

Dye-Sensitized TiO₂ Nanotube Solar Cells with Markedly Enhanced **Performance via Rational Surface Engineering**

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Highly ordered anodic TiO₂ nanotube arrays fabricated by electrochemical anodization were sensitized with ruthenium dye N-719 to yield dye-sensitized TiO₂ nanotube solar cells. Rational surface treatments on photoanode TiO_2 nanotubes markedly improved the device performance. With TiCl₄ treatment, in conjunction with oxygen plasma exposure under optimized conditions, dye-sensitized TiO₂ nanotube solar cells produced using 14- μ m-thick TiO₂ nanotube arrays in backside illumination mode subjected to simulated AM 1.5 G irradiation of 100 mW/cm² exhibited a pronounced power conversion efficiency (PCE) of 7.37%.

As one of the major renewable energy sources, solar energy has the potential to become an essential component of future global energy production. Dye-sensitized solar cells (DSSCs),¹ represent one of the most promising of several alternative, cost-effective concepts for solar-toelectric energy conversion that has been offered to challenge conventional silicon solar cells over the past decade. The configuration of a DSSC consists of a sintered, widebandgap semiconductor TiO₂ nanoparticle network film, a ruthenium-based dye (i.e., sensitizer), and an electrolyte. Upon the absorption of photons, the dye generates excitons (i.e., electron-hole pairs). Subsequently, the electrons inject into the TiO₂ photoanode to generate photocurrent; scavenged by a redox couple, holes transport to the cathode. The performance of a DSSC can be improved by optimizing the semiconductor TiO₂ nanoparticle film, sensitizer, and electrolyte. An overall power conversion efficiency (PCE) of > 10% for a DSSC, which is dictated by its light harvest efficiency, the quantum vield for charge injection, and the charge collection efficiency at the electrodes,² has been demonstrated. However, much research remains to be done to improve the efficiency and remove the practical problems related to DSSCs. For example, typically, a $10-\mu$ m-thick mesoporous TiO_2 (anatase nanocrystals) film with a porosity of 50% is employed as an electron-accepting species in a DSSC. The film is prepared by dispersing 15-30 nm colloidal TiO₂ particles on a conductive glass support consisting of a network of randomly dispersed nanocrystals.³ While versatile and robust, these sintered threedimensional TiO₂ nanoparticle films lead to enhanced

scattering of free electrons and electron trapping at the interfaces, thereby reducing electron mobility and exhibiting slow electron transport. The electron and hole transport across several ill-defined, heterogeneous interfaces in TiO₂ nanoparticle films is very complex.⁴

In this context, highly ordered, vertically oriented TiO₂ nanotube arrays of different aspect ratios and surface qualities have recently been fabricated as alternative nanoscale architectures to substitute the sintered TiO₂ nanoparticle films in DSSCs. They are produced by potentiostatic anodization of titanium (Ti) foil^{5,6} or Ti thin films that have been sputtered using radio-frequency (RF) sputter deposition on a variety of substrates with fluorine-containing electrolytes (e.g., fluorine-doped tin oxide (FTO)-coated glass).⁷ The nanotubular morphology of these arrays offers a large internal surface area with no concomitant decrease in geometric and structural order.⁵ The vertical orientation of the crystalline nanotube arrays after annealing makes them excellent electron percolation pathways for efficient, vectorial charge transport along the nanotube axis.⁵ A PCE of 2.9% was achieved using a 360-nm-thick transparent TiO₂ nanotube membrane to assemble DSSCs in a front side illumination mode,⁸ and the performance was further improved to 6.9% with the capability of growing thicker TiO₂ nanotube arrays on transparent substrates.⁹ A PCE of 6.89% was also obtained using $20-\mu$ m-thick TiO₂ nanotube arrays that were grown on Ti foil in a backside

- (6) Macak, J. M.; Tsuchiya, H.; Taveira, L.; Aldabergerova, S.; Schmuki, P. Angew. Chem., Int. Ed. 2005, 44, 7463.
 (7) Mor, G. K.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Adv.
- Funct. Mater. 2005, 15, 1291. (8) Mor, G. K.; Varghese, O. K.; Paulose, M.; Ong, K. G.; Grimes, C.

