Articles

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Freestanding TiO$_2$ Nanotube Arrays with Ultrahigh Aspect Ratio via Electrochemical Anodization

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Self-organized, freestanding titania (TiO$_2$) membrane with ultrahigh aspect ratio of the length/diameter (∼1500) was fabricated via electrochemical anodization of highly pure titanium (Ti) foil in fluorine-containing ethylene glycol, followed by a simple and safe detachment of the formed TiO$_2$ membrane from the metallic Ti substrate. The resulting membrane consists of highly ordered, vertically aligned, one-side open TiO$_2$ nanotube arrays. The pore diameter, wall thickness, and length of the nanotube arrays are 90 nm, 15 nm, and 135 μm, respectively, at a certain anodization condition.

Introduction

Because of the unique combination of wide band gap semiconductor properties with a high surface area, self-organized titania (TiO$_2$) nanotube arrays via electrochemical anodization of titanium (Ti) in fluorine-containing electrolyte have attracted tremendous attention for use in high-performance hydrogen sensors,[1–3] photocleavage of water,[4,5] photocatalytic,[6] and solar cells.[7–10] In the latter context, each individual TiO$_2$ nanotube is perpendicular to the membrane surface, thereby providing two separate channels for efficient electron and hole transport from interfaces to electrodes.[7] This is in sharp contrast to electron-hopping as in TiO$_2$ nanoparticles, which were widely used as electron-accepting species in dye-sensitized solar cells (DSSCs).[11,12]

Three generations of fluorine-containing electrolytes have been used for anodic oxidation of titanium foil to prepare TiO$_2$ nanotubes with different aspect ratio and surface quality. For the first generation, dilute hydrofluoride acid (HF) aqueous solution was used as electrolyte, the maximum thickness of TiO$_2$ nanotube arrays is limited to only several hundred nanometers because of fast chemical dissolution of TiO$_2$ by fluorine ions in aqueous host.[13–15] Later, it was demonstrated that TiO$_2$ nanotube arrays with a thickness of a few micrometers can be achieved in fluorine-containing buffer solution with controlled pH as a result of the reduced dissolution rate of formed TiO$_2$ in the buffer electrolyte.[16–18] Recently, TiO$_2$ nanotube arrays with an ultrahigh aspect ratio of the length/diameter (the length > 100 μm) has been successfully produced using a nonaqueous electrolyte with further reduced water content (i.e., ammonium fluoride, NH$_4$F dissolved in nonaqueous organic solvent, ethylene glycol).[5,8,19,20] Notably, the above-mentioned TiO$_2$ nanotubes were attached to the metallic Ti substrate (i.e., the Ti foil), which may limit their wider application.[21] Very recently, self-organized, freestanding TiO$_2$ nanotube arrays have been fabricated for flow-through photocatalytic application.[6] To obtain freestanding TiO$_2$ membrane, a corrosive bromine-containing methanol solution was employed for selective chemical etching of the metallic Ti substrate.[6]

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(1) Mor, G. K.; Carvalho, M. A.; Varghese, O. K.; Pishko, M. V.; Grimes, C. A. *J. Mater. Res.* **2004,** *19,* 628.
(2) Varghese, O. K.; Gong, D. W.; Paulose, M.; Ong, K. G.; Dickey, E. C.; Grimes, C. A. *Adv. Mater.* **2003,** *15,* 624.
(3) Varghese, O. K.; Gong, D. W.; Paulose, M.; Ong, K. G.; Grimes, C. A. *Sens. Actuators, B* **2003,** *93,* 338.
(4) Ruan, C.; Paulose, M.; Varghese, O. K.; Mor, G. K.; Grimes, C. A. *J. Phys. Chem. B* **2005,** *109,* 15754.
(5) Shankar, K.; Mor, G. K.; Prakasam, H. E.; Yoriya, S.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nanotechnology* **2007,** *18,* 065707.
(6) Albu, S. P.; Ghicov, A.; Macak, J. M.; Schmuki, P. *Nano Lett.* **2007,** *7,* 1286.
(7) Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2006,** *6,* 215.
(8) Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G.; Grimes, C. A. *J. Phys. D: Appl. Phys.* **2006,** *39,* 2498.
(9) Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G. K.; Hardin, B.; Grimes, C. A. *Nanotechnology* **2006,** *17,* 1446.
(10) Zhu, K.; Neale, N. R.; Miedaner, A.; Frank, A. J. *Nano Lett.* **2006,** *7,* 69.
(11) O'Regan, B.; Gratzel, M. *Nature* **1991,** *353,* 737.
(12) Gratzel, M. *Nature* **2001,** *414,* 338.

