Surface-Treated TiO\textsubscript{2} Nanoparticles for Dye-Sensitized Solar Cells with Remarkably Enhanced Performance

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\section*{ABSTRACT:}
Dye-sensitized solar cells (DSSCs) were prepared bycapitalizing on mesoporous P-25 TiO\textsubscript{2} nanoparticle film sensitized with N719 dyes. Subjecting TiO\textsubscript{2} nanoparticle films to TiCl\textsubscript{4} treatment, the device performance was improved. More importantly, O\textsubscript{2} plasma processing of TiO\textsubscript{2} film that was not previously TiCl\textsubscript{4}-treated resulted in a lower efficiency; by contrast, subsequent O\textsubscript{2} plasma exposure after TiCl\textsubscript{4} treatment markedly enhanced the power conversion efficiency, \textit{PCE}, of DSSCs. Remarkably, with TiCl\textsubscript{4} and O\textsubscript{2} plasma treatments dye-sensitized TiO\textsubscript{2} nanoparticle solar cells produced with 21 \textmu m thick TiO\textsubscript{2} film illuminated under 100 mW/cm\textsuperscript{2} exhibited a \textit{PCE} as high as 8.35\%, twice of untreated cells of 3.86\%.

\section{INTRODUCTION}

Dye-sensitized solar cells (DSSCs) are widely recognized as one of the most promising of several alternative, cost-effective concepts for solar-to-electric energy conversion that has been offered to challenge conventional Si solar cells over the past two decades.\textsuperscript{1} The major components of a DSSC include a n-type semiconductor, a sensitizer (i.e., dye), and a redox electrolyte. A sensitizer is chemically tethered to the semiconductor surface by functional anchoring moieties (usually a carboxyl group) to harvest a broad range of spectrally distributed light and transfer energy from absorbed photons to excite electrons. If the energy of excited electrons is sufficiently high, electrons will inject into the conduction band of a n-type semiconductor to generate photocurrent. The excited electron injection produces an oxidized sensitizer, which is reduced by the redox couple in electrolyte at the sensitizer/electrolyte interface. The Injected electrons return to the counter electrode through the external circuit at which they reduce the oxidized redox couple. The ability to promote a fast electron generation in sensitizer as well as a fast recovery of oxidized sensitizer, a rapid and efficient electron transport in n-type semiconductor, and a fast recovery and diffusion of redox couple in electrolyte is the key to achieve high power conversion efficiency, \textit{PCE}.

TiO\textsubscript{2} is one of the most widely used n-type large band gap semiconductor with an energy band gap of 3.2 eV.\textsuperscript{2} Different nanostructured TiO\textsubscript{2} have been utilized as photoanodes to produce DSSCs, including nanoparticles,\textsuperscript{1,3} nanorods,\textsuperscript{4–7} nanowires,\textsuperscript{8,9} and nanotubes.\textsuperscript{10–18} Notably, the highest \textit{PCE} was obtained from mesoporous P-25 TiO\textsubscript{2} nanoparticle film (\textit{PCE} = 11.20\%, in which a ruthenium-based dye, N719, was used as the sensitizer).\textsuperscript{19,20} High-performance dye-sensitized P-25 TiO\textsubscript{2} nanoparticle solar cells can be attributed to the cooperative effect of anatase and rutile phases, which facilitate charge separation and reduce charge recombination,\textsuperscript{7,21–23} and the higher surface to volume ratio of nanoparticle film,\textsuperscript{6} as compared to other nanostructures (e.g., nanowires).\textsuperscript{24} To enhance device performance, surface treatment on TiO\textsubscript{2} photoanodes was often performed to improve surface morphology and promote interaction between sensitizer and the TiO\textsubscript{2} surface.\textsuperscript{12,23} Immersing TiO\textsubscript{2} photoanode into TiCl\textsubscript{4} solution leads to formation of a thin TiO\textsubscript{2} blocking layer on the photoanode surface to suppress charge recombination and facilitate charge transport.\textsuperscript{5,12} Additionally, exposure to O\textsubscript{2} plasma has been proven very effective in increasing the surface hydrophilicity of TiO\textsubscript{2}, resulting in increased dye adsorption.\textsuperscript{26} In our previous study, the performance of dye-sensitized TiO\textsubscript{2} nanotube solar cells was significantly improved after sequential TiCl\textsubscript{4} treatment and O\textsubscript{2} plasma exposure, and an impressive \textit{PCE} of 7.37\% was obtained.\textsuperscript{15}

