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Surface Modification of TiO$_2$ Nanotube Arrays with Y$_2$O$_3$ Barrier Layer: Controlling Charge Recombination Dynamics in Dye-sensitized Solar Cells

Lu-Yin Lin, Min-Hsin Yeh, Chia-Yuan Chen, R. Vittal, Chun-Guey Wu and Kuo-Chuan Ho

Fast electron transport, large specific surface area, and slow interfacial electron recombination are indispensable features for an efficient photoanode of dye–sensitized solar cells (DSSCs). Highly–ordered TiO$_2$ nanotubes (TNT) with advanced architecture of high surface-to-volume ratio and open–up geometry for providing direct electrons/ions transport channels is applied on a flexible photoanode in this study. Due to several micrometers in the semiconductor are required for diffusion of electrons, which are surrounded by electron acceptors at a distance of only several nanometers, a wide band gap barrier layer of Y$_2$O$_3$ coated on TNT to retard back transfer of electrons to the electrolyte or to the oxidized dye molecules, by electrodepositing Y(OH)$_3$ on TNT surfaces and subsequently annealing the samples. By adjusting the charge capacity for Y(OH)$_3$ electrodeposition, the charge recombination dynamics in the pertinent DSSC can be easily controlled. This barrier layer also enhances the dye adsorption and therefore increases the volume of optically active component due to the more basic surface of Y$_2$O$_3$ for more carboxyl groups in a dye molecule adsorbing onto the surface. A higher light–to–power conversion efficiency ($\eta$) of 6.52% is obtained for the pertinent DSSC, with compared to a reference cell with non–coated TNT ($\eta = 5.35\%$), exhibiting a 22% enhancement on the $\eta$.

Introduction

Dye–sensitized solar cells (DSSCs) have been researched extensively since their first innovative report in 1991. The challenging issues lie not only on achieving high light–to–power conversion efficiency (\(\eta\)) but also on pursuing easy and low–cost manufacturing techniques. Flexible DSSCs with the photoanode composed of one–dimensional (1–D) TiO$_2$ nanotubes (TNT) have attracted much attention since the possibility of roll–to–roll production and the features of high surface–to–volume ratio and open–up geometry for TNT to provide higher dye loading amount and direct electrons/ions transport channels. Nakayama et al. applied TNT as an underlayer in the photoanode to raise the light harvesting efficiency of DSSCs. Xu et al. prepared a bilayered film with TiO$_2$ nanoparticles (TNP) and TNT respectively as the underlayer and the overlayer on the photoanode to realize rapid electron transfer. We have previously prepared a flexible photoanode with TNT as the underlayer and TNP as the overlayer on Ti foils to produce 1–D electron transfer paths at the interface between the Ti foil and TNP. To further improve electron transfer and minimize electron–hole recombination, surface modification of TiO$_2$ with other metal oxides, e.g., SrO, Nb$_2$O$_5$, NbTiO$_3$, ZnO, and MgO, have been studied for several years. The coated metal oxides allows the photo–injected electrons to tunnel through into TiO$_2$ core, and subsequently to the conducting oxide layer of the substrate. Simultaneously, the coated metal oxides form an energy barrier for the recombination reactions of the injected electrons from the TiO$_2$ core to triiodide ions in the electrolyte and also to the oxidized dye molecules. This process is energetically favourable only if the conduction band of the coated metal oxides lies above both the lowest unoccupied molecular orbital (LUMO) energy level of the sensitizer and the conduction band edge of the TiO$_2$ core. In addition, the surface of the metal oxide coating is often more basic, leading to higher adsorption of carboxyl groups in dye molecules and therefore to higher volume of optically active components. Guillon et al. developed a multistep wet–chemistry route to obtain ZnO nanowires arrays coated by a ZnO nanocrystalline layer. Decreased recombination rate and improved photovoltage are obtained for the pertinent cells. Gao et al. fabricated SnO$_2$/TiO$_2$ core–shell DSSCs to obtain fast and efficient charge collection. A $\eta$ of 5.11% was obtained for the core–shell DSSCs, which is above five times higher than that of the SnO$_2$ nanotube based DSSCs ($\eta = 0.99\%$). Chen et al. fabricated a TNT film filled with TNP coated by a thin SrO layer and got a $\eta$ of 5.39% for the pertinent DSSC. Lee et al. prepared porous TiO$_2$ films coated with ZrO$_2$ or Nb$_2$O$_5$ thin layers and found reduced charge injection and back electron transfer rates for the pertinent DSSCs with compared to those of...
the cell with a bare TiO₂ film. In this study, flexible photoanodes were prepared by anodizing Ti foils to obtain TNT on the surfaces. The TNT length was optimized in considering of the electron transport and the specific surface area for dye adsorption. It is well-known that the insulating yttrium oxide (Y₂O₃) has attractive features including high-κ dielectrical value, a wide bandgap energy of 6 eV, a relatively high dielectric constant, high thermal stability, and low leakage current. Therefore, to further reduce the interfacial electron recombination, Y(OH)₃ was electrodeposited on TNT and the resulting film was annealed subsequently to obtain a thin Y₂O₃ barrier layer on the surface of TNT. The charge recombination dynamics in the pertinent DSSC can be easily controlled via adjusting the charge capacity for Y(OH)₃ electrodeposition. In addition, the more basic surface of Y₂O₃ is favour for the carboxyl groups in a sensitizer adsorbing to increase the dye adsorption. A better η of 6.52% was achieved for the DSSC with Y₂O₃-coated TNT (Y–TNT) on a Ti foil as the photoanode, with reference to that of a cell with TNT (5.35%). The Y–TNT film was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Electrochemical impedance spectra (EIS), incident photon to current conversion efficiency (IPCE) curves, and laser-induced photo–potential transients were utilized to substantiate the explanations.