(13) Gong, D.; Grimes, C. A.; Varghese, O. K.; Hu, W.; Singh, R. S.; Chen, Z.; Dickey, E. C. *J. Mater. Res.* **2001,** *16,* 3331.
(14) Mor, G. K.; Varghese, O. K.; Paulose, M.; Mukherjee, N.; Grimes, C. A. *J. Mater. Res.* **2003,** *18,* 2588.
(15) Varghese, O. K.; Gong, D. W.; Paulose, M.; Grimes, C. A.; Dickey, E. C. *J. Mater. Res.* **2003,** *18,* 156.
(16) Cai, Q. Y.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *J. Mater. Res.* **2005,** *20,* 230.
(17) Macak, J. M.; Tsuchiya, H.; Schmuki, P. *Angew. Chem., Int. Ed.* **2005,** *44,* 2100.
(18) Macak, J. M.; Tsuchiya, H.; Taveira, L.; Aldabergerova, S.; Schmuki, P. *Angew. Chem., Int. Ed.* **2005,** *44,* 7463.
(19) Paulose, M.; Shankar, K.; Yoriya, S.; Prakasam, H. E.; Varghese, O. K.; Mor, G. K.; Latempa, T. A.; Fitzgerald, A.; Grimes, C. A. *J. Phys. Chem. B* **2006,** *110,* 16179.
(20) Prakasam, H. E.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *J. Phys. Chem. C* **2007,** *111,* 7235.

In addition to TiO$_2$ nanotubes that were grown on the top of Ti foil, TiO$_2$ nanotube arrays on a variety of substrates [e.g., fluorine-doped tin oxide (FTO)-coated glass] were also produced by anodizing Ti thin film that was predeposited on substrates by sputtering [e.g., radio frequency (RF)-sputter deposition].[21–23] Subsequent high-temperature annealing transformed the as-grown TiO$_2$ nanotubes into transparent anatase form,[21] which has been successfully exploited to fabricate front-side-illuminated DSSCs.[7,8] Thus, the incident light loss through redox electrolytes as in back-side-illuminated DSSCs was largely reduced.[7–9] An overall efficiency of 2.9% was obtained with only 360 nm thick TiO$_2$ nanotubes on the FTO-coated glass.[7,8] Because of the limitation on the ability to deposit thicker, high-quality Ti on the substrates, the maximum thickness of photoactive nanotube arrays that can be achieved was about several hundred nanometers.[7,21] In this context, to improve the incident light-harvesting efficiency, thicker TiO$_2$ nanotube arrays on top of a transparent, conductive substrate are highly desirable for use in the front-side-illuminated DSSCs. To this end, a possible approach is to produce a freestanding, much thicker TiO$_2$ nanotube membrane, followed by transferring the membrane onto a transparent conductive substrate to serve as the electrode.

