

# Size-Tunable, Fast, and Facile Synthesis of Titanium Oxide Nanotube Powders for Dye-Sensitized Solar Cells

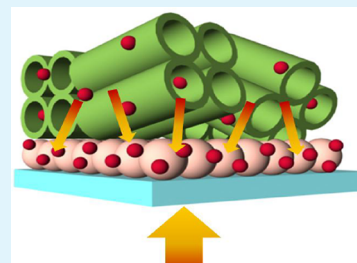
Kun Seok Lee,<sup>†</sup> Jeong Kwon,<sup>†</sup> Jeong Hyeok Im,<sup>†</sup> Chang Ryul Lee,<sup>†</sup> Nam-Gyu Park,<sup>†</sup>  
and Jong Hyeok Park<sup>\*,†,‡</sup>

<sup>†</sup>School of Chemical Engineering and <sup>‡</sup>SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea

## Supporting Information

**ABSTRACT:** Size-tunable titanium oxide (TiO<sub>2</sub>) nanotube powders offering both a light-scattering effect and a light-harvesting function were synthesized by a fast and facile anodizing method. When used to prepare the TiO<sub>2</sub> layer for a photoanode, their photovoltaic performances were much worse than that of a nanocrystal TiO<sub>2</sub> layer. However, when the TiO<sub>2</sub> nanotube powders were used as a light-scattering layer on a nanocrystal TiO<sub>2</sub> layer, the highest conversion efficiency was obtained because of more noticeable light absorption of the longer wavelength, which was not attainable from a pure nanocrystal TiO<sub>2</sub> layer or the combination of nanocrystal TiO<sub>2</sub>/commercialized light-scattering particles.

**KEYWORDS:** dye-sensitized solar cells, nanotube arrays, powder, light-scattering layer



## INTRODUCTION

With growing interest for green energy and alternative solar cell technologies, dye-sensitized solar cells (DSSCs) are of widespread interest as a cost-effective photovoltaic system. Typical DSSCs consist of thermally interconnected nc-TiO<sub>2</sub>, dye as a sensitizer, iodine/iodide electrolytes, and thin platinum (Pt) counter electrodes. Such device systems are generally less expensive than conventional silicon-based photovoltaic devices.<sup>1,2</sup> nc-TiO<sub>2</sub> nanoparticles provide a medium for electron transport, a stabilized interface with dye molecules, and contact points between the dye and electrolyte. Hence, the ability to control the structural characteristics of nc-TiO<sub>2</sub> photoelectrodes is crucial to maximize the cell efficiency. Because the surface area of nc-TiO<sub>2</sub> photoanodes has been considered to be very important, conventional nc-TiO<sub>2</sub> photoelectrodes are made of randomly networked and interconnected nc-TiO<sub>2</sub> nanoparticles with thicknesses in the range of 5–20 μm.<sup>3</sup> Although mesoporous films produced from nc-TiO<sub>2</sub> nanoparticles enable high-density loading of dye molecules, resulting in a large photocurrent density, such films generally exhibit a high transparency, which results in a decrease in the usage of visible light.<sup>4</sup> One effective method to increase the light harvesting efficiency is introducing other light scatters into the photoelectrode. A bilayer structure with a light-scattering film composed of ~400 nm sized particles has been widely adopted because it confines the incident light within an electrode and thereby enhances the light path length.<sup>5–10</sup> However, submicrometer-sized light-scattering particles barely aid light harvesting from charge generation because the number of dye molecules that can be adsorbed on these particles is much smaller than that on nc-TiO<sub>2</sub> nanoparticles because of their much smaller surface area.

