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COMMUNICATION

Dye-sensitized solar cells with TiO_2 nano-particles on TiO_2 nano-tube-grown Ti substrates†

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In the present work, dye-sensitized solar cells (DSSCs) were prepared with TiO_2 nano-particles on TiO_2 nano-tube-grown Ti substrates. A slow electron recombination and a light scattering effect might have simultaneously contributed to the DSSC performance and resulted in improvements in the short-circuit current (J_{sc}) and in the conversion efficiency.

The dye-sensitized solar cell (DSSC), which was originally developed by O'Regan and Grätzel in 1991,[1] is a novel photovoltaic device due to its low manufacturing cost and eco-friendly properties.[2] Furthermore, its certified photon-to-electron conversion efficiency recently reached 11.1%.[3] However, that conversion efficiency mark was established using a high-cost F/SnO_2 (FTO) glass substrate. A DSSC using a thin and light-weight substrate would have a greatly expanded degree of utility. Instead of conductive-layer-coated plastic films, Electronics and Telecommunications Research Institute has proposed metal substrates.[4] The metal foil has no temperature limitations, which makes it an excellent alternative. However, in the case of DSSCs based on metal substrates, light illumination should come from a counter electrode, *i.e.*, back illumination. Therefore, the light scattering layer,[5] which enhances the optical path length, should be located between 20 nm sized TiO_2 nano-particles (NPs) and conductive substrates. This structure causes poor adhesion of the scattering layer due to the large particle size of the scattering layer. In the meantime, vertically grown TiO_2 nano-tube (NT) arrays have also been studied because of the preferred reduced recombination and stronger light scattering effect.[6] Recently, the Grimes group has reported TiO_2 NT-based DSSCs with an overall conversion efficiency of 6.89%.[7] However, a sufficient amount of time is indispensable for the formation of a long TiO_2 NT array. The ability to achieve a longer TiO_2 NT increases with pH as long as the electrolyte remains acidic, but increasing the pH reduced the TiO_2 NT growth rate, and more time was required to achieve a growth–dissolution equilibrium.[8]

In this communication, we report the synergistic effect of a vertically grown TiO_2 NT and TiO_2 NP. Considering slow recombination and light-scattering,[6] TiO_2 NPs have been incorporated on short TiO_2 NT-grown Ti substrates (Fig. 1). For maximized dye uptake, a large surface area of a photoelectrode was attained by the TiO_2 NP, which was prepared by the well-known sol–gel method. TiO_2 NT-grown Ti foil performed as a substrate for the attachment of the TiO_2 NP. In our approach, therefore, the fabrication time and length of TiO_2 NT could be minimized while increasing, rather than diminishing, the surface area of the photoelectrode.

Ti foils (Goodfellow, 99.6 wt% purity) were prepared with the dimensions 15 × 15 × 0.1 mm^3. Prior to electrochemical anodizing, all samples were cleaned with a mixture of acetone and alcohol. A naturally formed oxide layer at the top of the Ti foil was removed using a 0.1% HF solution under ultrasonic waves. A Ti foil was dipped into a solution of ethylene glycol containing 0.25% ammonium fluoride (NH_4F) and 2% H_2O and then a voltage of 50 V was applied with a platinum (Pt) counter electrode for 15–60 min.[9] The anodized Ti foil was cleaned with acetone and alcohol. 20 nm TiO_2 NPs, including paste, were coated onto the TiO_2 NT-formed Ti substrates using a doctor blade technique, followed by thermal treatment at 550 °C for 30 min under an air atmosphere. The prototype DSSCs were fabricated using platinum (Pt)-coated SnO_2 : F glass as the counter electrode. The Pt coating was carried out with the spin-coating of an H_2PtCl_6 and ethanol solution, followed by heating at 400 °C for 30 min. Then, the DSSCs with TiO_2

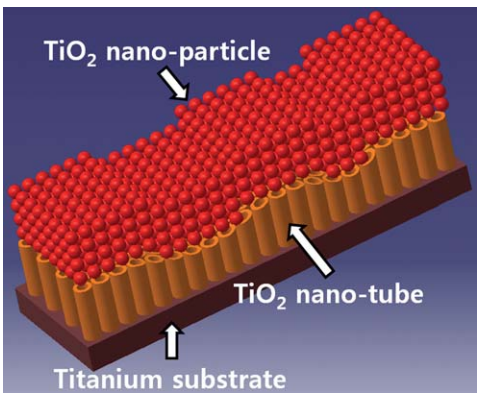

Fig. 1 Concept drawing of the photoelectrode for a DSSC composed of TiO_2 NP on the TiO_2 NT-grown Ti substrate (TiO_2 NP + NT/Ti).