Experimental Section

Materials

Lithium iodide (LiI, synthetical grade) and iodine (I₂, synthetical grade) were obtained from Merck. Tert–butyl alcohol (tBA, 96%) and 4–tert–butylpyridine (TBP, 96%) were obtained from Acros. Neutral cleaner, isopropanol alcohol (IPA, 99.5%) and yttrium nitride (Y(NO₃)₃ ⋅ 6H₂O) were obtained from Aldrich. 3– methoxypropionitrile (MPN, 99%) was obtained from Fluka. Acetonitrile (ACN, 99.99%) and ammonium fluoride (NH₄F, A. C. S. reagent) were obtained from J. T. Baker. Ethylene glycol (EG, extra pure) was obtained from Scharlau. 1–Propyl–2,3–dimethylimidazolium iodide (DMPH) was obtained from Soloranix. The organic solvent electrolyte contains a mixture of 0.1 M LiI, 0.6 M DMPH, 0.05 M I₂, and 0.5 M TBP in a solvent of 50 vol% MPN and 50 vol% ACN.

Preparation of photoanode/counter electrode and cell assembly

Ti foils (0.4 mm thick, 99.8% purity, Fuu Cheng Co. Ltd., Taiwan) were polished to remove residual metal oxides and other adhesive substances, and sequentially cleaned with a neutral cleaner, deionized–water (DI–water), acetone, and IPA. Highly ordered TNT was prepared on Ti foils using an anodization method. The anodization process was conducted at a constant applied potential of 50 V at the room temperature in an electrolyte consisting of 0.25 wt% NH₄F and 1.0 wt% H₂O in ethylene glycol (EG). The anodized sample sheet was ultrasonically cleaned in DI–water for 1 min to remove the surface debris. Y(OH)₃ was then electrodeposited on TNT using a conventional three electrode cell in a 0.01 M Y(NO₃)₃ solution at the deposition charge capacities of 10, 15, 20, and 25 mC cm⁻². (Equation (1)) The potential of the working electrode was fixed at −1.2 V vs. the Ag/AgCl reference electrode. The TNT film without the electrodeposition of Y(OH)₃ was used for the comparative purpose. The TNT films with and without Y(OH)₃ electrodeposition were gradually heated to a temperature of 500 °C in an oxygen atmosphere, and subsequently annealed at this temperature for 1 h. The Y(OH)₃ layer coated on TNT was then changed to a Y₂O₃ thin layer after annealing (Equation (2)).

\[
\text{Y(NO₃)₃} + 3 \text{H₂O} \rightarrow \text{Y(OH)₃} + 3 \text{HNO₃}
\]

\[
4 \text{Y(OH)₃} + 3 \text{O₂} \rightarrow 2 \text{Y₂O₃} + 12 \text{OH}^-
\]