Generally, conventional nc-TiO<sub>2</sub> nanoparticles have been prepared by a hydrothermal process that requires a reaction time of about 20 h at a high temperature of ~230 °C.<sup>11</sup> Therefore, it is a time-consuming process and a major obstacle in the commercialization of DSSCs. Moreover, the process also has some drawbacks including superfluously extended and nonoptimized electron transport paths among nc-TiO<sub>2</sub> nanoparticles due to randomly and irregularly distributed pores. To date, several research groups have reported the use of an electron collecting layer with the aid of one-dimensional semiconductor nanostructures such as nanorods,<sup>12–16</sup> nanowires,<sup>17–19</sup> and nanotubes<sup>20–23</sup> in DSSCs. These 1D structured materials can result in efficient electrical pathways from the TiO<sub>2</sub> to the transparent conducting oxide (TCO) electrode. As a result, reduced charge carrier recombination has been reported. Recently, several approaches have taken advantage of macroscale morphologies with typical feature sizes on the order of 100 nm.<sup>24,25</sup> However, since the surface areas of one-dimensional nanostructures and macropores are relatively small compared to that of zero-dimensional nanoparticles, the amount of dye adsorption and photoexcited electrons are limited as well. More importantly, the synthetic scheme of 1D macroporous materials is more complicated than the nc-TiO<sub>2</sub> nanocrystal system.

Therefore, in order to realize highly efficient DSSCs and eliminate the time-consuming TiO<sub>2</sub> synthesis step, it is required to develop a new synthetic scheme for TiO<sub>2</sub> photoelectrodes. Recently, a new synthetic scheme for vertically aligned TiO<sub>2</sub> nanotube (NT) arrays using an anodizing process has been

Received: May 18, 2012

Accepted: July 10, 2012

Published: July 10, 2012

utilized to realize highly efficient DSSCs.<sup>20–23</sup> However, the anodizing process takes several hours and the TiO<sub>2</sub> NT arrays have generally been formed on a nontransparent Ti substrate, requiring that back illumination to be used to operate the DSSCs.<sup>26</sup> The “detachment-transfer” technique for TiO<sub>2</sub> NT arrays directly grown on a FTO substrate has been recently proposed to construct front-illumination DSSCs.<sup>27</sup> However, this method is not a suitable approach for the commercialization of large-area TiO<sub>2</sub> NT-based DSSCs.

In this study, we made DSSCs using TiO<sub>2</sub> NT array powder synthesized within a very short time (several minute) as new light-scattering particles.<sup>28</sup> The as-prepared powders have a large particle size ranging from several micrometers to several tens of micrometers. This material is not acceptable as the light-scattering layer in DSSCs. We developed a preparation method to tear the aggregated TiO<sub>2</sub> NT arrays in the powder and demonstrated their potential for use as a light-scattering layer in DSSCs. Since our powders consist of a TiO<sub>2</sub> NT array structure, the particles possess a high surface area comparable to conventional TiO<sub>2</sub> nanoparticles.

## EXPERIMENTAL SECTION

### Preparation of TiO<sub>2</sub> Nanotube Powders and Pastes.

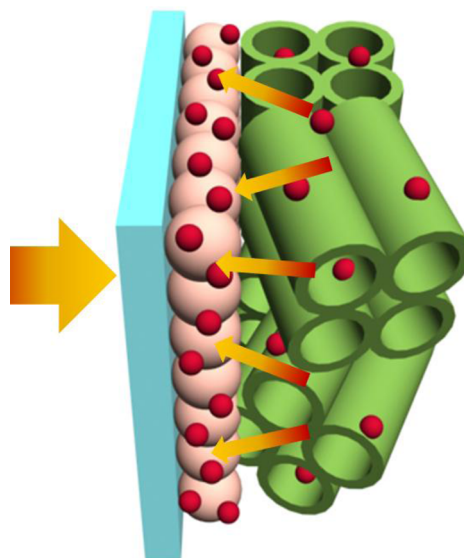
Amorphous TiO<sub>2</sub> NT powders were synthesized via an anodizing method using Ti foil. The Ti foil was cleaned by isopropyl alcohol and then anodized at 20 V in a 0.1 M HClO<sub>4</sub> solution using a platinum foil as a cathode for 5–10 min, as described previously.<sup>28</sup> Then, the powders were milled by zirconia beads as described in results and discussion part. The synthesized TiO<sub>2</sub> NT powders were washed using a centrifuge in DI water for 4–5 times, and then dried at 50 °C in oven. TiO<sub>2</sub> NT arrays powders were dispersed in  $\alpha$ -terpineol with ethyl cellulose as a binder to prepare NT based paste.

