Facile Synthesis and Morphology Control of Bamboo-Type TiO₂ Nanotube Arrays for High-Efficiency Dye-Sensitized Solar Cells

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S Supporting Information

ABSTRACT: We report fast synthesis of bamboo-type TiO₂ nanotube arrays via anodization of Ti in nonhazardous electrolyte under alternating voltage condition for applications as photoanodes in high-efficiency dye-sensitized solar cells (DSSCs). Formation mechanism of bamboo-type nanotubes is also explored. The low-voltage step reduces pH and ion-diffusion gradient inside TiO₂ nanotubes and induces formation of bamboo ridges on outer tube walls when a second high-voltage step is conducted. Ridge spacing and length of bamboo-type nanotubes can be facilely tuned by adjusting time of high-voltage step and electrolyte composition. All DSSCs based on bamboo-type TiO₂ nanotube arrays show higher efficiencies than those based on smooth-walled nanotubes with the same tube length due to enhanced surface area of bamboo-type nanotubes for dye loading. It is also noted that DSSC efficiency increases with the ridge density of bamboo-type nanotubes of the same length. For example, DSSC based on bamboo-type nanotubes (8 μm long) with the highest ridge density exhibits an efficiency of 5.64%, higher than the efficiency of 3.90% exhibited by DSSC based on smooth-walled nanotubes of the same length. Moreover, the DSSC efficiency can be further increased to 6.8% by growing significantly longer bamboo-type TiO₂ nanotubes (16.5 μm long) via decreasing water content in electrolyte.

1. INTRODUCTION

As fossil fuel reserves become depleted, the long-lasting and source-free solar energy is becoming an economically viable source of energy to offer a clean solution to the current energy crisis.^{1,2} However, conventional silicon solar cells are still expensive due to high production costs. Since dye-sensitized solar cell (DSSC) was first invented in 1991, it has attracted intensive attention for its low cost and easy fabrication.^{3–8} Hence, DSSC is regarded as one of the promising alternatives to traditional silicon solar cells. In DSSCs, electrons of dye are excited by solar energy adsorption and the electrons from photoexcited dye inject into the conduction band of photoanode titanium dioxide (TiO₂). The electrons then diffuse through the TiO₂ layer to the electrode and subsequently reach the counter electrode through an external circuit. The dye molecules regain electrons from a redox couple iodide/triiodide (I[−]/I₃[−]) in an electrolyte. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode, and this process requires a catalytic functionality of Pt on the cathode surface. This photoconversion process is regenerative.

Up to now, energy conversion efficiencies of DSSCs reported in literature are still lower than those of traditional silicon solar cells.⁹ One of the most efficient approaches to enhance DSSC efficiency is to reduce the recombination losses in the random network of TiO₂ nanocrystalline.^{10–12} To reduce electron recombination with excited dye and I₃[−] in electrolyte, 1D nanotubes have been investigated to enhance the electron transport owing to several advantages as follows.^{13–19} First, 1D nanotubes have less grain boundaries that electrons have to

pass; thus electron mobility is increased leading to fast transport of excited electrons. Second, ordered TiO₂ nanotubes provide a vertical pathway for electron transport along the tube and thus minimize electron loss during diffusion process. Third, the vertically ordered tubular structure will facilitate the filling of new sensitizer or solid-state electrolyte for a further increase in efficiency and improvement of stability, whereas the disordered mesoporous structure of conventional TiO₂ nanocrystalline film makes infiltration of solid or viscous electrolyte difficult and ineffective.^{20,21}

As such, self-aligned TiO₂ nanotube arrays have been widely studied for applications as photoanodes in DSSCs and anodic oxidation of Ti has been the most common method for synthesis of these nanotube arrays.^{17,22–28} However, the 1D nanotube structure typically has a low surface area compared to mesoporous films resulting in insufficient dye loading and low light-harvesting efficiency. In general, DSSCs based on TiO₂ nanotube arrays with a length of 10–30 μm only showed energy conversion efficiencies within a range of 1–3%. For example, Li et al. fabricated TiO₂ nanotube arrays of various lengths (10, 17, and 22 μm long) by anodic oxidation, and DSSCs based on these nanotube arrays exhibited efficiencies of 1.08%, 1.25%, and 1.39%, respectively.²⁹ Kim et al. also reported synthesis of TiO₂ nanotube arrays up to 10, 20, and 30 μm in length, with corresponding DSSC efficiencies of 2.33%, 2.88%, and 2.87%.³⁰ To increase the DSSC efficiency,