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NP on the TiO_2 NT-grown Ti substrate (TiO_2 NP + NT/Ti) were fabricated according to the method described in our previous work.[10] The measured active area of the photoelectrode was approximately 0.15 cm^2. The surface morphology of the Ti substrate and thickness of the TiO_2 layer were inspected using SEM (FEI, SIRION). The cross-sectional microstructures of the photoelectrode were characterized using scanning transmission electron microscopy (STEM) (Hitachi, HD2300A). Optical transmission was identified with UV-VIS-NIR spectrophotometers combined with an integrated sphere (Varian, Cary 100 and DRA-CA-300). Under a xenon lamp light source (Oriel, 91193), the *J–V* characteristics, electrochemical impedance, and voltage decay were measured using a Keithley 2400 source meter and a potentiostat/galvanostat (Gamry, Reference 600). The illumination intensity (100 mW cm^{-2}) was adjusted with a standard solar cell composed of a crystalline Si capped with a KG-5 glass.

TiO_2 NT can be realized using various methods, which include electrochemical anodizing,[11] hydrothermal synthesis,[12] and template-assisted synthesis.[13] In particular, anodizing is a relatively simple approach for the preparation of optimized TiO_2 NT in terms of pore diameter, wall thickness, inter-tube spacing, and tube length.[14] In this experiment, anodizing of the Ti foil was used for the simple fabrication of the short TiO_2 NT. The total process for the preparation of the photoelectrode can be completed in 4 steps: (1) electrochemical anodizing of the Ti foil for the formation of short TiO_2 NT arrays, (2) doctor blading of the TiO_2 NP paste onto the TiO_2 NT-formed Ti substrates, (3) thermal treatment of the photoelectrode prepared by steps (1) and (2), and (4) dye coating of the fabricated photoelectrode.

Fig. 2(a) and (b) are the SEM images of the TiO_2 NP and TiO_2 NT. Anodizing at 50 V in a solution of ethylene glycol containing ammonium fluoride (NH_4F) resulted in the formation of regular TiO_2 NT arrays. When the anodizing was performed for 30 min, the tube diameter and wall thickness were estimated to be about 100 and <50 nm, respectively. The lengths of the TiO_2 NT layers were controlled by the anodizing time. When the anodizing was performed for 15, 30, and 60 min, the lengths of the TiO_2 NTs were 1.53, 4.36, and 8.17 μm, respectively. After anodizing, TiO_2 NPs were coated onto the TiO_2 NT-grown Ti substrates. As shown in Fig. 2(d), TiO_2 NT and TiO_2 NP bonded well following thermal annealing at 550 °C for 30 min. It is well known that as-prepared TiO_2 NTs are composed of amorphous titanium oxide, but, independent of the electrolyte composition, crystallization of the TiO_2 NTs to the anatase TiO_2 phase occurred at temperatures >280 °C.[8]

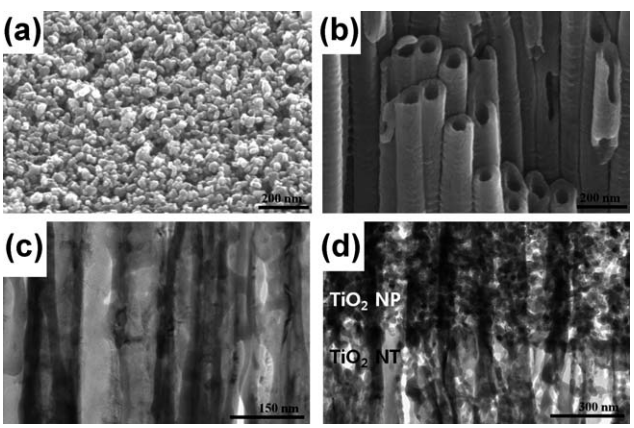

Fig. 2 SEM images of (a) TiO_2 NP and (b) TiO_2 NT. Cross-sectional TEM images of (c) TiO_2 NT and (d) interface between TiO_2 NP and TiO_2 NT.