**Fabrication of Dye-Sensitized Solar Cells (DSSCs).** The fluorine–tin-oxide (FTO) glass substrate was rinsed with acetone, ethanol, and deionized water each for 10 min and dried under nitrogen. Then, a barrier layer was coated on the FTO substrate with titanium tetrachloride (TiCl<sub>4</sub>, Aldrich) at 70 °C for 30 min and then rinsed with ethanol. Double layers of TiO<sub>2</sub> films were used as photoanodes. High surface area layer of TiO<sub>2</sub> paste (EnB Korea) was first printed onto a FTO substrate. Then, second light-scattering layer composed of TNT powders was overcoated on the nc-TiO<sub>2</sub>/FTO substrate. After heat treatment at 550 °C for 30 min, the TiO<sub>2</sub> films were treated with 20 mM TiCl<sub>4</sub> at 70 °C for 30 min again. Then, the nanocrystalline TiO<sub>2</sub> electrodes were immersed in a 50 mM N719 solution. Pt-based counter electrodes were prepared by coating a FTO substrate with a drop of H<sub>2</sub>PtCl<sub>6</sub> and subsequent heat treatment at 400 °C for 15 min. The dye-adsorbed nanocrystalline TiO<sub>2</sub> electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a molten polymer film (Surlyn, Dupont 1702). A drop of the electrolyte solution was introduced into a hole drilled in the counter electrode of the assembled cell followed by sealing the holes using a microcover glass and Surlyn. The electrolyte was composed of 0.6 M butylmethylimidazolium iodide, 0.03 M I<sub>2</sub>, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85:15).

**Characterization.** Images of the TiO<sub>2</sub> powders were obtained by SEM (JEOL JSM-7500F, Japan) to investigate the morphologies of the synthesized TiO<sub>2</sub> NT arrays powders. The surface area and pore volume of the TiO<sub>2</sub> films were analyzed by an ASAP chemisorption analyzer (Micromeritics, ASAP2020). The photovoltaic properties of the solar cells were measured using a Keithley model 2400 source measuring unit under 100 mW cm<sup>-2</sup> illumination using a 1,000 W xenon lamp (Spectra-Physics) as the light source. The IPCE was measured as a function of the wavelength ranging from 400 to 800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV Measurement, Inc.).

## RESULTS AND DISCUSSION

A schematic describing the device structure of DSSCs is shown in Figure 1. First, amorphous TiO<sub>2</sub> NT powders were

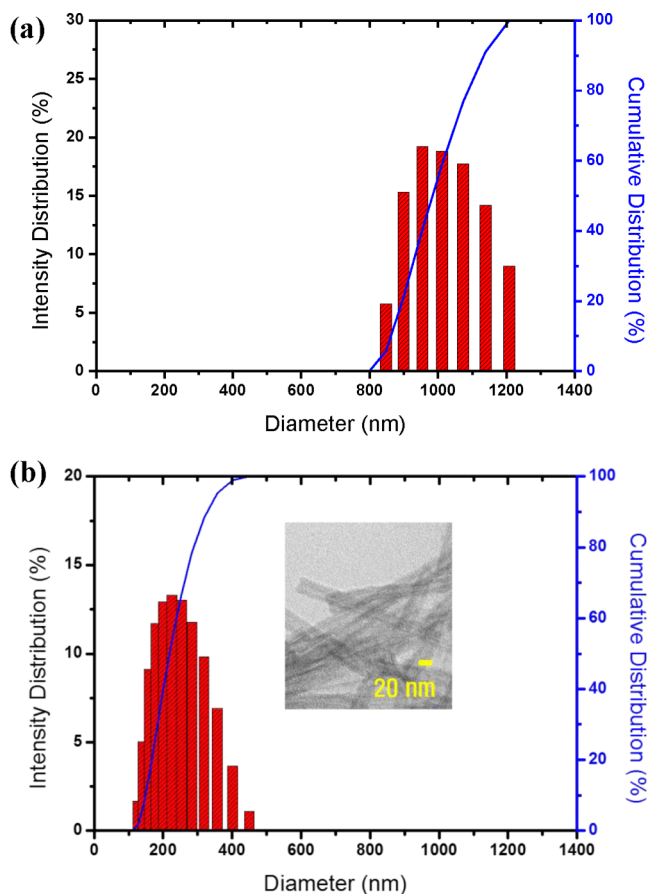


**Figure 1.** Schematic of the TiO<sub>2</sub> NT powder-based light-scattering layer on a preformed TiO<sub>2</sub> nanoparticle electrode.

