Collection Efficiency Enhancement of Injected Electrons in Dye-sensitized Solar Cells with a Ti Interfacial Layer and TiCl$_4$ Treatment

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This study attempts to enhance the performance of dye-sensitized solar cells (DSSCs) by integrating TiCl$_4$ treatment on porous TiO$_2$ and the Ti-deposited thin film metal on FTO. The electron conductance of the interface between the FTO glass and the electron transport on the porous TiO$_2$ film can be improved by sputtering the Ti interfacial layer. The modified DSSCs achieve significantly better short-circuit photocurrent density ($J_{sc}$), approximately 42% greater than that of the standard cell. This ultimately produces a 6.13% energy conversion efficiency ($\eta$), which is approximately 33% higher than that of a standard cell. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the modified DSSCs show a higher value than that of a standard cell, especially in the higher wavelength range.

Keywords: Dye-sensitized solar cell, TiCl$_4$ treatment, counter electrode, collection efficiency, excited electron

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) [1] are promising alternatives to silicon-based solar cells [2] because of their environmental friendliness, low manufacturing costs, and flexibility. Researchers have recently devoted considerable efforts to increasing the light harvesting efficiency (LHE) of photoelectrodes to achieve high photovoltaic performance.

Increasing the absorption path length of photons by light scattering is a conventional means of improving LHE [3-13]. Adding large particles as scattering layers improves absorption [8]. Light scattering can be enhanced by multilayer cells, which consist of TiO$_2$ particles of various sizes [10]. Previous research has also discussed mixing TiO$_2$ particles with TiO$_2$-Rutile and ZrO$_2$ as scattering
layers [12].

Another way to improve LHE is to improve the collection efficiency of the injected electrons using FTO. The electrical conductance and the surface connection of the porous TiO$_2$ photoelectrode [14,15] is likely the key subject. A well-known method is to use a thin TiO$_2$ film or metal thin film as the blocking layer to improve the interfacial conductance between the FTO glass and the porous TiO$_2$ film, preventing the back reaction of electrons with tri-iodide ions in the electrolyte and oxidized dye [16]. Sputtering titanium (Ti) thin film on the FTO glass to form a blocking layer can prevent the reverse reaction [17]. Non-noble metal grids of Ni, Cu, and Al can also be used to enhance the interfacial conductance [18]. Other researchers have reported depositing fine TiO$_2$ membranes by spray pyrolysis [19], and dense TiO$_2$ thin-film formed by chemical vapor deposition [20].

This study proposes the integration of a sputtered Ti interfacial layer method and TiCl$_4$ treatment on DSSCs. According to previous studies, TiCl$_4$ treatment enhances the connection between TiO$_2$ particles [21], increases the diameter of TiO$_2$ particles [22,23], and even improves the dye loading [22]. The interfacial layer should also consider the contact resistance, the work function match, and the transmittance. This study uses a 10 nm titanium metal film deposited on FTO, which has a work function of 4.33 eV titanium, to improve the electron conductance of the interface between the FTO glass and the porous TiO$_2$, and increase the electron transport on the porous TiO$_2$ film.

2. EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the modified DSSCs with a Ti interfacial layer over FTO and the TiCl$_4$ treatment on the photoelectrode. The Ti thin film was deposited by DC sputtering using Ti targets on FTO glass. The Ar flow and power were kept constant at 24 sccm and 150 W, respectively. The deposition thickness was 10 nm.

![Figure 1. Schematic of modified DSSCs with sputtered Ti thin film over FTO and TiCl$_4$ treatment on the photoelectrode.](image-url)
Colloidal TiO₂ paste was prepared using Degussa P25 powder mixed Triton X-100, acetylacetone, polyethylene glycol, and DI-water. The paste was spread on the FTO glass. After drying in an oven at 120 °C, the electrode was sintered for 30 min at 450 °C in air. The resulting film thickness was 12 μm, and the effective area was 0.25 cm². TiCl₄ treatment was then applied to the prepared TiO₂ films. The sintered TiO₂ films were dipped in an aqueous solution of 50 mM TiCl₄ at 70 °C for 30 min, and sintered again for 30 min at 450 °C. The sintered TiO₂ electrode was then immersed for 24 h in a 3×10⁻⁴ M ethanol solution of the dye, N719.

The counter electrode was prepared on a bare FTO substrate. The Pt precursor was prepared by H₂PtCl₆, and spread on the front side of the FTO glass. The electrolyte consisted of 0.1 M LiI, 0.03 M I₂, and 0.5M 4-tert-butylypyridine in 3-methoxypropionitrile.