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⁽¹⁾ Gratzel, M. Nature 2001, 414, 338.

⁽²⁾ O'Regan, B.; Gratzel, M. Nature 1991, 353, 737.

Nazeruddin, M.; Kay, A.; Rodicio, I.; Humpbry-Baker, R.; Miiller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. J. Am. Chem. (3)Soc. 1993, 115, 6382.

⁽⁴⁾ Martinson, A. B. F.; Hamann, T. W.; Pellin, M. J.; Hupp, J. T. *Chem.*—*Eur. J.* **2008**, *14*, 4458.
(5) Grimes, C. A. J. Mater. Chem. **2007**, *17*, 1451.

A. Thin Solid Films 2006, 496, 7.

Varghese, O. K.; Paulose, M.; Grimes, C. A. Nat. Nanotechnol. 2009, 4, 592.

illumination mode.¹⁰ Recently, an improved PCE in quantum-dot-sensitized solar cells was achieved by facilitating the charge transport through TiO₂ nanotube architecture (PCE \leq 1%) rather than sintered TiO₂ nanoparticle film.¹¹ Comparing solar cells produced from TiO_2 nanotube arrays with that from sintered TiO_2 nanoparticle films, enhanced charge collection efficiency and enhanced light scattering in TiO₂ nanotube-based DSSC was observed.¹² The use of TiO₂ nanotubes reduced carrier scattering loss and nonradiative recombination by eliminating unnecessary lateral transport (i.e., hopping between TiO₂ nanoparticles) and its resulting recombination loss. It is noteworthy that the dye absorption on TiO₂ nanotubes was found to be similar to that on TiO₂ nanoparticle films of identical film thickness, according to the dye loading measurement.¹²

Surface treatment on TiO₂ photoanodes not only increased the loading of sensitizers on the TiO₂ surface but also improved the electronic interaction between the sensitizer (i.e., dye) and the TiO_2 surface, thereby yielding improved device performance.^{13,14} For example, an increased PCE of the DSSC was obtained by exposing the TiO_2 nanoparticle film to O_2 plasma.¹³ The O_2 plasma treatment promoted the hydrophilicity on the TiO₂ surface, leading to the increased dye adsorption. It has been demonstrated that by exposing ZnO nanowires to O₂ plasma, the grafting density of CdSe quantum dots on the ZnO nanowire surface increased dramatically, resulting in an improved PCE.¹⁵ Notably, the treatment of TiO₂ nanotubes with O2 plasma has yet been studied. On the other hand, immersing photoanodes (e.g., TiO₂ or ZnO) in titanium tetrachloride (TiCl₄) solution led to the formation of a very thin TiO₂ blocking layer. As a result, the amount of dye adsorption was increased and the charge transfer from dye molecules to photoanodes was facilitated, and, ultimately, an enhanced PCE was readily obtained.14,16

In this article, we report dye-sensitized TiO₂ nanotube solar cells with enhanced performance based on highly ordered, vertically oriented TiO2 nanotube arrays after rational surface engineering, i.e., the TiCl₄ processing followed by O₂ plasma exposure. The TiO₂ nanotube arrays were fabricated by electrochemical anodization; subsequently, they were impregnated with ruthenium dye N-719 that was used as sensitizer and chemically anchored to the surface of TiO2 nanotubes via the reaction of carboxylate moieties on N-719 surface with

- (10) Shankar, K.; Mor, G. K.; Prakasam, H. E.; Yoriya, S.; Paulose, M.; Varghese, O. K.; Grimes, C. A. Nanotechnology 2007, 18, 065707.
- (11) Kongkanand, A.; Tvrdy, K.; Takechi, K.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2008**, *130*, 4007. (12) Zhu, K.; Neale, N. R.; Miedaner, A.; Frank, A. J. *Nano Lett.* **2007**,
- . 69
- (13) Boercker, J. E.; Enache-Pommer, E.; Aydil, E. S. Nanotechnology 2008, 19, 095604.
- (14) Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. Nano Lett. 2006, 6, 215.
- (15) Leschkies, K. S.; Divakar, R.; Basu, J.; Enache-Pommer, E.; Boercker, J. E.; Carter, C. B.; Kortshagen, U. R.; Norris, D. J.; Aydil, E. S. *Nano Lett*. **2007**, *7*, 1793.
- (16) Liu, B.; Aydil, E. S. J. Am. Chem. Soc. 2009, 131, 3985.