synthesized via an anodizing method from Ti foil. The as-prepared TiO<sub>2</sub> NT powders have a relatively larger particle size, ranging from 800 nm to 1200 nm (Figure 2a). In this study, one of the main functions of the TiO<sub>2</sub> NT powder is its light-scattering effect. The light-scattering effect in DSSCs has also been investigated theoretically where it was proposed that the scattering effect should be largest when the particle size is about  $k\lambda$ , where  $k$  is a constant and  $\lambda$  is the wavelength. In other words, the light-scattering efficiency is correlated to the size of the scattering particles in relation to the size of the wavelength of the incident solar light.<sup>29,30</sup> Hence, the optimum particle diameter of the light-scattering layer is between 300 and 500 nm.<sup>31</sup> To obtain a particle size between 300 and 500 nm, the TiO<sub>2</sub> NT powder was mixed with a 24 vol.% acetic acid aqueous solution and mechanically milled by 0.85 mm zirconia beads for the trituration of the TiO<sub>2</sub> NT powder. The NT powder was then obtained by centrifugation followed by washing several times using distilled water and drying overnight at 50 °C.

The resulting particle size of the TiO<sub>2</sub> NT powders was between 100 and 500 nm after the acid treatment method, as shown in the image in Figure 2b. The TiO<sub>2</sub> NT arrays powders were dispersed in  $\alpha$ -terpineol with ethyl cellulose as a binder to prepare the TiO<sub>2</sub> NT paste. The submicrometer-sized powder has a very large surface area because of the TiO<sub>2</sub> NT bundle inside the NT powders. As a result, the generated electrons in the TiO<sub>2</sub> NT scattering layer can contribute to the total photocurrent. The inset in Figure 2a shows scanning electron microscopic (SEM) images of the as-anodized TiO<sub>2</sub> NT particles consisting of NT bundles whose structure may contain nanopores and macropores. Macropores can be generated on the inside of the NTs and nanopores can be formed due to the interdistance between the NTs.

To quantitatively compare the synthesized NT particles and commercial nanoparticles (NP, P-25), we adopted the



**Figure 2.** Particle size distributions of the TiO<sub>2</sub> NT powders (a) before and (b) after the ball-milling process in an acidic solution. Inset figure shows TEM image of the TiO<sub>2</sub> NT powders after the ball-milling process.

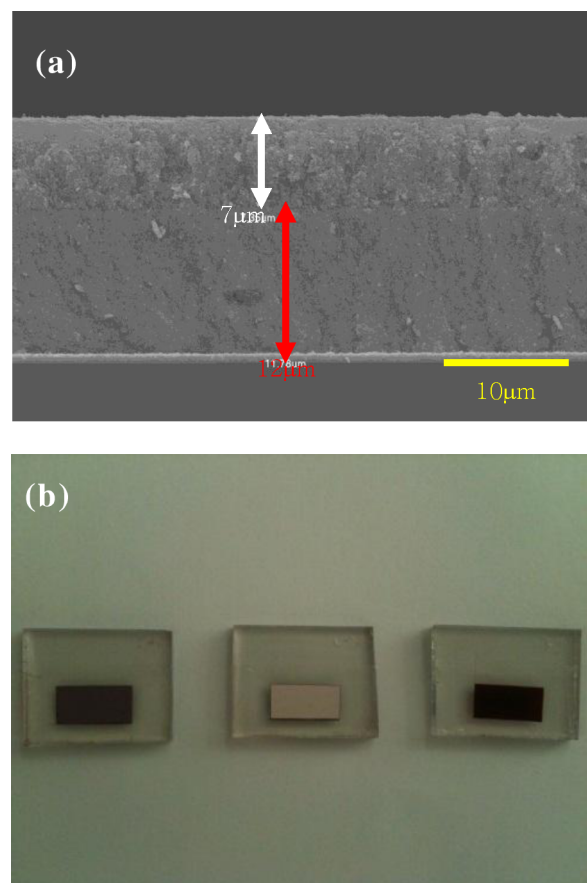
multipoint Brunauer–Emmett–Teller (BET) method to calculate the surface areas. As summarized in Table 1, the

