Improved Energy Conversion Efficiency of Dye-sensitized Solar Cells Fabricated using Open-ended TiO\textsubscript{2} Nanotube Arrays with Scattering Layer

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We prepared dye-sensitized solar cells (DSSCs) with enhanced energy conversion efficiency using open-ended TiO\textsubscript{2} nanotube arrays. As compared to closed-ended TiO\textsubscript{2} nanotube arrays, the energy conversion efficiency of the open-ended TiO\textsubscript{2} nanotube arrays was increased from 5.63% to 5.92%, which is an enhancement of 5.15%. With the TiO\textsubscript{2} scattering layer, the energy conversion efficiency was increased from 5.92% to 6.53%, which is an enhancement of 10.30%. After treating the open-ended TiO\textsubscript{2} nanotube arrays with TiCl\textsubscript{4}, the energy conversion efficiency was increased from 6.53% to 6.89%, a 5.51% enhancement, which is attributed to improved light harvesting and increased dye adsorption.

Key Words: Dye-sensitized solar cells, Scattering layer, Open-ended TiO\textsubscript{2} nanotube arrays

Introduction

Dye-sensitized solar cells (DSSCs) have attracted immense interest due to their high energy conversion efficiency and low cost.\textsuperscript{1,5} However, the energy conversion efficiency of DSSCs still needs to be improved so that it compares favorably with conventional photovoltaic devices.\textsuperscript{6} There are several parameters that can be investigated, including the dimensionality of TiO\textsubscript{2} for electron transport,\textsuperscript{7,8} light-harvesting capability,\textsuperscript{9,10} molar absorption coefficient,\textsuperscript{11} energetically suitable HOMO-LUMO levels,\textsuperscript{12} available surface area for dyes,\textsuperscript{13} transport kinetics of the electrons,\textsuperscript{14} regeneration by a redox couple,\textsuperscript{15} and losses due to recombination and back reactions.\textsuperscript{16}

TiO\textsubscript{2} nanotubes can enhance electron transport and charge separation by creating direct pathways and accelerating the charge transfer between interfaces.\textsuperscript{17-23} These properties make them an attractive candidate for DSSC applications. TiO\textsubscript{2} nanotube arrays that are prepared by electrochemical anodization have a highly oriented and vertically aligned tubular structure.\textsuperscript{11,12} Thus, the arrays have a high degree of electron transport and minor charge recombination in comparison to TiO\textsubscript{2} nanoparticle films.\textsuperscript{23} Hence, although current DSSCs fabricated using TiO\textsubscript{2} nanotube arrays have a low energy conversion efficiency as compared to DSSCs fabricated using TiO\textsubscript{2} nanoparticle films, they have immense potential. Recently, we prepared DSSCs using open-ended TiO\textsubscript{2} nanotube arrays and demonstrated that nanotube arrays whose barrier layers were removed by ion milling have 24% higher energy conversion efficiency.\textsuperscript{24}

Introducing a scattering layer such as TiO\textsubscript{2}, ZrO\textsubscript{2}, or SiO\textsubscript{2} can increase the total energy conversion efficiency of DSSCs.\textsuperscript{25} TiO\textsubscript{2} is a good material to use for a scattering layer due to its chemical stability and dye adsorption capability; hence, several DSSCs fabricated using TiO\textsubscript{2} nanoparticle films use a TiO\textsubscript{2} scattering layer on the active layer.

To the best of our knowledge, TiO\textsubscript{2} nanotube arrays have not been combined with scattering layers. In this paper, we report the improved energy conversion efficiency of DSSCs using open-ended TiO\textsubscript{2} nanotube arrays with a TiO\textsubscript{2} scattering layer. In this study, we compared the energy conversion efficiency of 1) closed- and open-ended TiO\textsubscript{2} nanotube arrays 2) with and without a TiO\textsubscript{2} scattering layer. In addition, we compared the energy conversion efficiency of fabricated DSSCs treated with TiCl\textsubscript{4} to untreated DSSCs.

Experimental

TiO\textsubscript{2} nanotube arrays were fabricated by anodizing thin Ti plates (99.7% purity, 2.5 cm \texttimes 4.0 cm \texttimes 100 \textmu m) in an electrolyte composed of 0.8 wt\% NH\textsubscript{4}F and 2 vol\% H\textsubscript{2}O in ethylene glycol at 25 °C and at a constant applied voltage of 60 V DC for 2 h. The TiO\textsubscript{2} nanotube arrays were annealed at 450 °C for 1 h under ambient conditions to improve crystallinity. To detach the free-standing TiO\textsubscript{2} nanotube arrays from the Ti plate, secondary anodization were carried out at a constant applied voltage of 30 V DC for 10 min, and then the plate was immersed in 10% H\textsubscript{2}O\textsubscript{2} for 24 h. The bottom layer of the TiO\textsubscript{2} nanotube arrays was removed by ion milling with Ar\textsuperscript{+} bombardment for 90 min.\textsuperscript{27}