Herein, we report a simple and safe method to achieve self-organized, freestanding, ultrahigh-aspect-ratio TiO$_2$ nanotube arrays without the need for a corrosive etching process to separate TiO$_2$ nanotubes from the metallic Ti substrate. TiO$_2$ nanotube arrays with the aspect ratio of length/diameter ~1500 was first grown on Ti foil by electrochemically anodizing Ti foil in a fluorine-containing nonaqueous electrolyte (i.e., ammonium fluoride, NH$_4$F, in ethylene glycol). The anodized Ti foil was rinsed extensively with DI water and methanol. Subsequent evaporation of methanol led to the delamination of the thin "barrier layer" of TiO$_2$, which was formed between the TiO$_2$ membrane and Ti foil during anodization. A gentle mechanical bending of anodized Ti foil may be applied to facilitate complete detachment of the membrane if necessary. As-grown TiO$_2$ nanotubes were amorphous and then transformed into photoactive anatase form after annealed at high temperature in air. The nanotubular structures of freestanding TiO$_2$ membrane was characterized by scanning electron microscopy (SEM, JEOL 5800 LV). The amorphous—anatase transformation was verified by confocal Raman spectroscopy measurement (Renishaw inVia Raman Microscopy). The integrity of nanotubes was retained after high-temperature annealing. It is noteworthy that the freestanding TiO$_2$ nanotube arrays may then be anchored to conductive glass by using a transparent conductive glue[24] to provide better interfacial electronic contact between nanotubes and conductive glass for use in front-side-illuminated DSSCs.[7] The thickness of freestanding TiO$_2$ nanotube arrays more than 100 μm can be readily fabricated;

Figure 1. Digital image of a freestanding TiO$_2$ nanotube membrane in brown (right). The lateral dimension of the membrane is comparable to a dime shown in the left.

thus, an enhanced incident light absorption efficiency is expected. Furthermore, the vertically aligned nanotube geometry not only provides a large interfacial area where excitons, that is, the bound electron–hole pairs, may effectively dissociate, but also has two separate channels for efficient electron and hole transport from interface to contacts. Finally, the absence of the "barrier layer" between the nanotubes and electrode imparts an enhanced charge collection at the electrode.[7] Taken together, we envision that by exploiting these freestanding TiO$_2$ nanotube arrays with ultrahigh aspect ratio fabricated in the present study in the front-side-illuminated DSSCs, an improved device performance may be anticipated.

Experimental Section

TiO$_2$ nanotube arrays with ultrahigh aspect ratio were grown on a Ti foil according to a modified procedure.[19] Briefly, Ti foil (Sigma-Aldrich; 250 μm thick, 99.7% purity) was cut into a 2.5 × 1.0 cm piece. It was degreased by ultrasonication for 30 min in a mixture of acetone, methanol, and methylene chloride, followed by a thorough rinse with DI water, and blow dried with N$_2$. Ethylene glycol (Fisher Scientific) was used as the electrolyte. A small amount of ammonium fluoride (Sigma-Aldrich) was added into the ethylene glycol electrolyte. All chemicals and materials in the experiment were used as received without further purification. Electrochemical anodization of Ti foil was carried out in a two-electrode cell at room temperature using a power source EC570-90 (Thermo Electron Corporation), in which a platinum foil was used as the counter electrode. The backside of Ti foil was protected by coating a layer of nail polish. Anodization was conducted at a constant potential of 60 V for a period of time until a desired thickness was reached (e.g., TiO$_2$ membrane with a thickness of ~135 μm was obtained after anodization for 60 h). After anodization, the Ti foil with the TiO$_2$ nanotubes grown on one side of its surfaces was thoroughly washed with a large amount of DI water and methanol and kept in a methanol bath overnight.

To achieve a freestanding membrane, the grown TiO$_2$ membrane was detached from the metallic Ti substrate as described in the following. The anodized Ti foil was taken out from methanol bath and washed again with a large amount of methanol, and then the foil was placed at the bottom of a big box with the anodized surface facing up. The brownish membrane (Figure 1) gradually separated from the Ti foil during

(21) Mor, G. K.; Varghese, O. K.; Paulose, M.; Grimes, C. A. *Adv. Funct. Mater.* **2005**, *15*, 1291.

(22) Leenheer, A. J.; Miedaner, A.; Curtis, C. J.; van Hest, M. F. A. M.; Ginley, D. S. *J. Mater. Res.* **2007**, *22*, 681.

(23) Macak, J. M.; Tsuchiya, H.; Berger, S.; Bauer, S.; Fujimoto, S.; Schmuki, P. *Chem. Phys. Lett.* **2006**, *428*, 421.