**Table 1.** Specific Surface Area and Dye Adsorption of nc-TiO<sub>2</sub> and TiO<sub>2</sub> Nanotube Powders

	nc-TiO <sub>2</sub> nanoparticles	TiO <sub>2</sub> nanotube powder
BET (m <sup>2</sup> /g)	22.5	46.9
adsorbed dye molecules (mol/cm <sup>3</sup> )	1.551 × 10 <sup>-4</sup>	1.082 × 10 <sup>-4</sup>

NT particles have a much higher specific surface area by more than a factor of 2. The adsorbed amounts of N719 dye were determined by measuring the eluted dye concentration from the TiO<sub>2</sub> photoelectrodes using UV–vis absorption spectroscopy. As shown in Table 1, the NT particle-based photoelectrode resulted in lower volumetric dye adsorption than the NP system. Because the dye absorption should be proportional to the surface area of the TiO<sub>2</sub>, the relatively small amount of volumetric dye absorption is due to the loosely packed film morphology. As a result, when approximately 12 μm thick TiO<sub>2</sub> films were fabricated from 20 nm sized NPs, whose paste was purchased from Dyesol Co., and submicrometer sized NT powders, the conversion efficiency of the NPs photoanode was much higher than that of the NT powder-based DSSCs (Figure 4).

The synthesized NT powders have a novel hierarchical pore structure which can simultaneously provide a large surface area, well oriented tubular structure, and large particle size. SEM cross-sectional images of the TiO<sub>2</sub> NT film on the nc-TiO<sub>2</sub> layer are shown in Figure 3a. To maximize the effectiveness of

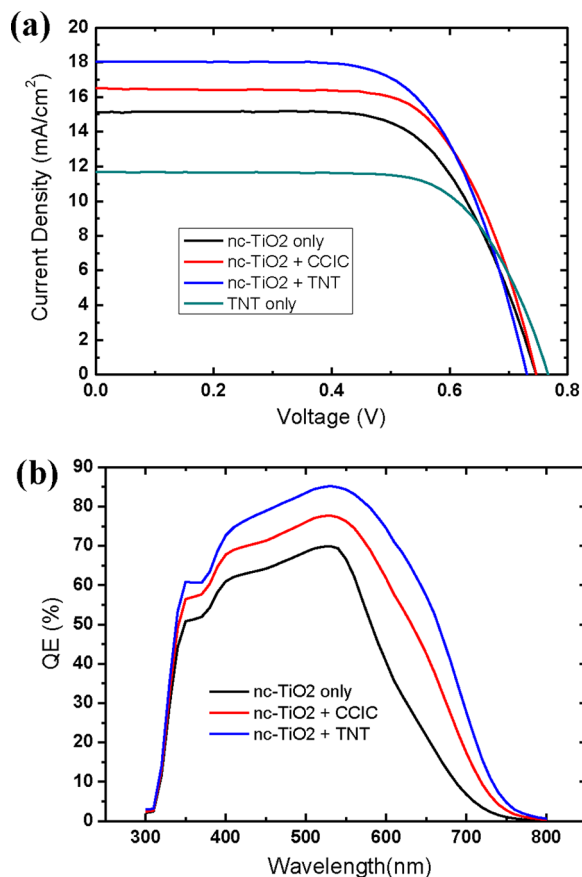


**Figure 3.** (a) Image of the cross-section of the nc-TiO<sub>2</sub>/NT double layer on the FTO substrate. (b) Photos of the photoanode after dye adsorption (left, nc-TiO<sub>2</sub>; middle, nc-TiO<sub>2</sub>/NP scattering layer; right, nc-TiO<sub>2</sub>/NT scattering layer).

the light-scattering layer, we prepared a light-scattering layer on a relatively thin (12 μm) nc-TiO<sub>2</sub> layer. The thickness of the scattering layer deposited on the semitransparent main layer was controlled to be 6–7 μm. For comparison, two additional samples were also prepared: a 12 μm thick nc-TiO<sub>2</sub> layer and a 12 μm -thick nc-TiO<sub>2</sub> layer with 4–5 μm-thick commercialized light-scattering layer (CCIC, Japan). Figure 3b shows pictures of the three different samples after the dye adsorption. From the pictures, it can be concluded that the commercial CCIC scattering layer cannot act as a light absorption layer like the TiO<sub>2</sub> NT film.

