

Surface-Treated TiO₂ Nanoparticles for Dye-Sensitized Solar Cells with Remarkably Enhanced Performance

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ABSTRACT: Dye-sensitized solar cells (DSSCs) were prepared by capitalizing on mesoporous P-25 TiO₂ nanoparticle film sensitized with N719 dyes. Subjecting TiO₂ nanoparticle films to TiCl₄ treatment, the device performance was improved. 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 μ m thick TiO₂ film illuminated under 100 mW/cm² exhibited a *PCE* as high as 8.35%, twice of untreated cells of 3.86%.



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.¹ The major components of a DSSC include an *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, PCE.

TiO₂ is one of the most widely used *n*-type large band gap semiconductor with an energy band gap of 3.2 eV.² Different nanostructured TiO₂ have been utilized as photoanodes to produce DSSCs, including nanoparticles,^{1,3} nanorods,^{4–7} nanowires,^{8,9} and nanotubes.^{10–18} Notably, the highest *PCE* was obtained from mesoporous P-25 TiO₂ nanoparticle film (*PCE* = 11.20%, in



which a ruthenium-based dye, N719, was used as the sensitizer). 19,20 High-performance dye-sensitized P-25 $\rm TiO_2$ nanoparticle solar cells can be attributed to the cooperative effect of anatase and rutile phases, which facilitate charge separation and reduce charge recombination,^{7,21–23} and the higher surface to volume ratio of nanoparticle film,⁶ as compared to other nanostructures (e.g., nanowires²⁴). To enhance device performance, surface treatment on TiO₂ photoanodes was often performed to improve surface morphology and promote interaction between sensitizer and the TiO₂ surface.^{12,25} Immersing TiO₂ photoanode into TiCl₄ solution leads to formation of a thin TiO2 blocking layer on the photoanode surface to suppress charge recombination and facilitate charge transport.4,12 Additionally, exposure to O2 plasma has been proven very effective in increasing the surface hydrophilicity of TiO₂, resulting in increased dye adsorption.²⁶ In our previous study, the performance of dye-sensitized TiO₂ nanotube solar cells was significantly improved after sequential TiCl₄ treatment and O₂ plasma exposure, and an impressive PCE of 7.37% was obtained.¹

Herein, we systematically explored the effects of TiCl₄ treatment and O₂ plasma exposure on device performance of DSSCs prepared by employing mesoporous P-25 TiO₂ nanoparticle film as a photoanode sensitized with N719 dyes. TiCl₄ treatment led to an increased *PCE* of DSSCs (e.g., *PCE* = 5.82% with a 21 μ m thick TiO₂ nanoparticle film) as compared to untreated sample

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(*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 μ m 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 sonicating in acetone, methanol, and isopropanol baths sequentially for 30 min. A number of 50 μ m 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.¹⁵ O₂ was regulated by a flow meter. Subsequently, the surface-treated TiO₂ nanoparticle 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*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis(tetrabutylammonium) (N719, 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 N719 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 μ m 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 nanoparticle photoanode). An ionic liquid electrolyte containing 0.60 M BMIM-I, 0.03 M I2, 0.50 M TBP, and 0.10 M GTC in acetonitrile/valeronitrile 85/15 (v/v) (ES-0004, purchased from io.li.tec, Germany) was injected between two electrodes driven by capillary force through holes on the Hot-Melt film.

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. J-V characteristics of DSSCs made of different thicknesses of TiO₂ nanoparticle films (open symbols, 21 μ m; solid symbols, 14 μ m) 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 μ m)

thickness	$V_{\rm OC}$ (V)	$J_{\rm SC} ({\rm mA/cm}^2)$	FF	PCE
14 μ m; none ^{<i>a</i>}	0.769	9.2	41.88%	2.98%
14 μ m; TiCl ₄ ^b	0.869	9.3	56.58%	4.56%
14 μ m; plasma ^c	0.658	4.9	33.98%	1.10%
14 μ m; both ^d	0.879	11.7	55.36%	5.70%
21 μ m; none	0.748	11.6	45.97%	3.86%
21 μ m; TiCl ₄	0.849	12.4	55.10%	5.82%
21 μ m; plasma	0.648	6.3	36.98%	1.51%
21 μ m; both	0.819	16.4	62.01%	8.35%

