Effect of TiOx compact layer with varied components on the performance of dye-sensitized solar cells

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A B S T R A C T
In this study, approximately 20 nm thick compact layers of TiOx with varied components are deposited by physical vapor deposition. The performance of these layers in solar cells is investigated. The TiOx compact layers consist of T1 (with Ti4+, Ti3+, and Ti2+), T2 (with Ti3+ and Ti4+), and T3 (with Ti4+). Results show that the optimum compact layer is T1, which exhibits an approximately 61% enhancement in energy conversion efficiency compared with the bare cell. Mott–Schottky plots indicate that the carrier concentration decreases and the flatband becomes less negative with decreasing x, which consequently increases the likelihood of charge transfer from the nanoporous TiO2 to the TiOx compact layers. Furthermore, a decrease in the x value of TiOx results in lower resistance. Voltage decay and electrical impedance spectrum (EIS) show that the electron-carrier lifetime and charge recombination reduction are improved the most by T1. Consequently, TiOx with smaller x works better as a compact layer. However, a solar cell with T2 shows weak enhancement of photovoltaic performance. Cyclic voltammetry and EIS illustrate that the low recombination blocking and high resistance of T2 may be a result of its large pore size and weak adhesion to fluorine-doped tin oxide glass.

1. Introduction
Over the past two decades, research on dye-sensitized solar cells (DSSC) has progressed [1,2]. Compared with the conventional p–n junction solar cell, DSSC has numerous advantages, such as reduced costs and simple fabrication procedures [3–6], particularly for building flexible devices. However, DSSC is also characterized by several limitations, such as the relatively narrow band of optical absorption in the effective dyes, poor stability, and the loss of photo-generated electrons. Charge recombination between the conductive substrate and the electrolyte or p-type transporting material is believed to be one of the main processes that result in electron loss [7,8]. This recombination process reduces the quantity and energy of electrons flowing out of the device under working conditions and therefore decreases the energy conversion efficiency.

A widely used and effective method of reducing recombination is the application of a compact layer between the conductive fluoroine-doped tin oxide (FTO) glass and the nanoporous film. The compact layer in DSSCs is generally composed of a dense TiO2 particle. The methods widely used in the fabrication of this particle include spray pyrolysis [9], hydrolysis [10,11], spin-coating [12], and sputtering deposition [13–16]. Among these methods, sputtering deposition is the most suitable for fabricating high-quality and fine compact layers, particularly for forming a uniform and fine layer for a large area at a relatively low temperature.

Most previous studies proposed the fabrication of the compact layer by Ti sputtering deposition and oxidization. Thus, the TiO2 compact layer prepared through the direct sputtering of the Ti target under an Ar/O2 atmosphere was introduced. The ratio of Ar/O2 is of great significance in the procedure as the resulting component is complicated and the optimization is very difficult [17]. Furthermore, some researchers employed the later-on oxidization on the sputtered film [18] or directly sputtered the TiO2 target under an Ar atmosphere [15,19]. Interestingly, Xia et al. found that the compact layer of TiOx with Ti3+, Ti2+, and Ti4+ made from the direct sputtering of Ti target under an Ar atmosphere effectively improved cell performance [14]. However, most recent studies focused on the optimization of the thickness and the depositing rate of the compact layers. No research has compared the performance of the TiOx compact layers with various x values, although such materials are ubiquitous in the compact layers applied in DSSCs. For example, the most widely used method, spray pyrolysis, also compels studies to confront this question as its oxidization process is not always sufficient and the ratio of Ti and O is difficult to control. Thus, understanding the effect of x values on TiOx compact layers is important.

In this work, the compact layer of titanium oxide with different components is called TiOx, where x changes along with the...
fabricating materials and atmospheres. To understand the effect of the TiOx compact layer produced by sputtering deposition, we fabricated approximately 20 nm thick TiOx compact layers with three different values of x by physical vapor deposition (PVD). These compact layers showed different functions in solar cells. The methods of Mott–Schottky plot, voltage decay, electrical impedance spectrum (EIS), and others were utilized to explore the possible reasons for the differences. An effective procedure for fabricating a compact layer using the PVD method was also formulated.