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nanotubes with lengths up to 100 μm have been produced to increase the surface area for dye loading.^{31,32} Shankar et al. even obtained ultralong TiO_2 nanotubes with length over 200 μm , which delivered significantly improved DSSC efficiency of 6.89%.³² However, synthesis of these ultralong nanotubes costs much time (more than 10 h) and electricity for anodization process, and the reported efficiencies of TiO_2 -nanotube-array-based DSSCs are still lower than DSSCs based on mesoporous TiO_2 films due to the relative low internal surface area for dye loading of nanotube arrays.^{33–35}

Some recent efforts have been made to further increase surface area of TiO_2 nanotube arrays for enhanced efficiencies of DSSCs, such as fabricating bamboo-type TiO_2 nanotube arrays with ridges on tube sidewalls. Schmuki's group reported an effective strategy to synthesize bamboo-type TiO_2 nanotube arrays via anodization under an alternating voltage (AV) condition.^{36,37} Such bamboo structure gained enhanced surface area owing to the ridges and yielded a photo conversion efficiency that was 55% higher than that of smooth-walled nanotubes with identical film thickness of 8.0 μm when used in DSSCs. However, these bamboo-type TiO_2 nanotube arrays were grown by using an electrolyte containing environmentally hazardous HF and a rather high voltage (120 V) for more than 10 h, and efficiency of DSSCs based on the bamboo-type TiO_2 nanotube arrays was still relatively low (2.96%). Zhang et al. synthesized bamboo-type TiO_2 nanotube arrays using an alternating current condition by using relatively high voltages (80 and 30 V), and reported a slightly improved DSSC efficiency of 3.47%.³⁸ It is noted that synthesis of these bamboo-type TiO_2 nanotube arrays is not very efficient as it takes a long time and high voltages. Though the formation process of bamboo-type TiO_2 nanotubes is outlined, there is no report about fundamental explorations about the growth mechanism and no clear understanding of factors that control morphological features such as ridge spacing. More importantly, the efficiencies of DSSCs based on these bamboo-type nanotubes have not shown appreciable improvement compared to DSSCs based on smooth-walled TiO_2 nanotube arrays.^{37–39}

In this report, we employ a facile anodic oxidation method to fabricate bamboo-type TiO_2 nanotube arrays for enhanced efficiencies of DSSCs. In comparison with former syntheses reported in literature,^{36–38} we use ethylene glycol-based electrolyte that contains NH_4F and H_2O but not the hazardous HF. In addition, the synthesis consumes much less energy and takes shorter time because our bamboo-type nanotubes with comparable lengths can be achieved by anodizing Ti at lower voltage (60 V) for less than 3 h. The formation mechanism of bamboo-type TiO_2 nanotubes synthesized via alternating high- and low-voltage anodization steps is explored as well. As the AV pulse duration is directly correlated to the tube/ridge growth, the morphological features of nanotubes such as ridge spacing can be precisely manipulated. The nanotube length can also be tuned by changing water content in electrolyte. Such fast synthesis and facile morphology control of bamboo-type TiO_2 nanotube arrays allows for optimization of nanotubes to achieve high-efficiency DSSCs.