complementary hydroxyl groups on the TiO₂ surface. The PCE of solar cells produced using 14-µm-thick TiO₂ nanotube arrays under simulated AM 1.5 G irradiation of 100 mW/cm² in backside illumination mode raised from 4.34% to 7.37% after immersion in the TiCl₄ solution followed by exposure to O_2 plasma. The TiCl₄ and O₂ plasma exposure processes led to increased photogenerated current and fill factor, ultimately, a higher PCE. To the best of our knowledge, the PCE of 7.37% is highest performance among dye-sensitized TiO₂ nanotube solar cells reported, thereby offering an avenue in developing high-efficiency solar cells for renewable energy production.

Experimental Section

Fabrication of TiO₂ Nanotube Arrays. High-purity Ti foil (250 µm thick, 99.7% purity, Sigma-Aldrich) was cut into pieces, each 1 in. \times 0.5 in. in size, and degreased by ultrasonication for 30 min in a mixture of acetone, methanol, and methylene chloride, followed by a thorough rinse with deionized (DI) water and blow-dried with N₂. Ethylene glycol (Fisher Scientific) was used as the electrolyte in which a small amount of ammonium fluoride (Sigma-Aldrich) was added. Electrochemical anodization of titanium was performed in a two-electrode cell at room temperature using a EC570-90 power source (Thermo Electron Corporation) at 60 V. A platinum foil was used as the counter electrode. After anodization, the Ti foil with TiO₂ nanotubes grown on one side of its surface was extensively washed with DI water and dried with N2 (the backside of the Ti foil was protected with a layer of insulate resin to prevent oxidation during the anodization process).

Surface Treatment. Prior to dye adsorption, anatase TiO₂ nanotubes were processed with TiCl₄ by immersing them in 50 mL of 0.2 M TiCl₄ aqueous solution in a beaker sealed with parafilm and kept in a 60 °C oil bath for 1 h, followed by rinsing with ethanol and annealed at 500 °C in air for 30 min. The TiCl₄treated TiO₂ nanotubes were further exposed to O₂ plasma at 30 W of power for different times.

TiO₂ Nanotube Solar Cell Fabrication. The surface-treated TiO₂ nanotube arrays were then immediately soaked in a 0.2 mM dye/ethanol solution for 24 h to allow complete dye adsorption. The dye used in the study was cis-diisothiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N-719, Solaronix). A semitransparent platinum (Pt)-coated ITO glass was used as the counter electrode, prepared by placing a drop of 0.5 mM chloroplatinic acid (H₂PtCl₆)/isopropanol solution on ITO glass and subsequently fired at 380 °C for 20 min. The dye-sensitized TiO₂ nanotube arrays were sandwiched between the Ti foil (anode) and the Ptcoated ITO glass (cathode) by applying a 25- μ m-thick hot-melt sealing foil as the spacer (SX1170-25, Solaronix). 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) (No. ES-0004, purchased from io.li.tec, Germany) was injected between two electrodes driven by capillary force through holes on the hot-melt sealing foil. The ionic liquid possesses high thermal stability, negligible vapor pressure, and low toxicity. The backside of the Ti foil was then scratched using sandpaper to remove the thin oxide layer, thereby exposing the underlying titanium that serves as the electrode.

Characterization. Scanning electron microscopy (SEM) imaging was performed with a JEOL Model LV 5800 microscope.



Figure 1. Structural characterization of highly ordered TiO₂ nanotube arrays: (a) SEM topology, scale bar = 1 μ m; (b) SEM cross-sectional view, scale bar = $10 \mu m$; (c) SEM cross-sectional view, scale bar = $1 \mu m$; and (d) Raman spectra of amorphous (black curve) and crystalline (red curve) TiO₂ nanotube arrays, where the Raman peaks at 145, 196, 399, 516, and 640 cm^{-1} suggest the formation of anatase TiO₂.