2. Experimental section

PVD was used to sputter the Ti and TiO2 targets under a gaseous atmosphere to fabricate a compact layer on FTO glass. Both Ti and TiO2 targets were 99.9% pure and had a round shape with a diameter of 76 mm. Nano-films with different thicknesses and components were deposited under a working pressure of 1.2 Pa at room temperature. The total gas flow was 50 sccm of pure Ar or mixed O2/Ar. The modified substrates were calcined at 450 °C for 2 h under ambient air. The construction details and resultant components of the TiOx compact layers are shown in Table 1. The thickness of the compact layers was measured using a Dektak 150 profilometer. Thickness about 20 nm was selected due to its relative good working functions in the DSSCs compared to other film thicknesses (Fig. S1, Supporting information).

A nanoporous TiO2 electrode was prepared by the application of doctor-blading on the bare FTO glass or compact layer modified substrates from colloidal P25 paste, which was made using the procedures proposed by Ito et al. [21]. After annealing the electrode in air at 450 °C for 30 min, its resulting thickness was 4.8 μm. The TiO2 electrodes were then immersed in 0.3 mM N719 (Ru(II)C2O4/2H2O) in acetonitrile/tert-butyl alcohol 50/50 (v/v) overnight at room temperature. A counter electrode was prepared by depositing 5 mM PtCl64– in isopropanol on FTO glass. The counter electrode was annealed at 400 °C for 30 min. The typical area of the electrode was 0.49 cm2. The liquid electrolyte for the DSSCs was composed of 0.5 M tert–4-butyllpyridine, 0.05 M LiI, 0.1 M LiI, and 0.7 M tert–butyl ammonium iodide in acetonitrile.

The optical transmittance measurements were conducted using UV-2450 (Shimadzu) at wavelengths ranging from 300 nm to 800 nm. The photocurrent–voltage characteristics were measured using a potentiostat (CH650C) by irradiating with simulated solar light (CEL-S500/350), that is, AM 1.5, 63 mW cm−2. The light density was monitored using a CEL-NP2000 full-spectrum light power meter and further verified by a standard DSSC sample. A light density of 63 mW cm−2 was used as certain study [22] proposed that a compact layer affects the DSSC performance more at low light densities. The cyclic voltammetric (C–V) curves and Mott–Schottky plots were obtained through another potentiostat (Galvanostat Model 273A) in 2 mM 1:1 potassium ferricyanide/potassium ferrocyanide aqueous solution with 137 mM KCl as the supporting electrolyte. In this work, the compact layer modified FTO glass, platinum plate, and Hg/HgCl2 were utilized as the working, counter, and reference electrodes, respectively. In addition, the EIS and open–circuit voltage decay of the solar cells were obtained using the potentiostat (CH650C). The EIS was measured in the dark with a frequency range of 0.1–10 kHz. The applied ac amplitude was set at 5 mV between the Pt counter electrode and the TiO2 working electrode. The voltage decay was detected by switching the light from on to off.

3. Results and discussion

3.1. Properties of the TiOx compact layer modified substrates

3.1.1. Optical properties

Fig. 1 shows the optical transmittance of the different substrates with or without compact layers as a function of wavelength from 300 nm to 800 nm. Compared with bare FTO glass, the T1 compact layer modified substrate slightly decreases the transmittance. By contrast, the T2 and T3 modified substrates show a transmittance that is lower by 4–5%. A substrate with a higher transmittance enables the absorption of more light by the dye molecules, along with the generation of more electrons. In addition, T3 red-shifts the curve the most, followed by T2 and T1. The red-shift is possibly a result of the penetration of the compact layers into the FTO glass [14].