A TiO\textsubscript{2}: blocking layer was formed on fluorine-doped tin oxide (FTO) glass by spin-coating with 5 wt\% titanium diisopropoxide bis(acetylacetonate) in butanol and then by heating at 450 °C for 30 min under ambient conditions. A TiO\textsubscript{2} paste (from Solaronix) was printed onto the FTO glass using a doctor blade and the closed- and open-ended TiO\textsubscript{2} nanotube arrays were introduced on the paste. The substrate was then sintered at 450 °C for 1 h under ambient conditions.
The TiO$_2$ scattering layer (~400-nm-diameter particles) was coated onto the closed- and open-ended TiO$_2$ nanotube arrays using a doctor blade and sintered at 450 °C for 30 min under ambient conditions. The substrate was dipped in 0.01 M of TiCl$_4$ aqueous solution at 50 °C for 30 min and sintered at 450 °C for 1 h under ambient conditions.

Dye molecules [0.5 mM (Bu$_4$N)$_2$Ru(dobpyH)$_2$(NCS)$_2$ (N-719, Solaronix)] were attached by immersing the substrate in absolute ethanol at 50 °C for 8 h. The composition of the electrolyte was as follows: 0.7 M of 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M of I$_2$, 0.1 M of guanidium thiocyanate (GSCN), and 0.5 M of 4-tert-butyl pyridine (TBP) in a mixture of acetonitrile and valeronitrile (85:15 V/V). The counter electrode was prepared using a Pt solution on the FTO glass. The working electrode was further sandwiched between the Pt-coated FTO glass, separated by a 60-μm-thick hot-melt spacer.

The morphology and thickness of the free-standing TiO$_2$ nanotube arrays, which were TiO$_2$ nanotube arrays after detachment from the Ti plate, were analyzed using a field-emission scanning electron microscope (FE-SEM, JSM-6330F, JEOL Inc.). The current density–voltage ($J$–$V$) characteristics of the DSSCs were measured by using an electrometer (KEITHLEY 2400) under AM 1.5 illumination (100 mW/cm$^2$) provided by a solar simulator (1 kW xenon with AM 1.5 filter, PEC-L01, Peccell Technologies). The incident photon-to-current conversion efficiency (IPCE) was measured by using a K3100 spectral IPCE measurement system (McScience Inc.) with reference to the calibrated diode.

Results and Discussion

Figure 1 shows the fabrication flow of the DSSCs using the closed- and open-ended TiO$_2$ nanotube arrays with the TiO$_2$ scattering layer for improved energy conversion efficiency. After sintering at 450 °C for 1 h under ambient conditions, the TiO$_2$ nanotube arrays have a crystalline form similar to anatase. To separate the closed-ended TiO$_2$ nanotube arrays from the Ti plate, secondary anodization was performed with subsequent immersion in H$_2$O$_2$ solution. After several hours, the amorphous TiO$_2$, which was formed under the TiO$_2$ nanotube arrays, dissolved in the H$_2$O$_2$ solution resulting in the formation of closed-ended TiO$_2$ nanotube arrays.

SEM images of the side, top, and bottom of the free-standing TiO$_2$ nanotube arrays are shown in Figures 2(a), (b), and (c), respectively. The length of the free-standing TiO$_2$ nanotube arrays was approximately 18 μm, as shown in Figure 2(a). The upper pores were well ordered and their diameter was ca. 100 nm. The morphology of the bottom layer under the closed-ended TiO$_2$ nanotube array was very rough due to chemical etching with the H$_2$O$_2$ solution after secondary anodization, as shown in Figure 2(c). To prepare the open-ended TiO$_2$ nanotube arrays, the bottom layer of the closed-ended TiO$_2$ nanotube array was eliminated by ion milling to remove the barrier layer. Most of the bottom tips were opened after ion milling for 90 min and they had an approximate diameter of 20 nm, as shown in Figure 2(d). Figure 2(e) shows the closed- and open-ended TiO$_2$ nanotube arrays on FTO glass after attachment using a TiO$_2$ paste and sintering at 450 °C for 1 h under ambient conditions.
DSSC using Open-ended TiO₂ Nanotube with Scattering Layer

Table 1. Photovoltaic properties of DSSCs fabricated using the closed-ended TiO₂ nanotube arrays

<table>
<thead>
<tr>
<th></th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed-ended TiO₂ nanotube arrays</td>
<td>9.44</td>
<td>0.82</td>
<td>0.73</td>
<td>5.63 ± 0.14</td>
</tr>
<tr>
<td>Closed-ended TiO₂ nanotube arrays with TiO₂ scattering layer</td>
<td>10.24</td>
<td>0.81</td>
<td>0.74</td>
<td>6.17 ± 0.18</td>
</tr>
<tr>
<td>Closed-ended TiO₂ nanotube arrays with TiO₂ scattering layer treated with TiCl₄</td>
<td>10.96</td>
<td>0.81</td>
<td>0.74</td>
<td>6.54 ± 0.20</td>
</tr>
</tbody>
</table>

Table 2. Photovoltaic properties of DSSCs fabricated using the open-ended TiO₂ nanotube arrays

<table>
<thead>
<tr>
<th></th>
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<td>6.89 ± 0.16</td>
</tr>
</tbody>
</table>

The TiO₂ scattering layer was coated onto the closed- and open-ended TiO₂ nanotube arrays using a doctor blade and then the dye (N719) was adsorbed. DSSCs were fabricated by assembling the working electrode (the closed- and open-ended TiO₂ nanotube arrays with TiO₂ scattering layer) and the counter electrode (Pt).