Raman spectroscopy measurements were performed using a Renishaw inVia Raman microscope excited with a 488-nm Ar^+ laser at 5 mW with an acquisition time of 10 s. The current-voltage (I-V) curves were measured using a Keithley Model 2400 multisource meter. A solar simulator (SoLux Solar Simulator) was used to simulate sunlight, with an illumination intensity of 100 mW/cm² (calibrated with Daystar Meter). The photoactive area for all solar cells was 0.125 cm^2 .

Results and Discussion

Highly ordered TiO₂ nanotube arrays were fabricated according to our previously reported procedure.¹⁷⁻¹⁹ The SEM images of as-prepared TiO₂ nanotube arrays are shown in Figures 1a-c. The nanotubes had an average inner diameter of 90 nm and an interpore distance of 120 nm (see Figures 1a and 1c). The membrane thickness can be readily controlled by the anodization time; the cross section of a 14- μ m-thick TiO₂ membrane obtained after 2 h of anodization is shown in Figure 1b. We note that TiO₂ nanotube arrays with thicknesses of 22 and 29 μ m were obtained after 3 h and 4 h of anodization, respectively. The as-prepared TiO₂ nanotubes were amorphous. To take advantage of nanotubular structures for use in solar cells, they should be converted to crystalline forms, i.e., anatase or rutile phase. The crystalline phase, induced by thermal annealing at 500 °C in air for 3 h,¹⁹ was confirmed by Raman spectroscopy. A broad spectrum was seen on amorphous TiO₂ nanotubes. By contrast, specific Raman peaks at 145, 196, 399, 516, and 640 cm^{-1} were





observed from annealed TiO2 nanotube arrays, signifying the formation of anatase TiO_2 (see Figure 1d).¹⁹ The TiO_2 nanotubular structures were maintained after high-temperature annealing.¹⁹

Anatase TiO₂ nanotube arrays were then utilized as photoanodes to assemble dye-sensitized nanostructured solar cells (see Scheme 1). Prior to dye adsorption, the nanotubes were processed with TiCl₄ using 0.2 M TiCl₄ aqueous solution.^{14,16} Subsequently, the TiCl₄-treated TiO_2 nanotube arrays were exposed to O_2 plasma for different time. The N-719 dye-sensitized TiO₂ nanotube solar cells were assembled and the performance was measured (see the Experimental Section).

Figure 2 shows the effects of TiCl₄ treatment on the I-V characteristics of dye-sensitized TiO₂ nanotube solar cells. The thickness of TiO₂ nanotube arrays was 14 μ m. For solar cell without subjecting to TiCl₄ processing, the measurement yielded an open circuit voltage $(V_{\rm OC})$ of 0.70 V, a short circuit current density $(J_{\rm SC})$ of 12.16 mA/cm², and a fill factor (FF) of 0.51; thus, the power conversion efficiency (PCE), which is defined as

⁽¹⁷⁾ Wang, J.; Lin, Z. Chem. Mater. 2008, 20, 1257.

 ⁽¹⁸⁾ Wang, J.; Lin, Z. Q. J. Phys. Chem. C 2009, 113, 4026.
 (19) Wang, J.; Zhao, L.; Lin, V. S. Y.; Lin, Z. Q. J. Mater. Chem. 2009, 19, 3682.



Figure 2. Current–voltage (I-V) characteristics of dye-sensitized TiO₂ nanotube solar cells. The thickness of TiO₂ nanotube membrane was $14 \,\mu\text{m}$. (a) the device in the dark; anatase TiO₂ nanotube arrays were not treated with TiCl₄ (the devices with and without TiCl₄ treatment were indistinguishable in the dark); (b) the device made of anatase TiO₂ nanotube arrays without TiCl₄ treatment under AM 1.5 G illumination, yielding a fill factor (FF) of 51% and power conversion efficiency (PCE) of 4.34%; and (c) the device made of the TiCl₄-treated TiO₂ nanotube arrays under AM 1.5 G illumination, yielding values of FF = 68% and PCE = 6.36%.