The TiO_2 NP film was made 15 μm thick, because that was the size that allowed DSSCs to exhibit optimal performance (Table 1). When the thickness of the TiO_2 NP was more than 15 μm, the DSSC with TiO_2 NP on the Ti substrate (TiO_2 NP/Ti) exhibited a lowered performance because the thick TiO_2 layer (>15 μm) provided additional electron recombination sites, resulting in a decreased open-circuit voltage (V_{oc}) and fill factor (FF).[15] However, the DSSC with TiO_2 NP + NT/Ti exhibited a different behavior. Fig. 3(a) and Table 2 show the *J–V* characteristics of DSSCs with TiO_2 NP + NT/Ti compared with the DSSC with TiO_2 NP/Ti. As anodizing time was increased to 30 min, *i.e.* increased thickness of the TiO_2 NT film, the results indicated an improvement in J_{sc} with a negligible effect on the V_{oc} and FF. The J_{sc} increased continuously with TiO_2 thickness[16] due to an increase in the number of dye molecules from the increased surface area of the TiO_2 film.[9] However, in spite of the superior surface area of the TiO_2 NP to TiO_2 NT, only the DSSC with TiO_2 NP + NT/Ti exhibited enhanced performance. This difference between the DSSC with TiO_2 NP + NT/Ti and the DSSC with TiO_2 NP/Ti can be attributed to the TiO_2 NT having an electron recombination that was reduced by comparison with the TiO_2 NP. The electron lifetime in the TiO_2 NT was longer than that in the TiO_2 NP because of the electron recombination suppression from the reduction in electron-hopping across the inter-crystalline contacts between the grain boundaries.[16]

Optical transmission is restricted to wavelengths >570 nm for a device with a TiO_2 layer that is more than 15 μm thick (Fig. 3(b)), resulting in a restricted increase in J_{sc}. However, strong internal light scattering within the TiO_2 NTs elongated the path length of the long-wavelength incident light to promote the capture of photons by the dye molecules.[6] Despite a surface area of the DSSC with TiO_2 NP on 30 min anodized TiO_2 NT/Ti that was smaller than that of DSSC with 20 μm thick TiO_2 NP/Ti, the increased J_{sc} could also be a result of stronger light scattering effects.

The reduced electron recombination at the interface of the TiO_2 NT/electrolyte was also represented in an electrochemical impedance measurement. To analyze the improved cell performance, electrochemical impedance spectra were evaluated (Fig. 3(c)). In addition, for the quantified estimation of the resistance from electrochemical impedance spectra, an equivalent circuit model including two constant phase elements has been adopted. The 1st semicircle (R_1) occurring in the high frequency range was closely related to charge transfer at the counter electrode and/or electrical contact between the conductive substrate and TiO_2.[17] Under the assumption that the TiO_2 NT is superior to TiO_2 NP in the interfacial contact with Ti substrates due to the *in situ* fabrication process, the largely reduced size of the 1st semicircle in a DSSC with TiO_2 NP + NT/Ti could be a result of the reduced electrical resistance at the interfacial contact. In the

Table 1 Summarized performance of the DSSC with TiO_2 NP/Ti according to the thickness of the TiO_2 NP layer under AM 1.5 irradiation (100 mW cm^{-2})

	V_{oc}/V	J_{sc}/mA cm^{-2}	FF (%)	Efficiency (%)
5 μm TiO_2 NP	0.81	5.65	71.6	3.29
10 μm TiO_2 NP	0.79	7.93	69.9	4.40
15 μm TiO_2 NP	0.80	10.73	68.2	5.90
20 μm TiO_2 NP	0.73	11.49	65.9	5.54

