Growth, detachment and transfer of highly-ordered TiO_2 nanotube arrays: use in dye-sensitized solar cells†

Jong Hyeok Park,*[a] Tae-Woo Lee[b] and Man Gu Kang*[c]

Received (in Cambridge, UK) 15th January 2008, Accepted 15th February 2008
First published as an Advance Article on the web 7th May 2008
DOI: 10.1039/b800660a

In the present work, we report a simple method of making glass-based dye-sensitized solar cells (DSSCs) with individual free-standing TiO_2 nanotube arrays.

Dye-sensitized solar cells (DSSCs) are promising subjects for commercialization in the near future due to their high energy conversion efficiency and low production cost, making them a cheaper alternative to silicon solar cells.[1–5] The electron-collecting layer in a DSSC is typically a 10–15 μm-thick nanoparticulate film, with a three-dimensional network of 15 nm-sized interconnected nanoparticles.[6] To obtain a high power conversion efficiency, a nanoporous film with a large surface area should be used to maximize the amount of photogenerated charge. Photoexcited ruthenium-based dyes inject electrons into the TiO_2. The injected electrons diffuse through a disordered TiO_2 film with a high grain boundary to the counter-electrode. Analysis of photocurrent measurements indicate that the light-harvesting efficiencies of vertically-grown nanotube-based DSSCs are higher than those found for DSSCs incorporating nanoparticles, owing to a stronger light scattering effect.[7] In addition, recombination between electrons injected from dyes and the electrolyte was much slower in the nanotube-based films, indicating that the nanotube-based DSSCs have significantly higher charge collection efficiencies than their nanoparticle-based counterparts.[7]

Highly-ordered vertically-oriented TiO_2 nanotube arrays fabricated by potentiostatic anodization constitute a material architecture that offers a large internal surface area without a concomitant decrease in geometric and structural order.[8–12] DSSCs with these oriented TiO_2 nanotube arrays have shown a 3.3% incident photon-to-current conversion efficiency and a 3% overall conversion efficiency.[13,14] Recently, Grimes' group achieved 4.4 and 6.89% overall conversion efficiency by using TiO_2 nanotube arrays made by the anodization of a Ti-foil in a backside-illuminated DSSC.[15,16] The application of TiO_2 nanotubes grown on Ti-foil requires backside illumination, a less than optimal approach for power conversion efficiency, because the Pt coated onto a fluorine-doped tin oxide (FTO) glass partially reflects light, while the iodine electrolyte absorbs photons in the near UV region. To resolve this drawback, a new methodology of fabricating nanotube arrays on FTO glass, and their application to DSSCs, has been reported.[14] However, the reported method involves the sputtering of Ti-films onto FTO glass, thus leading to a high fabrication cost. More recently, Albu *et al.* reported the preparation of a free-standing TiO_2 membrane by the selective dissolution of a metallic substrate.[17] This method is also very time consuming process, as it takes more than 10 h to remove the metallic substrate. Paulose *et al.* described a process including a critical point drying method by which nanotube array films can be transformed into free-standing membranes.[18] Through the use of their technique, free-standing TiO_2 nanotube arrays with 200 μm-thickness can be prepared and used to control the diffusion of phenol red.

Here we report a simple and inexpensive methodology for preparing TiO_2 nanotube arrays on FTO glass (Fig. 1). The prepared nanotube arrays are then used as photoanodes for a DSSC. This method is composed of four steps: (i) growth of TiO_2 nanotube arrays with various aspect ratios on Ti thin foil, (ii) detachment of the TiO_2 nanotube arrays, (iii) transfer and fixation of the TiO_2 nanotube arrays to FTO glass, and (iv) thermal annealing of the TiO_2 nanotube arrays onto FTO glass. For the first step, highly-ordered, 7–35 μm-thick TiO_2 nanotube arrays were made by the anodization of a thin film Ti foil (Goodfellow, England) in 0.25 wt% NH_4F and 2 vol% H_2O containing ethylene glycol.[16] Ti foils anodized at 60 V resulted in the formation of nanotube arrays, as shown in Fig. 2. The arrays consisted of very regular tubes, with a

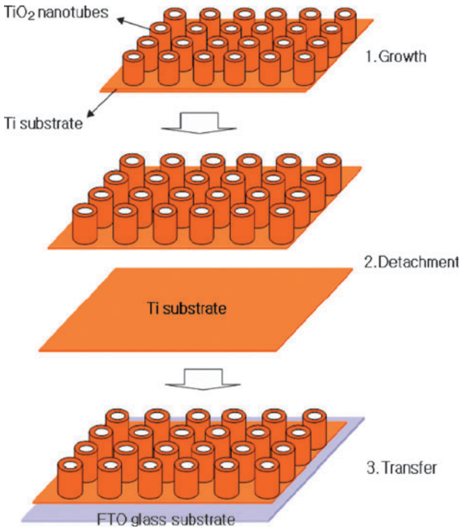

Fig. 1 Scheme for fabricating TiO_2 nanotube arrays on FTO glass.