Figure 3 presents the current density–voltage curves of three different DSSCs fabricated using the closed-ended TiO₂ nanotube arrays attached to the FTO glass using TiO₂ paste. The measurements were taken using AM 1.5-simulated sunlight. The values of the open-circuit voltage (V_oc), short-circuit current (J_sc), fill factor (ff), and energy conversion efficiency (η) are summarized in Table 1. For the DSSC fabricated using just the closed-ended TiO₂ nanotube arrays, the energy conversion efficiency was 5.63 ± 0.14%. For the DSSC fabricated using the closed-ended TiO₂ nanotube arrays and the TiO₂ scattering layer, the energy conversion efficiency was 6.17 ± 0.18%. By introducing the TiO₂ scattering layer on the closed-ended TiO₂ nanotube arrays, the energy conversion efficiency improved significantly, with a 9.59% enhancement. When the closed-ended TiO₂ nanotube arrays with the TiO₂ scattering layer were treated with TiCl₄, the energy conversion efficiency increased from 5.63 ± 0.14% to 6.54 ± 0.20%, corresponding to a 16.2% enhancement due to increasing dye adsorption on the surface of the TiO₂ nanotube arrays. By introducing the TiO₂ scattering layer on the closed-ended TiO₂ nanotube arrays, the energy conversion efficiency was improved due to increased light harvesting by the scattering layer.

Figure 4 presents the current density–voltage curves of three different DSSCs fabricated using the open-ended TiO₂ nanotube arrays attached to the FTO glass using TiO₂ paste. The values of V_oc, J_sc, ff, and η are summarized in Table 2. For the DSSC fabricated using just the open-ended TiO₂ nanotube arrays, the energy conversion efficiency was 5.92 ± 0.19%. For the DSSC fabricated using the open-ended TiO₂ nanotube arrays with the TiO₂ scattering layer, the energy conversion efficiency was 6.53 ± 0.13%, a 10.30% enhancement. When the open-ended TiO₂ nanotube arrays with the TiO₂ scattering layer were treated with TiCl₄, the energy conversion efficiency improved from 6.53 ± 0.13% to 6.89 ± 0.16%, corresponding to a 5.51% enhancement.

The energy conversion efficiency increased from 5.63 ± 0.14% for the DSSCs with the closed-ended TiO₂ nanotube arrays to 5.92 ± 0.19% for the DSSCs with open-ended TiO₂ nanotube arrays, a 5.15% enhancement. With the introdu-
tion of the scattering layer, the efficiency increased from 6.17 ± 0.18% for the DSSCs with the closed-ended TiO$_2$ nanotube arrays to 6.53 ± 0.13% for the DSSCs with open-ended TiO$_2$ nanotube arrays, an improvement of 5.83%. Upon treatment with TiCl$_4$, the enhancement was 5.35%, from 6.54 ± 0.20% for the DSSCs with the closed-ended TiO$_2$ nanotube arrays to 6.89 ± 0.16% for the DSSCs with open-ended TiO$_2$ nanotube arrays. In previous our works, the barrier layer in the closed-ended TiO$_2$ nanotube arrays affected the electron transport in the DSSCs, so the barrier layer was removed by ion milling in order to prepare the open-ended TiO$_2$ nanotube arrays.

The IPCE spectra of the DSSCs fabricated using the open-ended TiO$_2$ nanotube arrays and open-ended TiO$_2$ nanotube arrays with the TiO$_2$ scattering layer are shown in Figure 5. The IPCE spectra are similar but the DSSC with the TiO$_2$ scattering layer had a higher intensity.

**Conclusion**

In conclusion, we fabricated DSSCs using closed- and open-ended TiO$_2$ nanotube arrays and introduced a TiO$_2$ scattering layer. The energy conversion efficiency was enhanced by 5.15% due to the removal of the barrier layer, which was present in the closed-ended TiO$_2$ nanotube arrays, causing an improvement in electron transport. By introducing the TiO$_2$ scattering layer on the open-ended TiO$_2$ nanotube arrays, the energy conversion efficiency was enhanced by 10.30% due to improved light harvesting. Additionally, the energy conversion efficiency of the open-ended TiO$_2$ nanotube arrays treated with TiCl$_4$ was enhanced by 5.51% due to increased dye adsorption.

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**References**