3.1.2. Electrochemical characterization

The C–V curves of Fe(CN)63–/Fe(CN)64– redox couple reaction with the different substrates are shown in Fig. 2. The bare FTO glass shows a large current within the whole range of −0.5 V to +0.8 V. The current is almost completely suppressed by the TiOx compact layers, suggesting that the compact layer covers the surface of the FTO glass well. This finding was also verified through scanning electronic microscopy (SEM) (Fig. S3, Supporting information). More than T2, both T1 and T3 block the current at roughly the same thickness of approximately 20 nm.

3.2. Cell performance

The compact layer of TiOx blocked the current at FTO/electrolyte interface efficiently. DSSCs based on these compact layers show an impressively large improvement compared with non–compact-layer DSSC in terms of increased Jsc, Voc, and energy conversion efficiency (Fig. 3). Table 2 summarizes the photovoltaic properties of the cells. The error bar in this paper was calculated from the standard deviation of the two samples prepared for each case. The DSSC with the compact layer of T1 shows the highest Jsc, fill factor (FF), and relatively high Voc, resulting in the highest increase in power conversion efficiency at approximately 61%. DSSCs with these three compact layers do not show a significant difference in Voc except for the T2 cell, which shows a slightly lower Voc. However, the Voc values of all the cells are still higher than those of cells without a compact layer by approximately 60 mV. The T2 cell has a significantly lower fill factor than the T1 and T3 cells. The T1 cell exhibits the largest fill factor. Additionally, in our experiment, it was found that the energy conversion efficiency

![Fig. 1. Optical transmittance of the substrates with and without compact layers.](image)

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target</th>
<th>Power (W)</th>
<th>O2 (sccm)</th>
<th>Ar (sccm)</th>
<th>Thickness (nm)</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Ti</td>
<td>74</td>
<td>0</td>
<td>50</td>
<td>20 ± 5</td>
<td>Ti2+; Ti3+; Ti4+</td>
</tr>
<tr>
<td>T2</td>
<td>Ti</td>
<td>135</td>
<td>2</td>
<td>48</td>
<td>21 ± 5</td>
<td>Ti4+; Ti4+ (0.55:0.45)</td>
</tr>
<tr>
<td>T3</td>
<td>TiO2</td>
<td>100</td>
<td>0</td>
<td>50</td>
<td>27 ± 5</td>
<td>Ti4+</td>
</tr>
</tbody>
</table>

T1 components were adopted from those illustrated by Xia et al., and after being annealed at 450 °C, Ti4+ would disappear [14]; T2 was determined by X-ray photoelectron spectroscopy measurement (Fig. S2, Supporting information); and T3 was deposited by sputtering the TiO2 target, the component of which is TiO2 [20].
molecular orbital of the dye molecular and the conduction band of TiO$_2$. And the $\eta_{REC}$ is determined by the process that dye-molecules being regenerated by the $I_3^-$ in electrolyte. For all the solar cells, the $\eta_{INJ}$ and $\eta_{REC}$ should be the same because the only difference lies in the compact layers. Furthermore, if more dye molecules are excited by an increase in the penetrating light, the $J_{sc}$ may be higher. It is noteworthy that 4–5% more light penetrated the T1 compact layer. However, the corresponding solar cell shows a $J_{sc}$ that is better by approximately 10% and 18.5% than the T3 and T2 cells, respectively. Thus, the photo flux is not the only factor affecting the enhancement of $J_{sc}$. The collection efficiency should be considered as another main determinant. We know that $\eta_{COL}$ is related to the competition between charge transfer and charge recombination, $\eta_{COL} \propto Kt/(Kt + Kr)$, where $Kt$ and $Kr$ are the rate constants for transport and recombination, respectively [24]. The difference between $Kt$ and $Kr$ also influences the open-circuit voltage and fill factor of the solar cells. The performance of the charge transfer and recombination and their impact factor are discussed in the next section.