The photovoltaic performances of the DSSCs containing the different photoanodes are shown in Figure 4a. It can be seen that the short circuit current ( $J_{sc}$ ) of the DSSC with the single nc-TiO<sub>2</sub> layer in the photoanode is 15.1 mA/cm<sup>2</sup>. When the commercialized light-scattering film was added as the second layer, the DSSC demonstrated a  $J_{sc}$  value of 16.5 mA/cm<sup>2</sup>. Conspicuously, the DSSC containing the TiO<sub>2</sub> NT film as a light-scattering layer resulted in a  $J_{sc}$  as high as 18.05 mA/cm<sup>2</sup>. The increment of the  $J_{sc}$  value was also confirmed by the IPCE performance results shown in Figure 4b. As a result, the cell

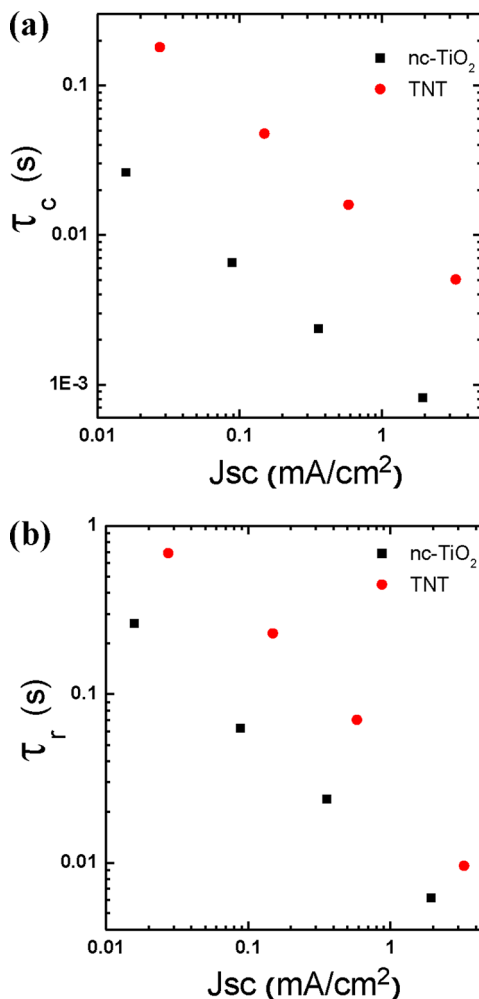




**Figure 4.** (a)  $J$ - $V$  characteristics and (b) IPCE of the DSSCs with different TiO<sub>2</sub> layers.

efficiency ( $\eta$ ) was improved to 8.7%. To investigate the effect of the particle size distribution of the TiO<sub>2</sub> NT powder on the light scattering in the DSSCs, we also fabricated DSSCs using the as-synthesized TiO<sub>2</sub> NT powder as the scattering layer. As shown in the Supporting Information, the effectiveness of the as-synthesized TiO<sub>2</sub> NT powder as the scattering layer was much worse than that of the TiO<sub>2</sub> NT powder treated with an acidic solution under mechanical crushing.

The transport and recombination behaviors of the pure NT powder- and NP-based DSSCs as a function of the incident photon flux ( $J_{sc}$ ) are shown in panels a and b in Figure 5, respectively. The thicknesses of the NT and NP films in the cells were about 10  $\mu\text{m}$ . For both DSSCs, the  $\tau_c$  values exhibited a power-law dependence on the light intensity. It is surprising that the transport time of the NT-based DSSC is larger than that of the NP-based DSSC because it is well-known that the 1D nanostructure should have much faster charge transport characteristics than randomly packed NP films for a given film thickness. Presumably, this behavior is attributed to the loosely packed film morphology in the NT powder photoanode. The electron diffusion coefficient,  $D$ , can be calculated using the expression  $D = L^2/2.35\tau_c$ .<sup>32</sup> The NT photoanode has a shorter electron diffusion length than the NP photoanode. Figure 4d shows that the recombination time constants,  $\tau_r$ , for the NT arrays have much higher time constant than those for the NP films over the light intensity range investigated. The large recombination time constant could indicate that the potential surface recombination sites in the NT is much less than NP photoanodes. Generally, the charge collection efficiency ( $\eta_{cc}$ ) can be expressed using the relation-