Herein, we systematically explored the effects of TiCl\textsubscript{4} treatment and O\textsubscript{2} plasma exposure on device performance of DSSCs prepared by employing mesoporous P-25 TiO\textsubscript{2} nanoparticle film as a photoanode sensitized with N719 dyes. TiCl\textsubscript{4} treatment led to an increased \textit{PCE} of DSSCs (e.g., \textit{PCE} = 5.82\% with a 21 \textmu m thick TiO\textsubscript{2} nanoparticle film) as compared to untreated sample.
(PCE = 3.86%). More importantly, O₂ plasma processing of TiO₂ film that was not previously TiCl₄ treated resulted in a lower efficiency; by contrast, subsequent O₂ plasma exposure after TiCl₄ treatment markedly enhanced the power conversion efficiency, PCE, of DSSCs. Remarkably, with TiCl₄ and O₂ plasma treatments, dye-sensitized TiO₂ nanoparticle solar cells produced with 21 μm thick TiO₂ film illuminated under 100 mW/cm² exhibited a PCE as high as 8.35%, twice that of untreated cells, 3.86%.

**EXPERIMENTAL SECTION**

**Fabrication of Solar Cells.** A 10 wt % TiO₂ nanoparticle paste was prepared by mixing 1 g of P-25 TiO₂ (Degussa) and 1 g of poly(ethylene glycol) in 4.5 mL of H₂O and 4.5 mL of ethanol. It was then deposited on a clean fluorine-doped tin oxide (FTO) glass. The FTO glass was cleaned by sonication in acetone, methanol, and isopropanol baths sequentially for 30 min. A number of 50 μm thick spacers (3M) was used to control the thickness of a P-25 TiO₂ nanoparticle film coated on the FTO glass by the doctor blade method. The P-25 TiO₂ nanoparticle paste was allowed to dry at room temperature for 15 min prior to removal of the spacer and then sintered at 500 °C for 2 h.

TiCl₄ solution was prepared by adding 2 mL of TiCl₄ into a mixture of 50 g of ice and 50 g of water. Prior to dye adsorption, TiO₂ nanoparticle films were immersed in TiCl₄ aqueous solution in a beaker and then kept in an oil bath at 60 °C for 1 h, followed by rinsing with ethanol and annealing at 500 °C in air for 30 min. The TiCl₄-treated samples were further exposed to O₂ plasma at 30 W (Harrick plasma machine) for 10 min to achieve best device performance according to our previous work. O₂ was regulated by a flow meter. Subsequently, the surface-treated TiO₂ nanoparticle film was immersed in 0.2 mM dye ethanol solution for 24 h to allow for sufficient dye adsorption. The dye used in the study was cis-dioctylcyanocarboxylato-(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis(tetrabutylammonium) (NT719, Solaronix). Platinum (Pt)-coated FTO glass was used as the counter electrode, prepared by placing a drop of 0.5 mM H₂PtCl₆ isopropanol solution on clean FTO glass substrate and subsequently sintered at 380 °C for 30 min.

The NT719 dye-sensitized solar cells were sandwiched between the TiO₂ nanoparticle paste-coated FTO glass (anode) and the Pt-coated FTO glass (cathode) by applying a 25 μm thick Hot-Melt film as the spacer (SX1170-25, Solaronix), yielding a front-side illumination mode (i.e., the incident photons directly encountered the dye-adsorbed TiO₂ film was immersed in a 0.2 mM dye ethanol solution for 24 h to allow for sufficient dye adsorption. The dye used in the study was cis-dioctylcyanocarboxylato-(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis(tetrabutylammonium) (NT719, Solaronix). Platinum (Pt)-coated FTO glass was used as the counter electrode, prepared by placing a drop of 0.5 mM H₂PtCl₆ isopropanol solution on clean FTO glass substrate and subsequently sintered at 380 °C for 30 min.

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**Characterization.** A digital optical power meter (Thor Laboratories Inc.) was used to measure the level of light emitted from a SoLux Solar Simulator. The light intensity was adjusted until 100 mW/cm² reached the sample. A small piece of indium was mechanically pressed onto the conductive side of FTO glass of the TiO₂ nanoparticle photoanode as well as the Pt-coated counter electrode to increase the contact area between the FTO glass and the testing tips. A Keithley source meter was used to create an input voltage and measure the output current of DSSCs. The anode of the source meter was placed on indium on the Pt-coated counter electrode, and correspondingly, the cathode was placed on indium on the photoanode. The current–voltage curves (J–V) were recorded with Keithley’s Lab Tracer 2.0. The photoactive area for solar cells was 0.125 cm². Dye loading measurement was conducted by immersing samples in 0.2 M NaOH solution (water/ethanol = 1/1; v/v) for 15 min and then measuring the absorbance of the dye solution by UV–vis absorption spectroscopy.