(24) Ouyang, H. Y.; Yang, Y. *Adv. Mater.* **2006**, *18*, 2141.

the course of methanol evaporation. In our experiment, the freestanding TiO$_2$ membrane can be successfully achieved upon evaporation of methanol once or twice. A possible mechanism of methanol-evaporation-induced membrane detachment can be rationalized as follows. A thin layer of TiO$_2$, known as the "barrier layer", was formed between the TiO$_2$ nanotube array and Ti foil during anodization. After anodization, although the Ti foil was thoroughly washed and kept in a methanol bath overnight, a small amount of H$^+$ and F$^-$ may still be present in the regions between adjacent nanotubes (i.e., the interpore regions). Thus, there existed a slow etching of the "barrier layer", which led to the formation of defects. On the other hand, methanol has low surface tension[25] (i.e., $\gamma_{CH_3}OH = 22.1$ dynes/cm at 20 °C), which makes it easy to infiltrate the interpore regions and wet the defects. Subsequent slow evaporation of methanol in the defect areas caused the delamination of the TiO$_2$ "barrier layer" driven by the surface tension. A slight mechanical bending of the foil may be applied if the membrane cannot separate completely after several repeated wetting and evaporation of methanol. The mechanical strength of TiO$_2$ is weak as compared to Ti; thus, the "barrier layer" can be easily delaminated upon methanol evaporation and/or destroyed by a gentle mechanical bending, resulting in a freestanding TiO$_2$ nanotube membrane. It is worth noting that the process is simple, safe, and without the use of corrosive etching solution.[6]

Results and Discussion

Figure 1 shows a digital image of a brownish freestanding TiO$_2$ nanotube membrane obtained directly after the electrochemical anodization in the NH$_4$F/ethylene glycol electrolyte. The lateral dimension of membrane is ∼1.0 × 1.0 cm^2. The top surface of the freestanding TiO$_2$ membrane was covered by a layer of TiO$_2$ nanowires (∼100 nm) as revealed by SEM (Figure 2a). The layer of TiO$_2$ nanowires was formed possibly because of electric-field-induced chemical etching of TiO$_2$ nanotubes in a "bamboo-splitting" mode (i.e., vertical splitting of anodically grown nanotubes during anodization).[26] In some region, that is, around the cracks of nanowires, TiO$_2$ nanotubes buried beneath nanowires were observed (Figure 2b). The cracks may be resulted from a slow but long period time of chemical dissolution of the TiO$_2$ nanowires[26] and/or damage during the membrane transferring process. To use the freestanding TiO$_2$ nanotubes for a variety of applications, e.g., DSSCs, this 100 nm top layer should be removed to infiltrate dye molecules and redox electrolytes into nanotubes in DSSCs.[7] Attempts to selectively chemical etch the top TiO$_2$ nanowires with HF aqueous solution, which was placed closely below the membrane, were unsuccessful (see Figure S1 in the Supporting Information). The HF treatment etched away not only the top nanowires but also the buried nanotubes (see Figure S1 in the Supporting Information). Microscopic holes were formed, leaving behind a highly rough membrane (see Figure S1 in the Supporting Information).

