would provide opportunity to improve the solar cell efficiency further.

J. Bandara acknowledges the Alexander von Humboldt Foundation fellowship. MT acknowledges SFB 840 and EURO-CORES (SONS II) SOHYDS research projects. B. Ghosler of University of Bayreuth, Germany is acknowledged for his help on SEM analysis of TiO₂ nanotube samples.

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