![Figure 1](image)  
**Figure 1.** J–V characteristics of DSSCs made of different thicknesses of TiO₂ nanoparticle films (open symbols, 21 μm; solid symbols, 14 μm) with and without TiCl₄ treatment. Untreated and TiCl₄-treated samples are represented by triangles and circles, respectively.

**Table 1. Summary of Device Performance of DSSCs Made of Two Different Thicknesses of TiO₂ Nanoparticle Films (i.e., 14 and 21 μm)**

<table>
<thead>
<tr>
<th>thickness</th>
<th>V_OC (V)</th>
<th>J_SC (mA/cm²)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 μm; none</td>
<td>0.769</td>
<td>9.2</td>
<td>41.88%</td>
<td>2.98%</td>
</tr>
<tr>
<td>14 μm; TiCl₄</td>
<td>0.869</td>
<td>9.3</td>
<td>56.58%</td>
<td>4.56%</td>
</tr>
<tr>
<td>14 μm; plasma</td>
<td>0.658</td>
<td>4.9</td>
<td>33.98%</td>
<td>1.10%</td>
</tr>
<tr>
<td>14 μm; both</td>
<td>0.879</td>
<td>11.7</td>
<td>55.36%</td>
<td>5.70%</td>
</tr>
<tr>
<td>21 μm; none</td>
<td>0.748</td>
<td>11.6</td>
<td>45.97%</td>
<td>3.86%</td>
</tr>
<tr>
<td>21 μm; TiCl₄</td>
<td>0.849</td>
<td>12.4</td>
<td>55.10%</td>
<td>5.82%</td>
</tr>
<tr>
<td>21 μm; plasma</td>
<td>0.648</td>
<td>6.3</td>
<td>36.98%</td>
<td>1.51%</td>
</tr>
<tr>
<td>21 μm; both</td>
<td>0.819</td>
<td>16.4</td>
<td>62.01%</td>
<td>8.35%</td>
</tr>
</tbody>
</table>

* None: no any surface treatments.  
* TiCl₄ treated by immersing in TiCl₄ solution.  
* Plasma: treated by exposing to O₂ plasma.  
* Both: sequential TiCl₄ and O₂ plasma treatments.

**RESULTS AND DISCUSSION**

Figure 1 compares the J–V characteristics obtained from DSSCs made of two different thicknesses of TiO₂ nanoparticle films that were treated with or without TiCl₄. Clearly, after TiCl₄ treatment, for the DSSC based on 14 μm TiO₂ nanoparticle film, the open-circuit voltage, V_OC increased from 0.769 to 0.869 V, the short-circuit current, J_SC, was almost the same (9.2 and 9.3 mA/cm² without and with TiCl₄ treatments, respectively), and the fill factor, FF, changed from 41.88% to 56.58%, resulting in a large increase in PCE from 2.98% to 4.56% (Table 1). A similar tendency was observed for the 21 μm TiO₂ nanoparticle film solar cell. The PCE was readily improved from 3.86% to 5.82% after TiCl₄ treatment.

A comparison of device performance from untreated solar cells and those treated solely with O₂ plasma processing showed a lowering of V_OC, J_SC, FF, and PCE (Table 1 and Figure 2). After treatment, V_OC decreased about 0.1 V (for example, from 0.748 to 0.648 V for the 21 μm TiO₂ nanoparticle sample); J_SC reduced almost one-half (for example, 11.6 (untreated) versus 6.3 mA/cm² (treated)). Correspondingly, FF decreased from 404% to 304%, and PCE of treated samples was lowered more than one-half of those untreated (i.e., 1.10% to 2.98% for 14 μm TiCl₄ and 1.51% to 3.86% for 21 μm TiO₂, respectively). Obviously, the O₂ plasma exposure alone decreased the PCE of the resulting DSSCs.