PCE = $\frac{I_{SC}V_{OC}FF}{D}$ is 4.34% (see curve b in Figure 2). In contrast, when TiCl₄-treated TiO₂ nanotube arrays were used, the performance sharply increased, yielding values of $V_{\rm OC} = 0.75$ V, $J_{\rm SC} = 12.48$ mA/cm², FF = 0.68, and PCE = 6.36% (see curve c in Figure 2), which represents a 47% increase in PCE, when compared to its non-TiCl₄treated counterpart (see curve b in Figure 2). The performance improvement can be rationalized as follows. Upon high-temperature annealing, there existed structural defects and cracks on the nanotubes, as well as on the barrier layer (i.e., structural disorders),^{17,20} which made it possible for the electrolyte to have direct contact with the Ti electrode on the bottom, leading to decreased shunt resistance and higher chance for charge recombination. By contrast, with TiCl₄ treatment, a thin blocking layer of TiO_2 can be formed on the uncovered region of Ti foil,¹⁶ thus reducing or eliminating the structural disorders. As a consequence, the shunt resistance increased and series resistance decreased; this improved the FF value, and, ultimately, a higher PCE was obtained.¹⁶ With TiCl₄ treatment, the increased electron transport through a TiO₂ nanotube wall to the bottom Ti electrode by decreasing the surface charge recombination, as well as the increased dye adsorption by facilitating improved bonding between TiO₂ and dye molecules, may also contribute to the enhanced performance.^{14,16}

 O_2 plasma treatment has been demonstrated as an effective approach to saturate the metal oxide surface with hydroxyl group,²¹ which increases the hydrophilicity at the metal oxide surface.¹⁵ In this regard, to further improve the performance of dye-sensitized nanostructured solar cells, O_2 plasma exposure was performed on the TiCl₄-treated TiO₂ nanotubes prior to infiltration of dye N-719. Specifically, the aforementioned TiCl₄-treated, 14- μ m-thick TiO₂ nanotube arrays were placed in an O₂ plasma cleaner (Harrick Plasma Model PDC-001;

a PlasmaFlo gas meter was used to control the O₂ flow in the reaction chamber). The plasma condition was optimized by tuning the O2 flow and vacuum until the brightest fluorescence was observed, i.e., with the O2 flow of 1 SCFH and a vacuum of 500 mTorr. After plasma exposure for different periods of time, TiO₂ nanotubes were immersed in the 0.2 mM N-719/ethanol solution for 24 h. All other steps for the construction of solar cells and the performance measurements were maintained the same. The I-V curves of resulting solar cells are shown in Figure 3. In comparison to curve c in Figure 2, in which TiO_2 nanotubes were not subjected to O_2 plasma (PCE = 6.36%), the PCE increased to 6.48% after 1 min O_2 plasma treatment. With longer time exposure to O_2 plasma, the PCE increased; the highest PCE value of 7.37% was achieved from the 10-min O_2 plasma-treated sample (see Table 1 for complete device characterization). The enhancement in PCE can be attributed to a large increase in the photocurrent density (J_{SC}) , while the photovoltage (V_{OC}) did not change much and the fill factor (FF) slightly decreased. Upon O₂ plasma treatment, the hydroxyl group on the TiO_2 surface increased and eventually saturated; this promoted the adsorption of the N-719 dye by forming interfacial bonding between N-719 and the TiO_2 via the coupling reaction of terminal carboxylic acid groups on N-791 with complementary hydroxyl groups on the TiO₂ surface, thereby substantially regulating the interfacial charge transfer from N-719 dye to TiO_2 and, therefore, the ultimate photophysical properties at the nanoscale.

Note that, upon lengthy O_2 plasma exposure (e.g., 20 min; see Figure 3d and Table 1), the device performance decreased, exhibiting a largely reduced J_{SC} value, compared to the sample after 10 min of O₂ plasma exposure (see Figure 3c and Table 1). The exact reason for this observation is not clear. It may be because the TiO₂ surface became less hydrophilic after a longer-time plasma exposure than that under the optimized condition.²² Consequently, the dye loading was reduced, which, in turn, the decreased device performance. Similar trends were seen in solar cells assembled using 22- and 29- μ m-hick TiO₂ nanotube arrays, that is, the PCE increased with time when nanotubes were subjected to O_2 plasma for < 10 min; otherwise, the PCE was reduced (see Table 1 and Figure S1 in the Supporting Information).