---

[a] *Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea. E-mail: lutts@skku.edu*
[b] *Samsung Advanced Institute of Technology, Mt. 14-1 Nongseo-Dong, Yongin-Si, Gyeonggi-Do 449-712, Republic of Korea*
[c] *Ionics Devices Team, IT-NT Group, Electronics and Telecommunications Research Institute, Daejeon 305-700, Korea. E-mail: 10009kang@etri.re.kr*

† Electronic supplementary information (ESI) available: IPCE of final cell and photos of free-standing membrane after thermal annealing, including the one that is stuck onto the FTO glass, and the final device. See DOI: 10.1039/b800660a

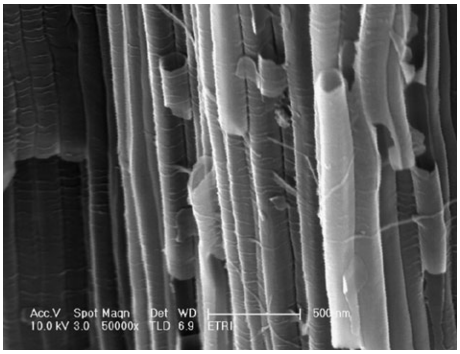

Fig. 2 Cross-sectional field emission scanning electron microscopy (FESEM) image of TiO_2 nanotube arrays.

diameter of $\sim$130 nm and a wall thickness of $\sim$15 nm. The thickness of the TiO_2 films was controlled by the anodization time.

In order to separate the TiO_2 nanotube arrays from the metallic Ti substrate, the arrays were immersed in 0.1 M aqueous HCl for 1 h (Fig. 3; (a) before, (b) after). After this simple process, a free-standing TiO_2 film, which had an opaque appearance and could be easily handled with tweezers, was obtained (Fig. 3(c)). The ease of oxide film detachment described in this process is a notable feature, particularly given that no pre-treatment of the Ti substrate was required.

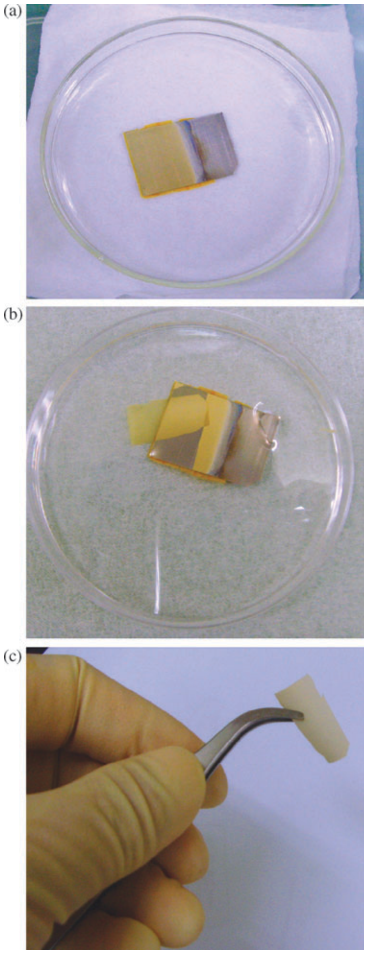

Fig. 3 Photographic images of the detachment process.

We have prepared and transferred TiO_2 nanotube arrays as large as 3 × 3 cm (the dimensions are limited only by the size of the substrate). In the next step, the films were transferred onto FTO glass, and two drops of 100 mM Ti-isopropoxide were subsequently applied to the TiO_2 films to form interconnections between the FTO glass and the TiO_2 film. Films were annealed at 500 °C for 30 min in air, with heating and cooling rates of 1 $^{\circ}C\ min^{-1}$ to induce crystallinity. To coat dye onto the TiO_2 films, the samples were immersed in a 3×10^{-4} M Ru(II)LL′$(NCS)_2$ (L = 2,2′-bipyridyl-4,4′-dicarboxylic acid; L′ = 2,2′-bipyridyl-4,4′-ditetrabutylammonium carboxylate, Solaronix) ethanol solution for 4 d. Photos for each step are provided in the ESI.† To prepare Pt counter-electrodes, hydrogen hexachloroplatinate(IV) hydrate (Aldrich, 99.9%) in a 2-propanol solution was coated on FTO glass (Pilkington, TEC 8), followed by heating at 450 °C for 30 min.[19] The dye-adsorbed TiO_2 electrode and Pt counter-electrode were assembled into a sealed sandwich-type cell by heating with a hot melt of a polymer film (Surlyn, Dupont 1702). Single drops of the electrolyte solution were, respectively, introduced into holes 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_2, 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85 : 15).