After annealing and cooling to the room temperature, a portion (0.4×0.4 cm²) of the resulting films was selected as the active area by removing the side portions carefully, and following the films were immersed in a 0.3 mM solution of TBA (Ru(4– carboxylic acid–4’–carboxylate–2,2’–bipyridine)(Ligand– 11)(NCS)) (CY C–B11) in a solvent mixture of ACN and tBA (volume ratio of 1:1), at room temperature for 24 h; 20 mM phenylenediamine (PCBM) was used as an adsorbent along with the dye. The dye–sensitized TiO₂ electrode was then coupled with a transparent Pt counter electrode. The counter electrode was prepared by sputtering Pt on an ITO glass (ITO, UR–IT0007–0.7mm, Uni–onward Corp., Taiwan, < 7 Ω sq⁻¹) which was first cleaned with a neutral cleaner, and then washed with DI–water, acetone, and IPA, sequentially; the sputtering was carried out for 5 s (under a sputter current of 40 mA), which was the optimized condition according to our previous study, in consideration of the catalytic ability of Pt and its transmittance for a back–illuminated DSSC. The two electrodes were separated by a 60 μm thick gasket made of ionomer Surlon (SX1170–25, Solaronix S.A., Aubonne, Switzerland) and sealed by heating. The electrolyte was injected into the gap between the electrodes by capillarity.

Measurements

The DSSCs were illuminated by a class A quality solar simulator (XES–301S, AM1.5G, San–Ei Electric Co., Ltd., Osaka, Japan) from the side of Pt/ITO (back–illumination) and the incident light intensity (100 mW cm⁻²) was calibrated with a standard Si cell (PECSI01, Pecell Technologies, Inc.). The photoelectrochemical characteristics of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco–Chemie, the Netherlands). The crystalline phase and the chemical bonding state of the films of TNT and Y–TNT were studied by X–ray diffraction (XRD, MO3XHF, MAC) and X–ray photoelectron spectroscopy (XPS, Theta Probe, Thermo Fisher Scientific, UK), respectively. Surface morphologies of TNT films were observed by scanning electron microscopy (SEM, Nova NanoSEM 230, FEI). Electrochemical impedance spectra (EIS) were obtained by the above–mentioned potentiostat/galvanostat equipped with an FRA2 module, under a constant light illumination of 100 mW cm⁻². The frequency range explored was 10 mHz to 65 kHz. The applied bias potential was set at the open–circuit potential of the DSSC, between the Pt counter electrode and the photoanode, starting from the short–circuit condition; the corresponding ac amplitude was 10 mV. The impedance spectra were analyzed using an equivalent circuit model. Pulsed laser excitation was applied by a frequency–doubled Q–switched Nd:YAG laser (model Quanta–Ray GCR–3–10, Spectra–Physics laser) with a 2 Hz repetition rate at 532 nm, and a 7 ns pulse width at half–height. The average electron lifetime could approximately be estimated by fitting a decay of the open–circuit potential transient with exp (−t/τ), where t is the time and τ is an average time.
Incident photo–to–current conversion efficiency (IPCE) curves were obtained at short–circuit condition. The light source was a class A quality solar simulator (PEC–L11, AM1.5G, Peccell Technologies, Inc.); light was focused through a monochromator (Oriel Instrument, model 74100) onto the photovoltaic cell. The monochromator was moved in steps through the visible spectrum to generate the IPCE (\(\lambda\)) as defined in Equation (3) as following,

\[
\text{IPCE} (\lambda) = \frac{J_{sc}}{\phi} \times \frac{100}{\lambda}
\]

where \(\lambda\) is the wavelength, \(J_{sc}\) is the short–circuit photocurrent (mA cm\(^{-2}\)) recorded with a potentiostat/galvanostat, and \(\phi\) is the incident radiative flux (W m\(^{-2}\)) measured with an optical detector (Oriel Instrument, model 71580) and a power meter (Oriel Instrument, model 70310).

## Results and Discussion

### Characteristics of yttrium oxide modified TiO\(_2\) nanotube arrays

Prior to deposit yttrium oxides on the TNT electrode, the performance of the DSSCs with bare TNT photoanodes was optimized by varying the anodization time for growing TNTs. The optimization results are described in the electronic supporting information (ESI). The best performance of the TNT–based DSSCs was obtained with 50 V and 240 min as the anodization voltage and period, respectively. Hence, for the following works the TNT was prepared with this best condition.

In order to further reduce the interfacial electron recombination, a post–treatment was performed with a thin barrier layer of Y\(_2\)O\(_3\) coated on TNT. Figure 1(a), (b), (c), and (d) show the SEM images of Y–TNT with the charge capacities of 10, 15, 20, and 25 mC cm\(^{-2}\), respectively. The wall thickness of the TNT slightly increases with increasing charge capacity for electrodepositing Y(OH)\(_3\) before annealing, indicating the formation of Y\(_2\)O\(_3\) thin film on TNT. The wall thickness of Y–TNT with the charge capacity of 10, 15, 20, and 25 mC cm\(^{-2}\) were respectively estimated to be 27, 37, 43, and 50 nm, which are larger than that of the TNT, i.e., 20 nm, as shown in the ESI.