3.3. Voltage decay

To understand the charge recombination of solar cells with different compact layers, the open-circuit voltage decay measurement was introduced. During the measurement, although the light densities were not the same because of the slightly different transmittance of the compact layers, the decay performance did not significantly change, as Zaban et al. [25] showed in their experiment. The decay and the related electron response time are shown in Fig. 4. The electron response time ($\tau$) was calculated by [25]:

$$\tau = -\frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

where $k_B$, $e$, and $T$ are the Boltzmann constant, electron charge, and temperature, respectively. The T1 solar cell reveals the slowest voltage decay and the largest response time in the whole voltage range of 0.45–0.75 V. The rate of the voltage decay corresponds to the charge recombination rate. Slower voltage decay implies a lower recombination rate. Thus, the charge recombination of the solar cells is $T1 < T3 < T2$. These results agree well with those of the dark currents shown in Fig. 3. Furthermore, these results explain the lower fill factor of the T2 cell.

Bisquert et al. [26] showed that the response time in the range of 0.6–0.75 V correlates with the electron from the conduction band of the nanoporous TiO$_2$, which indicates that the response time in this range can be estimated as the electron lifetime of the solar cells. Fig. 4(b) shows that the electron lifetime of the solar cells with three different compact layers is $T1 > T3 > T2$.

3.3.2. EIS

The only difference in the structure of the solar cells is the compact layer. Different recombination processes must be related to the distinctive compact layers. The properties of these layers can be identified in the EIS. As Fabregat–Santiago et al. [27, 28] proposed, the compact layer works like an insulator at a low-voltage region. This finding implies that the main recombination process occurs at the FTO/electrolyte interface when the voltage is low. The bode-phase plots of DSSCs at low voltages of 0.4 and 0.5 V are shown in Fig. 5. For all the cells with compact layers, the lower region of the peak frequency is presented, which demonstrates that the recombination is suppressed by the TiO$_2$ layer at the interface of FTO/electrolyte. The peak frequency is shifted to the lowest region by the T1 and T3 layers, followed by the T2 layer. This finding suggests that the T1 and T3 layers effectively block recombination, whereas the T2 layer does not reduce recombination as well. The measured cyclic voltammetry in Fig. 2 shows the same result.

![Fig. 2. Cyclic voltammograms of substrates with or without compact layer measured in 0.5 mM 1:1 K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ aqueous solution at a scan rate of 0.05 V s$^{-1}$.](image)

![Fig. 3. Photocurrent–voltage (J–V) curves of DSSCs with and without TiO$_x$ compact layer.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>Efficiency ($\eta$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare FTO glass</td>
<td>4.01 ± 0.04</td>
<td>687 ± 4</td>
<td>0.681 ± 0.005</td>
<td>3.13 ± 0.05</td>
</tr>
<tr>
<td>20 nm T1</td>
<td>6.04 ± 0.09</td>
<td>756 ± 10</td>
<td>0.702 ± 0.006</td>
<td>5.05 ± 0.19</td>
</tr>
<tr>
<td>21 nm T2</td>
<td>5.14 ± 0.03</td>
<td>749 ± 6</td>
<td>0.654 ± 0.028</td>
<td>3.99 ± 0.16</td>
</tr>
<tr>
<td>27 nm T3</td>
<td>5.52 ± 0.04</td>
<td>757 ± 11</td>
<td>0.692 ± 0.009</td>
<td>4.56 ± 0.08</td>
</tr>
</tbody>
</table>

The short-circuit current ($J_{sc}$) of the solar cells under the light with a wavelength range of $\lambda 1$ to $\lambda 2$ and spectral photon flux of $\phi(\lambda)$ can be expressed as [23]:

$$J_{sc} = q \int_{\lambda 1}^{\lambda 2} \phi(\lambda) \eta_{INJ}(\lambda) \eta_{REC}(\lambda) \eta_{COL}(\lambda) d\lambda$$

where $\eta_{INJ}$ is the electron injection efficiency, $\eta_{REC}$ is the dye regeneration efficiency, and $\eta_{COL}$ is the electron collection efficiency. The $\eta_{INJ}$ is related to the energy gap between the lowest unoccupied