Quite intriguingly, as clearly evident in Figure 3, a markedly improved device performance was achieved for TiCl₄-treated
DSSCs that were further processed by exposing to O2 plasma. The primary advantage of O2 plasma treatment was represented in a largely increased JSC (Table 1). JSC went up approximately 25% from 9.3 to 11.7 mA/cm² for 14 μm TiO2 and 12.4 to 16.4 mA/cm² for 21 μm TiO2, respectively. The overall PCE of DSSCs produced after both TiCl4 and O2 plasma treatments was higher than those of solar cells with only TiCl4 treatment. As noted in Table 1, TiCl4 treatment increased VOC and FF while JSC remained almost the same. By contrast, subsequent O2 plasma processing after TiCl4 treatment increased JSC by 25% while only marginally altering VOC and FF (Figure 3). The synergistic effect of TiCl4 and O2 plasma treatments led to a remarkable increase of approximately twice PCE compared to untreated solar cells (i.e., 5.7% to 2.98% for 14 μm TiO2 and 8.35% to 3.86% for 21 μm TiO2, respectively). This experimental observation on DSSCs made of P-25 TiO2 nanoparticles was consistent with our previous study on those fabricated based on TiO2 nanotubes.15 It is noteworthy that the efficiencies of DSSCs in the present study were not as high as those reported previously by Grätzel et al. (PCE ≈ 11%).19 This is not surprising as our DSSCs did not have a scattering layer on top of the TiO2 nanoparticle film and a compact block layer of TiO2 between the TiO2 nanoparticle film and the FTO glass as compared to the record DSSCs.17 The presence of a scattering layer could enhance the light harvesting,27 and the coating of a compact block layer could decrease the charge recombination between the electrolyte and the FTO glass.28 The performance of our DSSCs is expected to be further improved if the scattering layer and block layer are applied; however, this is not the focus of the present investigation and will be the subject of a future study.

We now turn our attention to elucidate the effects of TiCl4 and O2 plasma treatments on device performance. It is well known that structural defects and cracks may occur during the process of high-temperature annealing of TiO2 nanoparticle networks.14,29 Accordingly, the defects and cracks may induce a higher chance of charge recombination by trapping electrons at the surface of defects and cracks. With TiCl4 treatment a thin blocking layer of TiO2 was deposited on the TiO2 surface30 and thus improved the surface morphology. Consequently, charge recombination was reduced and charge transport was enhanced, thereby leading to increased VOC and FF. Moreover, additional O2 plasma treatment was advantageous as it increased the surface hydrophilicity of TiO230 by saturating the TiO2 surface with hydroxyl groups,26 which in turn substantially promoted attachment of N719 dye to the TiO2 surface via reaction of carboxyl moieties on the N-719 surface with complementary hydroxyl groups on the TiO2 surface. Thus, the dye loading increased considerably after O2 plasma exposure. For DSSCs, the capacity of dye loading exerts a profound influence on the photocurrent. The dye loading measurement by UV—vis absorption spectroscopy revealed that a 21 μm thick TiCl4-treated TiO2 sample had a dye concentration of 0.148 μmol/cm², while for (TiCl4 +O2 plasma)-treated sample, the dye concentration was 0.176 μmol/cm², which accounted for the 25% increase in JSC after additional treatment with O2 plasma (Table 1). TiCl4 treatment and O2 plasma processing collectively increased VOC, JSC, and FF and thus markedly enhanced the PCE of dye-sensitized surface-treated TiO2 nanoparticle solar cells. It is worth noting that without prior TiCl4 treatment the device efficiency of O2 plasma-treated samples decreased dramatically as compared to untreated, TiCl4-treated, and (TiCl4 + O2 plasma)-treated samples. The exact reason for this observation was not clear. One possible reason may be that the oxygen plasma generated high electric field during the process, which led to the damage to TiO2, thus increased the existence of defects and cracks on untreated TiO2 surface, created high trap density, and degraded the bonding strength. The surface hydrophilicity may also be increased upon O2 plasma exposure; however, the damage induced by O2 plasma dominated over this advantageous effect and thus decreased the PCE.