Thus, as an alternative approach, mild ultrasonication of the freestanding TiO$_2$ nanotube membrane in methanol was performed for a few minutes. A very thin gray layer on top
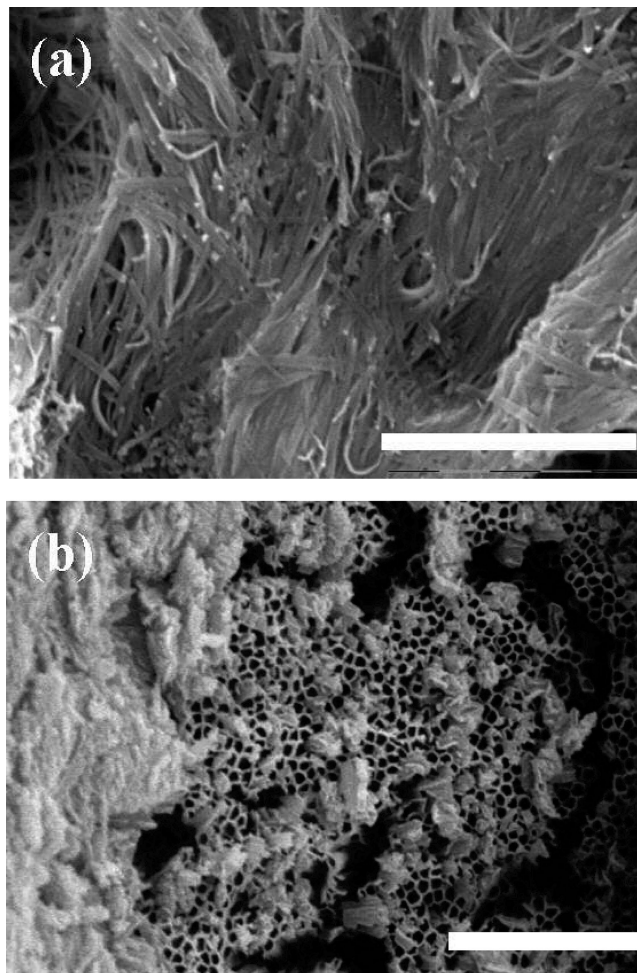
(25) Dilmohamud, B. A.; Seeneevassen, J.; Rughooputh, S. D. D. V.; Ramasami, P. *Eur. J. Phys.* **2005**, *26*, 1079.
(26) Lim, J. H.; Choi, J. *Small* **2007**, *3*, 1504.

Figure 2. SEM images of the freestanding TiO$_2$ nanotube membrane right after anodization (top view). (a) Thin layer of TiO$_2$ nanowires formed because of chemical dissolution of TiO$_2$ and covered on the top of nanotubes; scale bar = 2 μm. (b) In some regions (e.g., around the cracks of nanowires), TiO$_2$ nanotubes were revealed. The TiO$_2$ nanowires can be seen on the left of the image; scale bar = 5 μm.

of the membrane was seen to gradually break and disperse into methanol during ultrasonication. The process was repeated several times to ensure complete removal of the top TiO$_2$ nanowire layer. Figure 3 shows a topological SEM image of the sonicated freestanding TiO$_2$ membrane. Highly ordered arrays of nanotubes are clearly evident. The average tube diameter, D, is 90 nm, with an average wall thickness of 15 nm. The average interpore distance, λ_{C-C}, is 120 nm. The cross-sectional SEM image confirms closely packed arrays of nanotubes perpendicular to the membrane surface. The bottom of nanotubes was closed (Figure 4). The nanotube arrays go straight from the top to the bottom of the membrane as shown in Figure 5. The vertically oriented, close-packed morphology of nanotubes provides a direct pathway for electron transport at the nanotube walls as compared to the "electron-hopping" in TiO$_2$ nanoparticles that are commonly used in DSSCs. The thickness of the freestanding membrane is ∼135 μm after 60 h of anodization.