![Table 2: Properties of all the DSSCs including short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and power conversion efficiency ($\eta$) measured at AM 1.5, with a light density of 63 mW cm$^{-2}$.](table)
This phenomenon can be explained by the pore size of the T2 film, which is larger than that of the T1 and T3 films. The larger pore size enables more electrolytes to penetrate the film and recombine with the electrons in the FTO glass or compact layer. The larger pore size of the film may be a result of the fabricating procedure. Depositing a TiO$\text{x}$ compact layer by sputtering the titanium target using a mixture of O$_2$/Ar gas introduces an additional kinetic reaction between the titanium atom and the oxygen, resulting in a slower deposition rate, which in turn forms larger particles and decreases the contact and adhesion between the TiO$\text{x}$ film and the FTO glass.

EIS measurements at the open-circuit voltage provide more details of the charge transport of the solar cells. Fig. 6 shows the Nyquist plots of the EIS. Table 3 summarizes the resistance of the cells at open-circuit voltage from Fig. 6. The series resistance, $R_s$, expresses the charge transport through the complete cells, which is primarily associated with the charge transfer capability of the compact layer and their contact with or adhesion to the FTO glass [29]. The T1 cell shows the lowest $R_s$, which in turn suggests that T1 facilitates the fastest transport of the electrons. This result is consistent with Bally’s findings that electrical resistivity decreases rapidly with decreasing oxygen concentration in TiO$\text{x}$ [30]. Nevertheless, T2 shows a larger $R_s$ than T3. This result may be attributed to the larger pore size of T2, which decreases the interconnections among TiO$\text{x}$ particles and impedes the charge transport across the particles. The charge transfer resistance in the second semicircle of the lower frequency, $R_{\text{second semicircle}}$, is related to the resistance $R_{\text{FTO-TiO}_2} + R_{\text{FTO}}$. The value of $R_{\text{second semicircle}}$ represents the charge transfer resistance of $R_{\text{FTO-TiO}_2}$ because $R_{\text{TiO}_2}$ is kept constant in all cells [28,31]. T3 shows the largest $R_{\text{second semicircle}}$, followed by T2 and T1, which implies that the electron transfer from the nanoporous TiO$_2$ to the modified substrate is T1 > T2 > T3.

In this system, the charge transport capability of the compact layer and the charge transfer from the nanoporous to the substrate are the two main factors that determine the charge transport rate, $K_t$. We suggest that the charge transfer from the nanoporous TiO$_2$
Table 3

Summary of the resistance measured at open-circuit voltage by EIS: $R_s$ is the series resistance and $R_{\text{second semicircle}}$ is the resistance from the second semicircle in impedance analysis.

<table>
<thead>
<tr>
<th></th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>10.9</td>
<td>15.1</td>
<td>13.2</td>
</tr>
<tr>
<td>$R_{\text{second semicircle}}$</td>
<td>49.9</td>
<td>52.7</td>
<td>58.1</td>
</tr>
</tbody>
</table>

4. Conclusions

The performance of TiO$_2$ compact layers with varied components made by sputtering deposition was investigated. The best compact layer is T1 with the smallest $x$, which showed an approximately 61% increase in energy conversion efficiency compared with the bare cell. The TiO$_2$ compact layer with smaller $x$ shows a lower surface carrier concentration, more positive flatband, and reduced resistance, resulting in better charge transfer and less charge recombination in the corresponding solar cells. Furthermore, the transmittance is decreased less by the TiO$_2$ film with a smaller $x$ value. As a result, the recombination at the FTO/electrolyte interface is blocked more effectively, leading to a longer electron-carrier lifetime. Meanwhile, the photocurrent significantly increases with the enhanced energy conversion efficiency. This study facilitates understanding of the effects of the TiO$_2$ compact layer made through PVD, spray pyrolysis, and other commonly used methods. The suggestions in this work should also help produce more effective compact layers.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2013.12.013.

References