3. RESULTS AND DISCUSSION

Figure 2 shows the current density-voltage (J-V) characteristics of the DSSCs of the FTO and FTO/Ti substrate, and with TiCl₄ treatment on the photoelectrode. These results were measured under 100 mW/cm² irradiation by a solar simulator. Table 1 presents a summary of the important photovoltaic characteristics and parameters. The average characteristic values, including the short-circuit photocurrent density (J_sc), open-circuit voltage (V_oc), and fill factor (FF) of the FTO standard cell are 9.37 mA/cm², 0.73 V, and 0.66, corresponding to a conversion efficiency of 4.61%. After the Ti thin film was deposited on the FTO substrate, the device exhibited a great improvement conversion efficiency of 5.31%, which is approximately 15% higher than a standard cell. The average photovoltaic characteristic of J_sc, V_oc, and FF for the TiCl₄-treated DSSCs are 11.54 mA/cm², 0.73 V, and 0.63, respectively. The TiCl₄ treatment was also applied to a DSSC based on FTO/Ti substrate, achieving a higher short-circuit photocurrent density of 13.28%. Finally, the DSSC with TiCl₄ treatment and the Ti interfacial layer shows a 6.13% has higher energy conversion efficiency.
Table I  Photovoltaic parameters of the DSSCs of FTO and FTO/Ti substrate, and with TiCl₄ treatment on the photoelectrode.

<table>
<thead>
<tr>
<th></th>
<th>η(%)</th>
<th>FF</th>
<th>J(sc)(mA/cm²)</th>
<th>Voc(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO STD Cell</td>
<td>4.61(±0.10)</td>
<td>0.66</td>
<td>9.37(±0.11)</td>
<td>0.73</td>
</tr>
<tr>
<td>FTO/Ti Cell</td>
<td>5.31(±0.08)</td>
<td>0.63</td>
<td>11.54(±0.13)</td>
<td>0.73</td>
</tr>
<tr>
<td>FTO Cell (TiCl₄)</td>
<td>5.59(±0.15)</td>
<td>0.60</td>
<td>13.02(±0.46)</td>
<td>0.72</td>
</tr>
<tr>
<td>FTO/Ti Cell (TiCl₄)</td>
<td>6.13(±0.02)</td>
<td>0.61</td>
<td>13.28(±0.15)</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Figure 3 shows the scanning electron microscope (SEM) surface morphologies of porous TiO$_2$ films with and without TiCl$_4$ treatment. Figure 3(a) shows that the untreated TiO$_2$ has particle diameters of approximately 25 nm. After TiCl$_4$ treatment, the TiO$_2$ particles increased in diameter (Fig. 3(b)). For the enlarged area of the surface morphology of the treated porous TiO$_2$, the maximum diameter was approximately 250 nm. Moreover, the formation of large particles ensured greater light harvesting in the photoelectrode because of light scattering.

Figure 3. SEM photographs of (a) standard porous TiO$_2$ films, (b) with TiCl$_4$ treatment.

Figure 4 presents the XPS analysis of the FTO/Ti substrate after it was sintered for 30 min at 450 °C in air. Figure 4(a) shows the curve-fitted XPS spectra of the Ti 2p regions: only the Ti$^{4+}$ (464.7 and 459.0 eV) signal is observable. Figure 4(b) shows the O 1s feature, which consists of two peaks. The strongest peak appears at 530.3 eV, and corresponds to the oxygen in O$^{2-}$. The second peak appears at 532 eV, and corresponds to the oxygen in OH$^-$ groups. Curve fitting shows that the O$^{2-}$ account for the majority of the O species. Figures 4(a) and 4(b) demonstrate the presence of Ti$^{4+}$ and O$^{2-}$, and confirm that the sintered FTO/Ti forms TiO$_2$ on the FTO substrate.
Figure 4. XPS spectra and curve fits of (a) Ti 2p and (b) O 1s of Ti on FTO/Ti after sintering.

Figure 5. XRD patterns of Si wafer/Ti substrate before and after sintering at 450 °C
Figure 5 shows the XRD analysis of the Ti-sputtered wafer after it was sintered for 30 min at 450 °C in air. Because it is difficult to detect a new phase on the FTO substrate with XRD technology, the XRD analysis was measured on the Ti-sputtered wafer. The results show two peaks, the signal 26.01 eV and the signal 38.00 eV, which are in the range of the TiO$_2$ rutile form and the TiO$_2$ anatase form. This means that after 450 °C sintering, the Ti thin film was transformed into semiconductor oxide (TiO$_2$) with a form between that of the rutile and anatase forms. It would be a dense TiO$_2$ film to compare with the porous TiO$_2$ film, and it is suitable as a blocking layer to help electrons transport smoothly.

Figure 6 shows the energy-band diagrams of a structure with an FTO electrode, a dense TiO$_2$ layer, and a porous TiO$_2$ electrode structure (FTO/BL-TiO$_2$/TiO$_2$). The work function ($\phi$) of FTO is 4.4 eV [24]. The electron affinity ($\chi$) and work function of the porous anatase n-type semiconductor TiO$_2$ are 4.1 eV and 4.2 eV, respectively [25,26]. The dense TiO$_2$ layer is between the anatase and the rutile form, and the electron affinity of the dense TiO$_2$ layer is a little higher than the anatase structure porous TiO$_2$ of 4.1 eV, but lower than the rutile form TiO$_2$. Thus, this dense TiO$_2$ layer forms a proper conduction band offset. These results show that the excited electrons can transport from the porous TiO$_2$ to the FTO substrate smoothly because of the work function match of the dense TiO$_2$ layer. This work likes an electron blocking layer (BL), and can also prevent the electrons from reacting with the electrolyte and excited dye. Therefore, Ti-deposited DSSC has a higher $J_{sc}$ and efficiency than the standard cell.