The as-prepared TiO$_2$ nanotube membrane was amorphous, as revealed by Raman spectroscopy, in which broad spectra ranging from 100 to 1000 cm^{-1} is clearly evident (black curve in Figure 6). To take advantage of nanotubular structures of TiO$_2$ for use in DSSCs, the initially amorphous
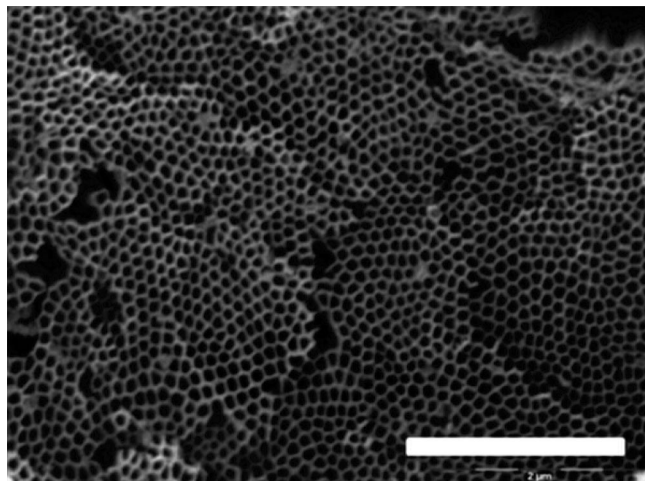
Figure 3. SEM image of the freestanding TiO$_2$ nanotube arrays after mild ultrasonication treatment to remove the top TiO$_2$ nanowires (top view). The average diameter is 90 nm, with a wall thickness of 15 nm. The average interpore distance is 120 nm. Scale bar = 2 μm.
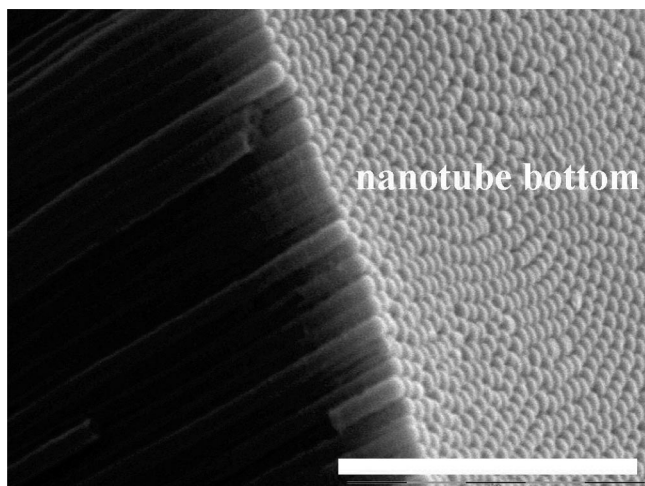

Figure 4. SEM image of the freestanding TiO$_2$ nanotube arrays (side view). The closed end of nanotube bottoms is clearly evident. The nanotubes are perpendicular to the membrane surface. Scale bar = 2 μm.
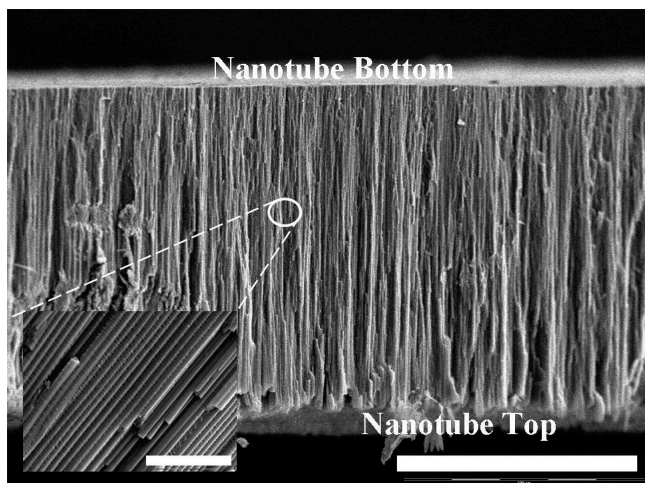

Figure 5. SEM image of the freestanding TiO$_2$ nanotube membrane (side view). A close-up of nanotubes marked in a circle is shown as an inset. The scale bars in the main image and inset are 100 and 2 μm, respectively.

TiO$_2$ nanotubes should be converted into photoactive anatase or rutile phase.[15] Thus, thermal annealing of the membrane
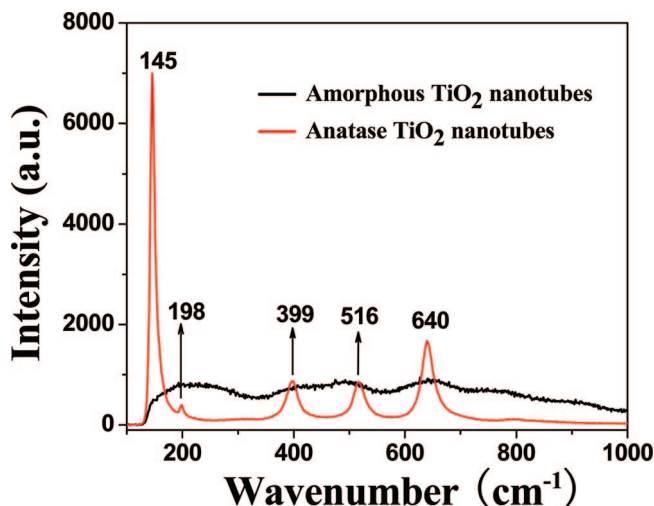