^{*a*} None: no any surface treatments. ^{*b*} TiCl₄: treated by immersing in TiCl₄ solution. ^{*c*} Plasma: treated by exposing to O₂ plasma. ^{*d*} 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 μ m TiO₂ nanoparticle film, the opencircuit voltage, V_{OC} , increased from 0.769 to 0.869 V, the shortcircuit 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 μ m 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 $V_{\rm OC}$, $J_{\rm SC}$, FF, and PCE (Table 1 and Figure 2). After treatment, $V_{\rm OC}$ decreased about 0.1 V (for example, from 0.748 to 0.648 V for the 21 μ m TiO₂ nanoparticle sample); $J_{\rm SC}$ reduced almost one-half (for example, 11.6 (untreated) versus 6.3 mA/cm² (treated)). Correspondingly, FF decreased from 40+% to 30+%, and *PCE* of treated samples was lowered more than one-half of those untreated (i.e., 1.10% to 2.98% for 14 μ m TiO₂ and 1.51% to 3.86% for 21 μ m 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

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Figure 2. J-V characteristics of DSSCs made of different thicknesses of TiO₂ nanoparticle films (open symbols, 21 μ m; solid symbols, 14 μ m) 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 μ m; solid symbols, 14 μ m). TiCl₄-treated and (TiCl₄ + O₂ plasma)-treated samples are represented by triangles and squares, respectively.

DSSCs that were further processed by exposing to O₂ plasma. The primary advantage of O₂ plasma treatment was represented in a largely increased J_{SC} (Table 1). J_{SC} went up approximately 25% from 9.3 to 11.7 mA/cm² for 14 μ m TiO₂ and 12.4 to 16.4 mA/cm² for 21 μ m 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, $TiCl_4$ treatment increased V_{OC} and FFwhile J_{SC} remained almost the same. By contrast, subsequent O_2 plasma processing after TiCl₄ treatment increased J_{SC} by 25% while only marginally altering V_{OC} 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 TiO_2 and 8.35% to 3.86% for 21 μ m 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* = $\sim 11\%$).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.¹⁹ 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 surface⁴ and thus improved the surface morphology. Consequently, charge recombination was reduced and charge transport was enhanced, thereby leading to increased V_{OC} and FF. Moreover, additional O₂ plasma treatment was advantageous as it increased the surface hydrophilicity of TiO_2^{30} by saturating the TiO_2 surface with hydroxyl groups,² 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 μ m thick TiCl₄-treated TiO₂ sample had a dye concentration of 0.148 μ mol/cm², while for (TiCl₄ + O₂ plasma)-treated sample, the dye concentration was 0.176 μ mol/cm², which accounted for the 25% increase in J_{SC} after additional treatment with O_2 plasma (Table 1). TiCl₄ treatment and O_2 plasma processing collectively increased V_{OC} , J_{SC} , 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, $TiCl_4$ -treated, and $(TiCl_4 + O_2 \text{ plasma})$ -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 O_2 plasma exposure; however, the damage induced by O_2 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 O_2 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 μ m were prepared. It is not surprising that the thinnest TiO₂ film (i.e., $7 \mu m$) had the lowest efficiency (PCE = 3.78%). As the thickness increased from 7 to 21 μ m, I_{SC} 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 μ m), J_{SC} and PCE decreased from 16.4 to 12.1 mA/cm² and from 8.35% to 6.38%, respectively. The decrease in J_{SC} and *PCE* can be rationalized as



Figure 4. J-V characteristics of DSSCs made of different thicknesses of TiO₂ nanoparticle films.

Table 2. Summary of Device Performance of DSSCs with Both TiCl₄ and O₂ Plasma Treatments^{*a*}

thickness	$V_{\rm OC}$ (V)	$J_{\rm SC} ({\rm mA/cm}^2)$	FF	PCE
7 μ m; both ^b	0.889	7.8	54.63%	3.78%
14 μ m; both	0.879	11.7	55.36%	5.70%
21 μ m; both	0.819	16.4	62.01%	8.35%
28 μ m; both	0.859	12.1	61.57%	6.38%
^{<i>a</i>} The thicknesse	s of nanopar	ticle films were from	n 7 to 28 μ i	n. ^b Both:
sequential TiCl ₄	and O ₂ plass	na 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 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 V_{OC} and *FF*, while O₂ plasma treatment increased J_{SC} 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 μ m 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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