![Energy-band diagrams of FTO/Dense-TiO$_2$/TiO$_2$/Dye.](image)

**Figure 6.** Energy-band diagrams of FTO/Dense-TiO$_2$/TiO$_2$/Dye.
Figure 7 shows the impedance spectra of DSSCs with and without TiCl$_4$ treatment in the complex plane. $Z_1$ and $Z_2$ are the impedances related to charge-transfer processes at the surface of the CE and at the TiO$_2$/dye/electrolyte interface, respectively. The resistances of each impedance ($Z_1$ and $Z_2$) for the standard DSSC are 11.7 and 28.7 Ωcm$^2$, and the resistances related to each impedance ($Z_1$ and $Z_2$) of the TiCl$_4$-treated DSSC are 11.6 and 27.7 Ωcm$^2$, respectively. After TiCl$_4$ treatment, the impedance in the second semi-circle ($Z_2$) decreases apparently. The TiCl$_4$ treatment can enhance the connection of TiO$_2$ particles, enhancing the charge transportation through the TiO$_2$ electrode.

![Impedance Spectra](image)

**Figure 7.** Electrochemical impedance spectra of DSSC with and without TiCl$_4$ treatment under illumination.

![IPCE Spectra](image)

**Figure 8.** IPCE spectra for the DSSCs of FTO and FTO/Ti substrate, and with TiCl$_4$ treatment on the photoelectrode.
Figure 8 shows the IPCE spectra for the DSSCs of FTO and FTO/Ti substrates and with TiCl$_4$ treatment on the photoelectrode. After the Ti interfacial layer was deposited on the FTO substrate, the cells raise the IPCE compared to the IPCE of FTO-based cells in the whole wavelength. Similarly, the TiCl$_4$-treated cells also raise the IPCE curve compared to the IPCE of untreated cells. Because the Ti interfacial layer and the TiCl$_4$ treatment technologies were both integrated using in the DSSC, the IPCE curve presents the highest value in the whole wavelength.

Generally, $J_{sc}$ can be expressed using the following equation [10];

$$J_{sc} = \int q \cdot F(\lambda) \cdot [1 - r(\lambda)] \cdot IPCE(\lambda) \, d\lambda$$  

(1)

where $q$ denotes the electron charge, $F(\lambda)$ denotes the incident photon flux density at wavelength $\lambda$, and $r(\lambda)$ denotes the loss of the incident light by the light absorption and reflection of the FTO glass. Three other factors also influence IPCE($\lambda$), and their correlation is given by the following equation [27];

$$IPCE(\lambda) = LHE(\lambda) \cdot \phi_{inj} \cdot \eta_{coll}$$  

(2)

where LHE($\lambda$) denotes the light harvesting efficiency of the dye absorbed, $\phi_{inj}$ denotes the injection efficiency of the electron from the excited dye into the TiO$_2$, and $\eta_{coll}$ denotes the collection efficiency of the injected electrons by the FTO. This study adopts $\phi_{inj}$ with an identical value because of the identical dye (N719) used. The TiCl$_4$-treated cells enhanced the dye loading of the TiO$_2$ film and light scattering, explaining the increase of the LHE($\lambda$) of the TiCl$_4$-treated cells.

Conversely, $\eta_{coll}$ can be estimated using the transport ($k_t$) rate and the recombination ($k_r$) rate as $\eta_{coll} \sim k_t / (k_t + k_r)$ [28]. Because the TiCl$_4$-treated cells improve the connection between TiO$_2$ particles, the treated cells enhance the transport rate and decrease the recombination rate of excited electrons [16]. Therefore, the overall IPCE after TiCl$_4$ treatment is higher than that of the untreated cell. The Ti thin film can supply the dense TiO$_2$ film with an interfacial layer, and may reconstruct the interface between the FTO substrate and the porous TiO$_2$ film. The Ti thin film can also be used as a blocking layer to improve electron conduction and suppress interfacial electron recombination. Therefore, the term $\eta_{coll}$ in the IPCE equation increases with the enhancement of the rate for transport ($k_t$) and decreases with the recombination ($k_r$) rate.

Thus, applying TiCl$_4$ treatment to porous TiO$_2$ and applying the Ti-deposited thin film metal on FTO can achieve a higher LHE($\lambda$), $\phi_{inj}$, and $\eta_{coll}$ value, which in turn improves the IPCE and $J_{sc}$ values.

4. CONCLUSIONS

In summary, this study reports the successful application of TiCl$_4$ treatment to porous TiO$_2$ and the Ti-deposited thin film metal on FTO to improve the performance of DSSCs. After sintering, Ti oxidizes to form TiO$_2$ and serves as a blocking layer to prevent back reaction. This also increases the electron conduction and suppresses the interfacial electrons recombination because of conduction band
matching. TiCl$_4$ treatment enhances the transport of excited electrons on the porous TiO$_2$. These processes are simple and cost-effective, and can be integrated in current DSSCs with glass or flexible substrates.

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References


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