**Figure 5.** Comparison of (a) transport and (b) recombination time constants of the pure nc-TiO<sub>2</sub> and TiO<sub>2</sub> NT films as a function of the incident photon flux.

ship  $\eta_{cc} = 1 - \tau_c/\tau_r$ .<sup>33</sup> From the equation, the light-scattering film based on NTs must have a relatively lower charge correction efficiency compared to the NP-based photoelectrode. Nevertheless, the NP/NT double layer photoanode showed considerably higher cell efficiency than that of pure NP-based photoanode because the NT light-scattering layer can increase the light absorption ability of the photoanode, which was confirmed by the  $J$ - $V$  characteristics. One may expect that electron diffusion can be enhanced by reducing the pore volume of the NT powder-based photoelectrodes by applying post treatment such as pressing. So, the positive effects due to the NT-based light-scattering layer can be further maximized by controlling the porosity of the NT layer.

## CONCLUSIONS

We prepared a TiO<sub>2</sub> NT bundle powder with a controlled particle size. The fabricated TiO<sub>2</sub> electrode from the NT powder provided a novel hierarchical pore structure as well as a large particle size suitable for inducing effective light scattering and the light absorption of the longer wavelength of solar light. The pure TiO<sub>2</sub> NT-based DSSC demonstrated a relatively lower cell efficiency compared to the NP-based DSSC because of the high free volume, which decreases the amount of dye adsorption and the electron diffusion coefficient, as confirmed

by the BET, dye desorption, and frequency-resolved modulated photocurrent/photovoltage spectroscopy analyses. Interestingly, the NP/NT double layer structure demonstrated a considerably higher  $J_{sc}$  value due to the enhanced light scattering as well as the charge generation from the NT light-scattering layer. In addition, because the preparation procedures for the TiO<sub>2</sub> NT powder are simple and low cost, this novel approach is promising as an alternative light-scattering material.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

$J$ - $V$  characteristics of DSSCs with a light-scattering layer based on as-prepared NT powder (without the ball-milling process in an acidic solution) (12  $\mu\text{m}$  nc-NP and 7  $\mu\text{m}$  NT powder scattering). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [lutts@skku.edu](mailto:lutts@skku.edu). Fax: (+82) 31-290-7272.

### Author Contributions

K. S. Lee and J. Kwon contributed equally to this work.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by an NRF grants funded by the Korea Ministry of Education, Science and Technology (MEST) (2009-0092950), the NCRC program (2011-0006268), and Future-based Technology Development program (2010-0029321). N.G.P. acknowledges the New and Renewable Energy Program through the KETEP funded by the Ministry of Knowledge Economy (MKE) (008NPV08J010000). Additional  $J$ - $V$  characteristics of DSSCs with a light-scattering layer based on as-prepared NT powder. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ REFERENCES