Furthermore, the crystalline phases of the TNT and Y–TNT films were examined by XRD patterns, as shown in Figure 2. Peaks corresponding to (101), (103), (004), (200), (105), (211), and (118) of the TiO\(_2\) structure associated with the anatase phase are observed in this figure for all the XRD patterns, indicating the TNT and Y–TNT are crystallized in pure anatase phase. The peaks of Ti foil substrate also present in this figure. However, no obvious peaks were found for Y\(_2\)O\(_3\) in the case of Y–TNT. It is presumed that the Y\(_2\)O\(_3\) film is too thin to be detected. Therefore, EDX was applied to further investigate the composition of Y–TNT. Figure 3(a) and (b) illustrate the EDX data of Y–TNT and TNT, respectively. Ti and O peaks were found in both Figure 3(a) and (b), while Y peak was only observed in Figure 3(a), indicating the existence of yttrium element on TNT in the case of Y–TNT. In addition, the formation of Y\(_2\)O\(_3\) was verified by XPS. The Y 3d and Ti 2p core–level XPS spectra of Y–TNT annealed at 500 °C are shown in Figure 4(a) and (b), respectively. Oxide Y 3d peaks located around 161 and 159 eV respectively for Y\(_2\)O\(_3\) and 3d\(_{x2}\) and 3d\(_{yz}\) characterized for Y\(_2\)O\(_3\) were found in Figure 4(a), while TiO\(_2\) features at 458.9 eV for Ti 2p\(_{3/2}\) and at 464.5 eV for Ti 2p\(_{1/2}\) in Figure 4(b) reveal the presence of TiO\(_2\) in Y–TNT.
Figure 4 XPS spectra of (a) Y 3d and (b) Ti 2p for the Y–TNT.

Photovoltaic performance and incident photon–to–electron conversion efficiency of dye-sensitized solar cells with Y₂O₃ modified TiO₂ nanotube arrays

Figure 5 shows J–V curves of the DSSCs with TNT and Y–TNT obtained with the charge capacity of 10, 15, 20, and 25 mC cm⁻², and the corresponding photovoltaic parameters are summarized in Table 1. All the DSSCs with Y–TNTs show higher V_OC compared that of the cell with TNT. These increases in V_OC are due to energy barrier at the interface between Y–TNT and the electrolyte or the oxidized sensitizer enabled by the presence of Y₂O₃, which has a higher conduction band edge by about 3.2 V, i.e., the conduction band edges of TiO₂ and Y₂O₃ are −0.20 V and −2.58 V vs. normal hydrogen electrode (NHE) respectively, as shown in Scheme 1. This energy barrier reduces the back electron transfer from the conduction band of TiO₂ to triiodide ions or oxidized sensitizers. Also, with the increase in charge capacity for the deposition of Y(OH)₃, i.e., with the increase of Y₂O₃ amount on TNT, the V_OC increases considerably, indicating the more efficient reduction for the back electron transfer with thicker Y₂O₃ layers. It is also successfully confirmed that by simply adjusting the charge capacity for Y(OH)₃ electrodeposition on TNT, the charge recombination dynamics can be easily controlled. On the other hand, the J_SC increases with the increase in charge capacity up to 15 mC cm⁻², and decreases with further increases in charge basic than TiO₂, i.e., the pzc are pH 9 and pH 6.2 for Y₂O₃ and capacity. It was reported by Kay and Grätzel that Y₂O₃ is more TiO₂, respectively. The surface of Y–TNT should be more basic than that of the individual structure of TiO₂, so more acidic dye molecules can adsorb on the surface, leading to higher J_SC. However, the J_SC decreases with further increases in the charge capacity for Y(OH)₃ electrodeposition, i.e., 20 and 25 mC cm⁻². This may be ascribed to the serious tunnelling barrier in the case of thick Y₂O₃ layers, which would inhibit the electron

Table 1 Photovoltaic parameters of the DSSCs with bare TNT and Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻², measured at 100 mW cm⁻².

<table>
<thead>
<tr>
<th>Deposited charge capacity (mC cm⁻²)</th>
<th>V_OC (V)</th>
<th>J_SC (mA cm⁻²)</th>
<th>FF</th>
<th>η (%)</th>
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<td>0.55</td>
<td>5.35</td>
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<td>6.27</td>
</tr>
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<td>0.67</td>
<td>17.06</td>
<td>0.67</td>
<td>6.52</td>
</tr>
<tr>
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<td>5.22</td>
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<tr>
<td>25</td>
<td>0.70</td>
<td>12.31</td>
<td>0.58</td>
<td>4.89</td>
</tr>
</tbody>
</table>

Scheme 1 Schematic diagram of the energy levels of a core–shell structure on the photoelectrode in DSSCs.
transferring from dye to TiO₂. The best η of 6.52% was achieved for the DSSC with Y–TNT obtained with a charge capacity of 15 mC cm⁻², while the cell with TNT shows an η of only 5.35%.