We note that increasing the thickness of TiO₂ nanotube arrays may be a good strategy to improve the performance of solar cells by allowing more dye molecules to be adsorbed on the TiO₂ nanotube surface and, thus, a higher light harvesting efficiency. To this end, thicker TiO₂ nanotube arrays 22 and 29 μ m in thickness were prepared and used to fabricate solar cells; they were processed with TiCl₄ and oxygen plasma. Quite intriguingly, the use of thicker TiO₂ nanotube arrays yielded progressively decreased performance (PCE = 6.29% for

⁽²⁰⁾ Zhu, K.; Vinzant, T. B.; Neale, N. R.; Frank, A. J. Nano Lett. 2007, 7, 3739.

⁽²¹⁾ Tsoi, S.; Fok, E.; Sit, J. C.; Veinot, J. G. C. *Langmuir* 2004, 20, 10771.

⁽²²⁾ Lu, D.; Wu, Y.; Guo, J. H.; Lu, G.; Wang, Y.; Shen, J. C. Mater. Sci. Eng. B 2003, 97, 141.



Figure 3. I-V characteristics of dye-sensitized TiO₂ nanotube arrays assembled using TiCl₄- and oxygen-plasma-treated, 14- μ m-thick TiO₂ nanotube arrays, for oxygen plasma exposures of (a) 1 min, (b) 2 min, (c) 10 min, and (d) 20 min.

Table 1. Summary	of the D	evice Performance	of Dye-Sensitized	TiO ₂ Nanotube Solar	Cells
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TiCl ₄	O ₂ plasma exposure time (min)	open circuit voltage, $V_{\rm OC}$ (V)	short-circuit current density, $J_{\rm SC}~({\rm mA/cm^2})$	fill factor, FF	power conversion efficiency, PCE (%)
		TiO ₂	Nanotube Thickness = $14 \mu m$		
no	0	0.70	12.16	0.51	4.34
ves	0	0.75	12.48	0.68	6.36
ves	1	0.81	11.76	0.68	6.48
ves	2	0.74	13.36	0.68	6.72
ves	10	0.77	15.44	0.62	7.37
yes	20	0.76	12.45	0.62	5.87
		TiO ₂	Nanotube Thickness = $22 \mu m$		
ves	0	0.73	8.10	0.63	3.73
ves	1	0.67	8.48	0.67	3.81
ves	2	0.75	8.30	0.69	4.29
ves	5	0.72	9.2	0.71	4.70
ves	10	0.77	11.84	0.69	6.29
yes	20	0.72	9.6	0.70	4.84
		TiO ₂	Nanotube Thickness = $29 \mu \text{m}$		
yes	10	0.75	11.52	0.70	6.05

22- μ m-thick nanotubes and PCE = 6.05% for 29- μ m-thick nanotubes; see Table 1), compared to the device produced using 14- μ m-thick nanotubes (PCE = 7.37%). The *I*-*V* characteristics of solar cells assembled using 14-, 22-, and 29- μ m-thick TiO₂ nanotubes are shown in Figures 4a, 4b, and 4c, respectively. For the 22- μ m-thick TiO₂ nanotube arrays, although the device performance increased as a function of O₂ plasma exposure time (see Table 1 and Figure S1 in the Supporting Information), the PCE value was less than that using 14- μ m-thick TiO₂ nanotubes. When even thicker TiO₂ nanotube arrays were used (i.e., 29 μ m), the PCE value decreased further. The decrease in PCE with increased TiO₂ thickness may be likely due to the limitations of the current device configuration, as depicted in Scheme 1. In the backside

illumination mode, the incident photons had to pass through semitransparent platinum-coated ITO glass and the ionic liquid electrolyte (i.e., ES-0004). Thus, a portion of incident photons was lost before reaching the sensitizer N-719 dye and the photoanode TiO₂ nanotube arrays. Therefore, as the thickness of nanotubes increased, the remaining photons may be fully absorbed by the dyes that were anchored on the top part of TiO₂ nanotube; however, the dyes on the bottom part of nanotubes will not be excited. A solution to this problem may be the use of freestanding TiO₂ nanotube arrays (i.e., detached from Ti foil after anodization)¹⁷ or TiO₂ nanotubes directly grown on transparent conductive substrate^{7,14} in a front-side illumination mode, where the dye-adsorbed TiO₂ nanotube arrays are directly