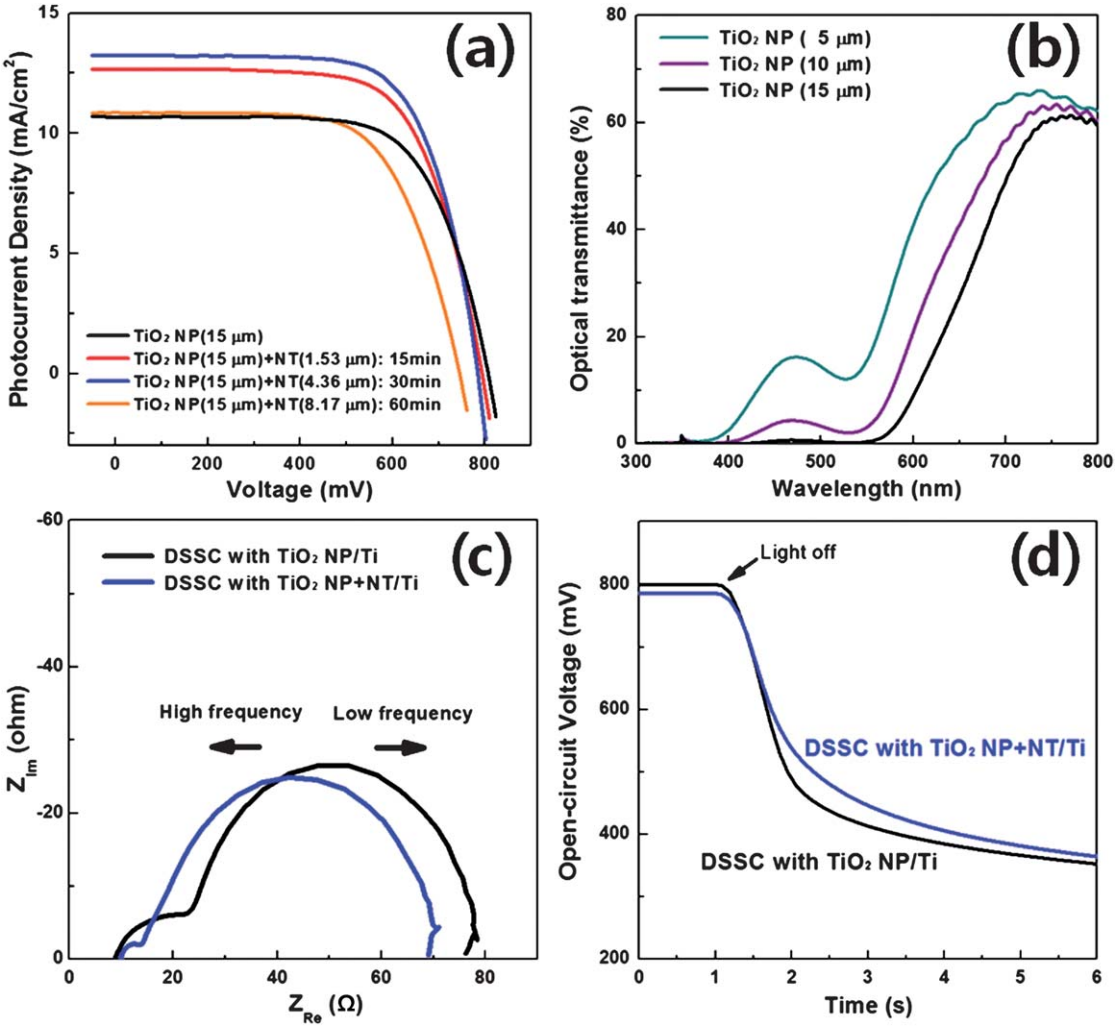

Fig. 3 (a) *J–V* characteristics of the DSSC with TiO_2 NP/Ti and TiO_2 NP + NT/Ti. (b) Under light from the photoelectrode direction (front illumination), optical transmission of FTO-glass-based DSSC. (c) Electrochemical impedance spectra in frequencies ranging from 10^{-1} to 10^{6} Hz. (d) Open-circuit voltage decay measurement.