**Figure 5** also illustrates the current density–voltage curves of the DSSCs with TNT and Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻² measured in dark. The onsets of the dark current densities for the DSSCs with Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻² occur at 0.56, 0.59, 0.60, 0.61, and 0.54 V, respectively. These values were obtained by drawing tangent lines to the curves, starting from the potential scale, and a zero current line to the same curves, and by measuring the potentials that correspond to the intersection points of the tangent lines with the zero current line. The onset of the dark current for the DSSC with TNT occurs at the lowest forward bias, indicating the most serious charge recombination in this case, while the forward bias for the onset of the dark current of the DSSCs with Y–TNT increases with increasing charge capacity, confirming again that the charge recombination can be reduced with more Y₂O₃ deposition. All the onset potentials of the cells measured in dark are in consistency with their V_OC values.

**Figure 6** shows IPCE curves of the DSSCs with TNT and Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻². The maximum efficiency at the wavelength of 580 nm is in coincidence with the absorption maximum wavelength of CYC–B11 dye. The IPCE for the DSSC with Y–TNTs (15 mC cm⁻²) at 580 nm is 89.71%, which is higher than that of the DSSC with TNT (79.43%), and also IPCE over the whole wavelength region of 400 nm to 800 nm exhibits higher value for the former case, resulting from the more basic surface of Y–TNT for more dye adsorption and therefore more electrons can be excited. All the IPCE values at 580 nm are in consistency with the J_SC value of the cells.

**Transmitent photovoltage curves of dye-sensitized solar cells with Y₂O₃ modified TiO₂ nanotube arrays**

Transmitent photovoltage curves were obtained to estimate average electron lifetimes of the DSSCs with TNT and Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻², as shown in **Figure 7**. The average electron lifetimes could approximately be estimated by fitting a decay of the open circuit potential transient with exp (–t/τₑ), where t is time and τₑ is an average time constant before recombination. The τₑ values of 13.18, 24.41, 30.65, 38.77, and 46.69 ms are obtained for the photoanodes with TNT and Y–TNT obtained with the charge capacities of 10, 15, 20, and 25 mC cm⁻², respectively. The longer electron life time for the Y–TNT based DSSCs is due to the Y₂O₃ barrier layer to inhibit back transfer of electrons from TiO₂ to triiodide ions. Also, the increasing electron life time for the photoanode with thicker Y₂O₃ barrier layer again confirms that the charge recombination dynamics can be easily controlled by varying the charge capacity for electrodeposition Y(OH)₃ and be reduced with more amount of Y₂O₃ on TNT surface. The longer electron life times are in consistency with the higher Ψ Sc value of the corresponding cells.

**Conclusions**

TNT obtained on Ti foils exhibits a nearly constant diameter and increasing length for longer anodization periods. The V_OC value decreases while the J_SC value increases for the DSSC with longer anodization period to obtain TNT on the photoanode, due to the increasing longer electron diffusion path and larger surface area, but the J_SC value decreases for the anodization period reaches 300 min due to the serious recombination. Thin layers of Y(OH)₃ were electrodeposited on TNT and subsequently the films were annealed to obtain the Y₂O₃ barrier layers to reduce charge recombination. Higher V_OC values were found for the Y–TNT based DSSCs with compared to that of the cell with TNT, demonstrating the reduced recombination for the former cases with the help of Y₂O₃ barrier layers. Also, the V_OC value increases considerably with increasing amount of Y₂O₃ on TNT, indicating the charge recombination dynamics can be simply controlled by adjusting the charge capacity for Y(OH)₃ electrodeposition. The J_SC value increases with increasing charge capacity to deposit Y(OH)₃ up to 15 mC cm⁻², and decreases with further increases in the charge capacity, due to the more basic surface of Y₂O₃ for more dye adsorption but serious electron transfer inhibition for higher charge capacity. The best η of 6.52% was achieved for the Y–TNT based DSSC with a charge capacity of 15 mC cm⁻².
while the cell with TNT shows an $\eta$ of 5.35%. The tendency of $V_{OC}$ is in consistency with the dark current and the electron lifetime, while IPCE values shows the same trend with the $J_{SC}$ value for all the cells.

**Notes and references**

Table of content

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