The effect of TiO2 thickness on the device performance of DSSCs was examined (Figure 4 and Table 2). The samples used in this phase of study were processed with sequential TiCl4 and O2 plasma treatments. We note that increasing thickness of TiO2 nanoparticle film may be a good strategy to improve the performance of DSSCs. The thicker TiO2 active layer suggested that more dye molecules can be adsorbed and thus a higher light harvesting efficiency. To this end, DSSCs with TiO2 nanoparticle film thicknesses of 7, 14, 21, and 28 μm were prepared. It is not surprising that the thinnest TiO2 film (i.e., 7 μm) had the lowest efficiency (PCE = 3.78%). As the thickness increased from 7 to 21 μm, JSC increased from 7.8 to 16.4 mA/cm² and PCE increased from 3.78% to 8.35%. However, when an even thicker TiO2 nanoparticle film was employed (i.e., 28 μm), JSC and PCE decreased from 16.4 to 12.1 mA/cm² and from 8.35% to 6.38%, respectively. The decrease in JSC and PCE can be rationalized as

Figure 2. J–V characteristics of DSSCs made of different thicknesses of TiO2 nanoparticle films (open symbols, 21 μm; solid symbols, 14 μm) with and without treatments by O2 plasma exposure. Untreated and O2 plasma-treated samples are represented by circles and diamonds, respectively.

Figure 3. J–V characteristics of DSSCs made of different thicknesses of TiO2 nanoparticle films after surface treatments (open symbols, 21 μm; solid symbols, 14 μm). TiCl4-treated and (TiCl4 + O2 plasma)-treated samples are represented by triangles and squares, respectively.
The thicknesses of nanoparticle films were from 7 to 28 μm. Both: sequential TiCl4 and O2 plasma treatments

Table 2. Summary of Device Performance of DSSCs with Both TiCl4 and O2 Plasma Treatments

<table>
<thead>
<tr>
<th>thickness</th>
<th>VOC (V)</th>
<th>JSC (mA/cm²)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 μm; both</td>
<td>0.889</td>
<td>7.8</td>
<td>54.63%</td>
<td>3.78%</td>
</tr>
<tr>
<td>14 μm; both</td>
<td>0.879</td>
<td>11.7</td>
<td>55.36%</td>
<td>5.70%</td>
</tr>
<tr>
<td>21 μm; both</td>
<td>0.819</td>
<td>16.4</td>
<td>62.01%</td>
<td>8.35%</td>
</tr>
<tr>
<td>28 μm; both</td>
<td>0.859</td>
<td>12.1</td>
<td>61.57%</td>
<td>6.38%</td>
</tr>
</tbody>
</table>

The thicknesses of nanoparticle films were from 7 to 28 μm. Both: sequential TiCl4 and O2 plasma treatments

follows. First, the increased thickness of TiO2 nanoparticle film may give rise to better light absorption; however, in the present front-side illumination mode (i.e., light entered the cell through the transparent FTO glass on which TiO2 nanoparticle photoanode was directly deposited (see Experimental Section)), as the TiO2 nanoparticle thickness greatly increased, most of the photons may be absorbed by the dyes anchored on TiO2 photoanode that was near the FTO glass (i.e., the bottom part of the TiO2 nanoparticle film), while the dyes on the top part of the nanoparticle film that was near the TiO2/electrolyte interface may not have enough photons to be absorbed. As a result, the advantage of a thick film decreased with largely increased thickness. Second, a thicker TiO2 film implied that electrons had to undergo a longer pathway before reaching the FTO glass and therefore a higher chance to recombine during the transport process. Finally, the thicker TiO2 film may hinder the electrolyte to penetrate all the way down to the bottom of the TiO2 film and the transport of the triiodide ions in electrolyte to the Pt-coated counter electrode and thus impeded the recovery of dye molecules after injection of exited electrons to TiO2. Taken together, the device performance decreased with further increased nanoparticle thickness.

**CONCLUSIONS**

In summary, the synergy of TiCl4 treatment and O2 plasma processing on TiO2 nanoparticle films markedly enhanced the performance of the resulting DSSCs. TiCl4 treatment induced an improved surface morphology of TiO2, which increased VOC and FF, while O2 plasma treatment increased JSC by promoting the dye loading on the TiO2 surface. However, O2 plasma processing on the sample alone without undergoing TiCl4 treatment alone lowered PCE. In stark contrast to a PCE of 3.86% from a 21 μm thick untreated TiO2 sample, a maximum PCE of 8.35% was achieved after sequential TiCl4 and O2 plasma treatments. Use of thinner or thicker TiO2 films did not yield a higher performance. This work reflects the great importance of rational surface engineering with TiCl4 and O2 plasma in producing high-efficiency DSSCs. In addition to ruthenium-based dyes, in principle, conjugated polymers and semiconductor quantum dots or rods can be readily utilized as alternative photosensitizers to yield a variety of dye-sensitized surface-treated TiO2 nanoparticle solar cells; this is the subject of a future study.

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