The photocurrent (J) and photovoltage (V) of the DSSCs were measured with an active area of 0.03–0.15 cm^2 using simulated solar light at AM 1.5, produced by a 1000 W xenon lamp (Oriel, 91193). The J–V characteristics of the devices with 35 μm TiO_2 nanotube arrays are shown in Fig. 4. At 1 sun illumination, the nanotube DSSC exhibited a J_{sc} (short-circuit current) of 16.8 mA cm^{-2}, a V_{oc} (open-circuit voltage) of 0.733 V and a fill factor (FF) of 62%, with an overall conversion efficiency of 7.6%. In a previous paper, a TiO_2 nanotube/FTO glass-based DSSC without $TiCl_4$ treatment showed a five-times higher value compared to that of a non-treated DSSC.[14] In our study, when FTO glass treated with a 40 mM $TiCl_4$ solution was used as a substrate, a roughly 30% enhanced photocurrent was observed. We believe that this enhancement can be attributed to a reduction of the charge recombination between photo-injected electrons in the substrate and the oxidized dye.[20] Open

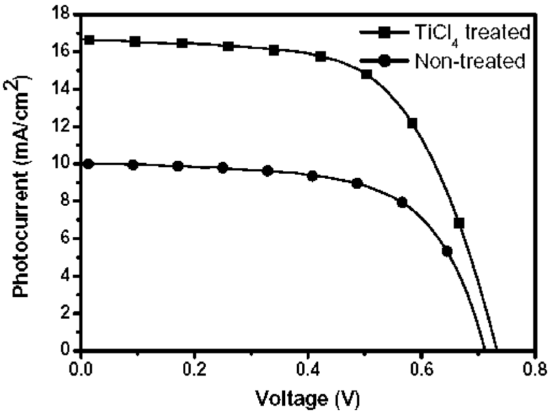

Fig. 4 Photocurrent–photovoltage characteristics of transparent nanotube array-based DSSCs.

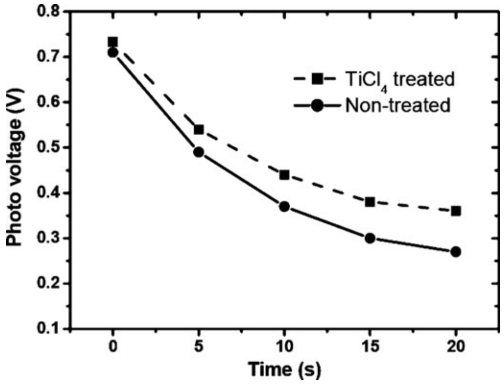

Fig. 5 Photovoltage–decay measurement of transparent nanotube array-based DSSCs.

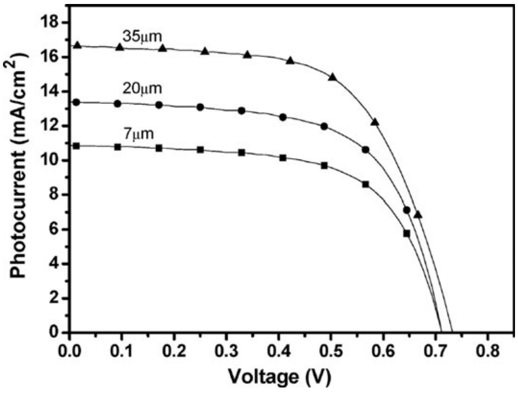

Fig. 6 Photocurrent–photovoltage characteristics of transparent nanotube array-based DSSCs as a function of tube length.

circuit voltage decay measurements were conducted to investigate the recombination kinetics of the nanotube-based DSSCs, with and without the underlayer (Fig. 5).[14] Zaban *et al.* proposed that the rate of photovoltage decay is inversely proportional to the lifetime of the photoelectron in the DSSC, and that the lifetime of the electron is inversely proportional to the rate of recombination.[21] A DSSC with FTO glass treated with a 40 mM $TiCl_4$ solution exhibited superior recombination characteristics with a longer lifetime, indicating that the recombination rate had been reduced. However, the effect of $TiCl_4$ treatment was weak compared to that described in previous work.[14] We conclude that Ti-isopropoxide, used to connect the substrate and the TiO_2 nanotubular film, can also reduce charge recombination.