- (1) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166.
- (2) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- (3) Miki, T.; Nishizawa, K.; Suzuki, K.; Kato, K. *Mater. Lett.* **2004**, *58*, 2751.
- (4) Wang, Z. S.; Kawauchi, H.; Kashima, T.; Arakawa, H. *Coord. Chem. Rev.* **2004**, *248*, 1381.
- (5) Wei, S.; Feng, G.; Li, G. L.; Li, C. Z. *Chem. Commun.* **2011**, *47*, 5046.
- (6) Qiu, Y. C.; Chen, W.; Yang, S. H. *Angew. Chem., Int. Ed.* **2010**, *122*, 4753.
- (7) Luo, J.; Gao, L.; Sun, J.; Liu, Y. *RSC Adv.* **2012**, *2*, 1884.
- (8) Liao, J. Y.; Lin, H. P.; Chen, H. Y.; Kuang, D. B.; Su, C. Y. *J. Mater. Chem.* **2012**, *22*, 1627.
- (9) Shin, K.; Jun, Y.; Moon, J. H.; Park, J. H. *ACS Appl. Mater. Interfaces* **2010**, *2*, 288.
- (10) Yan, K. Y.; Qiu, Y. C.; Chen, W.; Zhang, M.; Yang, S. H. *Energy Environ. Sci.* **2011**, *4*, 2168.
- (11) Padinger, F.; Brabec, C. J.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Opto-electron. Rev.* **2000**, *8*, 280.
- (12) Liu, B.; Aydil, E. S. *J. Am. Chem. Soc.* **2009**, *131*, 3985.
- (13) Jiu, J.; Isoda, S.; Wang, F.; Adachi, M. *J. Phys. Chem. B* **2006**, *110*, 2087.
- (14) Song, M. Y.; Ahn, Y. R.; Jo, S. M.; Kim, D. Y.; Ahn, J. P. *Appl. Phys. Lett.* **2005**, *87*, 113113.

- (15) Adachi, M.; Yoshida, K.; Kurata, T.; Adachi, T.; Tsuchiya, K.; Mori, Y.; Uchida, F. *J. Mater. Res.* **2012**, *27*, 440.
- (16) Kurata, T.; Mori, Y.; Isoda, S.; Jiu, J. T.; Tsuchiya, K.; Uchida, F.; Adachi, M. *Curr. Nanosci.* **2010**, *6*, 269.
- (17) Feng, X.; Shankar, K.; Varghese, O. K.; Paulose, M.; Latempa, T. J.; Grimes, C. A. *Nano Lett.* **2008**, *8*, 3781.
- (18) Jiang, C. Y.; Sun, X. W.; Tan, K. W.; Lo, G. Q.; Kyaw, A. K. K.; Kwong, D. L. *Appl. Phys. Lett.* **2008**, *92*, 143101.
- (19) Adachi, M.; Murata, Y.; Takao, J.; Jiu, J.; Sakamoto, M.; Wang, F. *J. Am. Chem. Soc.* **2004**, *126*, 14943.
- (20) Mor, G. M.; Shankar, M.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2006**, *6*, 215.
- (21) Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G. K.; Grimes, C. A. *J. Phys. D: Appl. Phys.* **2006**, *39*, 2498.
- (22) Stergiopoulos, T.; Ghicov, A.; Likodimos, V.; Tsoukeris, D. S.; Kunze, J.; Schmuki, P.; Falaras, P. *Nanotechnology* **2008**, *19*, 235602.
- (23) Park, J. H.; Lee, T. W.; Kang, M. G. *Chem. Commun.* **2008**, 2867.
- (24) Lee, S. H. A.; Abrams, N. M.; Hoertz, P. G.; Barber, G. D.; Halaoui, L. L.; Mallouk, T. E. *J. Phys. Chem. B* **2008**, *112*, 14415.
- (25) Kwak, E. S.; Lee, W.; Park, N. G.; Kim, J.; Lee, H. *Adv. Funct. Mater.* **2009**, *19*, 1093.
- (26) Kuang, D.; Brillet, J.; Peter, C.; Takata, M.; Uchida, S.; Miura, H.; Sumioka, K.; Zakeeruddin, S. M.; Grätzel, M. *ACS Nano* **2008**, *2*, 1113.
- (27) Park, J. H.; Kim, S.; Bard, A. J. *Nano Lett.* **2006**, *6*, 24.
- (28) Fahim, N. F.; Sekino, T. *Chem. Mater.* **2009**, *21*, 1967.
- (29) Lee, B. H.; Song, M. Y.; Jang, S. Y.; Jo, S. M.; Kwak, S. Y.; Kim, D. Y. *J. Phys. Chem. C* **2009**, *113*, 21453.
- (30) Ferber, J.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 265.
- (31) Usami, A. *Sol. Energy Mater. Sol. Cells* **1999**, *59*, 163.
- (32) Koo, H. J.; Park, J.; Yoo, B.; Yoo, K.; Kim, K.; Park, N. G. *Inorg. Chim. Acta* **2008**, *361*, 677.
- (33) van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2001**, *105*, 11194.