quantified estimation, a large amount of the R_1 has been varied, 16.6 Ω and 5.7 Ω in the DSSC with TiO_2 NP/Ti and TiO_2 NP + NT/Ti, respectively. However, the size of the 2nd semicircle (R_2, low frequency range) was almost the same, 53.0 Ω in the DSSC with TiO_2 NP/Ti and 56.0 Ω in the DSSC with TiO_2 NP + NT/Ti. The 2nd semicircle represents the recombination of injected electrons to the TiO_2 film with an electrolyte.[18] Under open-circuit conditions, the recombination kinetics could also be investigated by the evaluation of the rate of photovoltage decay, which is proportional to the rate of recombination.[17] As shown in Fig. 3(d), DSSCs with TiO_2 NP/Ti and TiO_2 NP + NT/Ti exhibited a similar rate of photovoltage decay. The overall TiO_2 film in the DSSC with TiO_2 NP + NT/Ti was thicker than that of the DSSC with TiO_2 NP/Ti due to the introduction of the TiO_2 NT layer at the interface of the TiO_2 NP and Ti substrate. Therefore, it seems that the small variation in the 2nd semicircle in the electrochemical impedance spectra (Fig. 3(c)) and the rate of photovoltage decay (Fig. 3(d)) can be attributed to the slow recombination characteristics of the TiO_2 NT.

Table 2 Summarized performance of the DSSCs with TiO_2 NP/Ti and TiO_2 NP + NT/Ti under AM 1.5 irradiation (100 mW cm^{-2})

	V_{oc}/V	J_{sc}/mA cm^{-2}	FF (%)	Efficiency (%)
Only TiO_2 NP (15 μm)	0.80	10.73	68.2	5.90
TiO_2 NP (15 μm) + TiO_2 NT (1.53 μm)	0.79	12.71	67.4	6.80
TiO_2 NP (15 μm) + TiO_2 NT (4.36 μm)	0.79	13.30	69.3	7.23
TiO_2 NP (15 μm) + TiO_2 NT (8.17 μm)	0.75	10.86	65.4	5.30

The DSSCs with TiO_2 NP + NT/Ti were prepared for the synergistic effect of vertically grown TiO_2 NT and TiO_2 NP films. The slow electron recombination at the interface of the TiO_2 NT/electrolyte and the light scattering effect might have simultaneously contributed to DSSC performance, and could have resulted in improvements to the J_{sc} and to the conversion efficiency with only a negligible effect on the V_{oc} and FF. Consequently, an overall conversion efficiency of 7.23% was achieved by the use of the DSSC with TiO_2 NP + NT/Ti.

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Notes and references

1 O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
2 M. K. Nazeerudden, P. Pechy, T. Renouard, S. M. Zakeeruddin, B. R. Humphry, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613.
3 Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, *Jpn. J. Appl. Phys.*, 2006, **45**, L638.
4 M. G. Kang, N.-G. Park, K. S. Ryu, S. H. Chang and K.-J. Kim, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 574.
5 S. Ito, S. M. Zakeeruddin, R. H. Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1202.
6 K. Zhu, N. R. Neale, A. Miedaner and A. J. Frank, *Nano Lett.*, 2007, **7**, 69.
7 K. Shankar, G. K. Mor, H. E. Prakasam, S. Yoriya, M. Paulose, O. K. Varghese and C. A. Grimes, *Nanotechnology*, 2007, **18**, 065707.
8 Q. Y. Cai, M. Paulose, O. K. Varghese and C. A. Grimes, *J. Mater. Res.*, 2005, **20**, 230.
9 J. H. Park, T.-W. Lee and M. G. Kang, *Chem. Commun.*, 2008, 2867.
10 H.-G. Yun, Y. Jun, J. Kim, B.-S. Bae and M. G. Kang, *Appl. Phys. Lett.*, 2008, **93**, 133311.
11 D. Gong, C. A. Grimes, O. K. Varghese, W. C. Hu, R. S. Singh, Z. Chen and E. C. Dickey, *J. Mater. Res.*, 2001, **16**, 3331.
12 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Langmuir*, 1998, **14**, 3160.
13 P. Hoyer, *Langmuir*, 2006, **12**, 1411.
14 G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2005, **5**, 191.
15 R. Kato, A. Furube, A. V. Barzykin, H. Arakawa and M. Tachiya, *Coord. Chem. Rev.*, 2004, **248**, 1195.
16 C.-J. Lin, W.-Y. Yu and S.-H. Chien, *Appl. Phys. Lett.*, 2008, **93**, 133107.
17 J. H. Park, Y. Jun, H.-G. Yun, S.-Y. Lee and M. G. Kang, *J. Electrochem. Soc.*, 2008, **155**, F145.
18 T. Hoshikawa, M. Yamada, R. Kikuchi and K. Eguchi, *J. Electrochem. Soc.*, 2005, **152**, E68.