Figure 4. Effects of thickness (h) of TiO₂ nanotube arrays on I-V characteristics of dye-sensitized TiO₂ nanotube solar cells. All the TiO₂ nanotubes were treated with TiCl₄ and 10 min of O₂ plasma exposure prior to N-719 dye adsorption: (a) $h = 14 \,\mu$ m and PCE = 7.37%; (b) $h = 22 \,\mu$ m and PCE = 6.29%; and (c) $h = 29 \,\mu\text{m}$ and PCE = 6.05%.

illuminated from the TiO₂ nanotube arrays before incident photons encounter the electrolyte and the counter electrode,¹⁴ thereby ensuring good light harvesting efficiency. Note that, currently, both transferring mechanically brittle freestanding TiO₂ nanotube arrays to solid transparent substrates by detaching them from Ti foil and directly growing thick TiO₂ nanotube arrays on transparent substrates remain challenging for us. In the later context, the direct growth of TiO₂ nanotubes on transparent substrate was hindered by the difficulty in depositing thick, high-quality Ti films at the moment.^{7,23} In addition to the constraint imposed by the device configuration, the one-side-open nature of TiO₂ nanotubes may cause air to be trapped inside, making it, probably, less accessible by the dye and the electrolyte; moreover, with the increased thickness of nanotubes, longer pathways for electron and hole transport to electrodes may result in a higher chance for charge recombination. These compensate the advantage of using O₂ plasma to increase the surface hydrophilicity of TiO₂ nanotubes and facilitate the infiltration of dyes and electrolytes. Taken together, the device performance decreased as the nanotube thickness increased.

Conclusions

In summary, we have assembled ruthenium dye (N-719)sensitized nanostructured solar cells, using highly ordered anodic TiO₂ nanotube arrays as the photoanode. Rational surface engineering on TiO2 nanotubes with TiCl4 treatment together with O_2 plasma activation under optimized

condition dramatically enhanced the performance of resulting devices. A solar cell in backside illumination mode produced using 14- μ m-thick TiO₂ nanotube arrays after surface treatments with TiCl₄ and O₂ plasma yielded a power conversion efficiency (PCE) of 7.37%, which is the highest promising efficiency for solar cells made of TiO₂ nanotube arrays reported in the literature. The use of thicker TiO₂ nanotube arrays did not give rise to higher performance, as expected. We attribute this observation to the limitation of current device configuration, as well as the possible air trapped in one-side-open nanotubes. In addition to ruthenium-based organic dyes, in principle, conjugated homopolymers (e.g., regioregular poly(3-hexyl thiophene)), conjugated block copolymers, and semiconducting nanocrystals (e.g., quantum dots)^{24,25} can be employed as alternative photosensitizers to create a variety of dye-sensitized TiO_2 nanotube solar cells. This work is currently under investigation. Such rational design and materials engineering of dye-sensitized TiO2 nanotube solar cells create new opportunities for understanding and manipulating the molecular and electronic pathways of solar energy conversion.

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Supporting Information Available: I-V characteristics of dye-sensitized TiO₂ nanotube solar cells in which the nanotube arrays were treated with TiCl4 before exposure to O2 plasma for different period of time. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽²³⁾ Shankar, K.; Bandara, J.; Paulose, M.; Wietasch, H.; Varghese, O. K.; Mor, G. K.; LaTempa, T. J.; Thelakkat, M.; Grimes, C. A. Nano Lett. 2008, 8, 1654.

⁽²⁴⁾ Sun, W. T.; Yu, Y.; Pan, H. Y.; Gao, X. F.; Chen, Q.; Peng, L. M. J. *Am. Chem. Soc.* **2008**, *130*, 1124. Gao, X. F.; Li, H. B.; Sun, W. T.; Chen, Q.; Tang, F. Q.; Peng, L.

⁽²⁵⁾ M. J. Phys. Chem. C 2009, 113, 7531.