Fig. 6 compares the *J–V* properties of the TiO_2 nanotube-based DSSCs as a function of film thickness. With increasing TiO_2 film thickness, J_{sc} increased linearly up to 35 μm, even though the film thickness reached several tens micrometers. This is directly attributed to the increase in the number of dye molecules from the increased surface area of the film. Moreover, this increased light-harvesting efficiency in TiO_2 nanotube-based DSSCs could also be a result of stronger light scattering effects.[7] Hence, these factors lead to significantly higher charge collection efficiencies of the nanotube-based DSSCs relative to those of nanoparticle-based DSSCs.

In summary, we have introduced a simple and cost-effective method of making free-standing TiO_2 nanotube arrays that allows remarkable control over their thickness. To date, several researchers have demonstrated the strengths of TiO_2 nanotubular systems compared with TiO_2 nanoparticle systems in DSSCs. However, the use of TiO_2 nanotube arrays for DSSCs has been hindered by difficulties in fabricating the arrays on transparent substrates. We believe that the ease of oxide film detachment and transfer to FTO glass in this process will facilitate increasing the power conversion efficiency of DSSCs.

This work was supported by the Ministry of Information and Communications under contract 2006-S-006.

Notes and references

1. M. Gratzel, *Nature*, 2001, **414**, 338.
2. H. Yang, C. Yu, Q. Song, Y. Xia, F. Li, Z. Chen, X. Li and C. Huang, *Chem. Mater.*, 2006, **18**, 5173.
3. L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito and M. Gratzel, *Adv. Mater.*, 2005, **17**, 813.
4. T. Yamaguchi, N. Tobe, D. Matsumoto and H. Arakawa, *Chem. Commun.*, 2007, 4767.
5. S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann and R. Kern, *Chem. Commun.*, 2005, 2011.
6. M. Gratzel, *J. Photochem. Photobiol., A*, 2004, **168**, 235.
7. K. Zhu, N. R. Neale, A. Miedaner and A. J. Frank, *Nano Lett.*, 2007, **7**, 69.
8. J. H. Park, S. Kim and A. J. Bard, *Nano Lett.*, 2006, **6**, 24.
9. J. H. Park, S. Kim and O. O. Park, *Appl. Phys. Lett.*, 2006, **89**, 163106.
10. Q. Y. Cai, M. Paulose, O. K. Varghese and C. A. Grimes, *J. Mater. Res.*, 2005, **20**, 230.
11. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2005, **5**, 191.
12. M. Paulose, K. Shankar, S. Yoriya, H. E. Prakasam, O. K. Varghese, G. K. Mor, T. A. Latempa, A. Fitzgerald and C. A. Grimes, *J. Phys. Chem. B*, 2006, **110**, 16179.
13. J. M. Macak, H. Tsuchiya, H. Ghicov and P. Schmuki, *Electrochem. Commun.*, 2005, **7**, 1133.
14. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 2006, **6**, 215.
15. M. Paulose, K. Shankar, O. K. Varghese, G. K. Mor and C. A. Grimes, *J. Phys. D: Appl. Phys.*, 2006, **39**, 2498.
16. K. Shankar, G. K. Mor, H. E. Prakasam, S. Yoriya, M. Paulose, O. K. Varghese and C. A. Grimes, *Nanotechnology*, 2007, **18**, 065707.
17. S. P. Albu, A. Ghicov, J. M. Macak, R. Hahn and P. Schmuki, *Nano Lett.*, 2007, **7**, 1286.
18. M. Paulose, H. E. Prakasam, O. K. Varghese, L. Peng, K. C. Popat, G. K. Mor, T. A. Desai and C. A. Grimes, *J. Phys. Chem. C*, 2007, **111**, 14992.
19. N. Papageorgiou, *Coord. Chem. Rev.*, 2004, **248**, 1421.
20. K. Zhu, E. A. Schiff, N. G. Park, J. van de Lagemaat and A. J. Frank, *Appl. Phys. Lett.*, 2002, **80**, 685.
21. A. Zaban, M. Greenshtein and J. Bisquert, *ChemPhysChem*, 2003, **4**, 859.