Figure 6. Raman spectra of amorphous (black curve) and anatase (red curve) TiO$_2$ nanotubes. After annealed at 500 °C in air for 3 h, amorphous TiO$_2$ was transformed into the anatase phase, as verified by the specific Raman peaks at 145, 198, 399, 516, and 640 cm^{-1}.

was carried out at 500 °C in air for 3 h to induce crystallinity. The Raman spectrum of the annealed membrane (red curve in Figure 6) shows the specific peaks of anatase TiO$_2$ at 145, 198, 399, 516, and 640 cm^{-1}.[27,28] The nanotubular structures were retained after high-temperature annealing, as evidenced in SEM measurement (see Figure S2 in the Supporting Information).

In summary, we report a simple and safe method to obtain self-organized, freestanding TiO$_2$ nanotube arrays with ultrahigh aspect ratio of the diameter/length (~1500) by simply using solvent-evaporation-induced delamination of the TiO$_2$ "barrier layer", which was formed between the TiO$_2$ membrane and Ti foil during anodization. A gentle mechanical bending of anodized Ti foil may be applied to facilitate complete detachment of the membrane from the metallic substrate if necessary. As-grown TiO$_2$ nanotubes were amorphous and transformed into photoactive anatase form after annealed at high temperature in air. The amorphous–anatase transformation of TiO$_2$ nanotubes was verified by confocal Raman spectroscopy. The nanotubular structures of the freestanding TiO$_2$ membrane were retained after annealing. Currently, we are constructing quantum dot-sensitized nanostructured solar cells (QDSNSC) in a front-side-illuminated mode using quantum dots[29–33] as sensitizers and impregnating them into these vertically aligned, ultra-high-aspect-ratio TiO$_2$ nanotubes. The use of TiO$_2$ nanotubes with an ultrahigh aspect ratio improves the incident light absorption efficiency. Moreover, the vertically aligned nano-

(27) Aggour, M.; Dittrich, T. H.; Belaidi, A.; Sieber, I.; Rappich, J. *Phys. Status Solidi C* **2005**, *2*, 3344.
(28) Zhao, J.; Wang, X.; Chen, R.; Li, L. *Solid State Commun.* **2005**, *134*, 705.
(29) Xu, J.; Xia, J. F.; Wang, J.; Shinar, J.; Lin, Z. Q. *Appl. Phys. Lett.* **2006**, *89*, 133110.
(30) Xu, J.; Xia, J.; Lin, Z. Q. *Angew. Chem., Int. Ed.* **2007**, *46*, 1860.
(31) Xu, J.; Wang, J.; Mitchell, M.; Mukherjee, P.; Jeffries-EL, M.; Petrich, J. W.; Lin, Z. Q. *J. Am. Chem. Soc.* **2007**, *129*, 12828.
(32) Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z. Q.; Tsukruk, V. V. *Langmuir* **2007**, *23*, 4509.
(33) Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z. Q.; Zhang, L.; Tsukruk, V. V. *Langmuir* **2007**, *23*, 10176.

tubes not only offer a large interfacial area for excitons to effectively dissociate but also facilitate efficient electron transports from the tube walls to electrodes. Thus, an enhanced photoconversion efficiency may result.

Supporting Information Available: SEM images of the freestanding TiO_2 nanotubes obtained after treated with concentrated HF solution to chemically etch the top TiO_2 nanowires that were formed by chemical dissolution of TiO_2 during electrochemical anodization (Figure S1) and SEM images of the freestanding TiO_2 nanotubes after thermal annealing at 500 °C in air (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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