2. EXPERIMENTAL SECTION

Ti foils (0.25 mm thickness, 99.5 wt % purity, Alfa Aesar) were degreased by sonicating in acetone, deionized (DI) water, and ethanol for 15 min, respectively, then rinsed with ethanol and dried in a nitrogen stream. Electrochemical anodization of the Ti foils was carried out in a two-electrode cell with a platinum

mesh as the counter electrode at room temperature. The electrolyte for anodization was prepared with anhydrous ethylene glycol (EG) with NH_4F (0.3 wt %) and H_2O (5 vol % for shorter TiO_2 nanotube arrays, 2 vol % for longer TiO_2 nanotube arrays). The voltage was supplied by a dc power supply with digital display (Model 1623A, PK Precision). To prepare bamboo-type TiO_2 nanotube arrays, the anodization process consists of multiple cycles of alternating high- and low-voltage steps as shown in Figure 1. The voltage is first increased

Figure 1. Anodization sequence for the formation of bamboo-type TiO_2 nanotube arrays.

from zero to V_{high} (60 V) and being kept at V_{high} for a time t , then drops to V_{low} (10 V) and is also held at V_{low} for a time t , followed by increasing to V_{high} (60 V) again and being kept at for a time t . Each voltage alternate from 60 to 10 V is regarded as one cycle. High voltage of 60 V in the first cycle is reached via a voltage ramp of 1 V/s, whereas other voltage steps are switched without ramp. The AV pulse duration, t , is kept the same for V_{high} and V_{low} during the anodization process. To produce bamboo-type TiO_2 nanotube arrays with different ridge spacing, t is varied (1, 2, and 4 min). For comparison purposes, a smooth-walled TiO_2 nanotube array was prepared by anodization of Ti under constant-voltage conditions (CV) at 60 V for 1 h. After anodization, the samples were rinsed in deionized water and dried in air, followed by heat treatment at 450 $^{\circ}\text{C}$ in air for 3 h to produce the anatase phase. The annealed TiO_2 nanotube arrays were soaked in 100 mL of 0.2 M TiCl_4 aqueous solution at 70 $^{\circ}\text{C}$ for 30 min and then annealed in at 450 $^{\circ}\text{C}$ in air for 30 min.

To fabricate DSSCs, the as-prepared TiO_2 nanotube arrays were soaked in anhydrous ethanol containing 0.2 mM N719 dye ($\text{Ru}[\text{LL}'-(\text{NCS})_2]$, $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid, $\text{L}' = 2,2'$ -bipyridyl-4,4'-ditetrabutylammonium carboxylate, Solaronix Co.) and sensitized for 24 h at room temperature. Afterward, these films were rinsed with acetonitrile in order to remove physisorbed N719 dye molecules. Platinized counter electrode was fabricated by drop casting 0.5 mM $\text{H}_2\text{PtCl}_6/\text{isopropanol}$ solution on FTO glass substrate that has a hole for electrolyte injection later on, followed by heating at 400 $^{\circ}\text{C}$ in air for 20 min. The dye-sensitized TiO_2 nanotube arrays were sandwiched together with Pt-coated FTO glass by applying a 100 μm thick hot-melt sealing film as the spacer (Meltonix 1170–100, Solaronix Co.). DSSCs were sealed by applying heat and pressure with a hot press at 110 $^{\circ}\text{C}$. A I^-/I_3^- based electrolyte, which contained 0.10 M GTC in a mixture of

acetonitrile and valeronitrile (85:15 v/v) (No. ES-0004, IoLiTec Inc., Germany) was injected through the hole on the Pt-coated FTO into DSSC.

A FEI Quanta 3D FEG scanning electron microscope (SEM) was used to characterize morphology of TiO_2 nanotube arrays. Crystal structure of TiO_2 nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with $\text{Cu K}\alpha$ radiation operated at 30 kV and 15 mA with a scan rate of $2^\circ/\text{min}$. The current–voltage (J – V) characteristics of DSSCs were recorded using a Keithley 2400 source meter. A solar light simulator (Model: 67005, Oriel) was used to simulate sunlight under one sun AM 1.5 G ($100 \text{ mW}/\text{cm}^2$) illumination provided by a 150 W xenon arc lamp (Model: 6256, Oriel) and calibrated using a Si solar reference cell (Model: 91150 V, Oriel). Backside illumination mode was used, since the photoanode consists of TiO_2 nanotube array on Ti substrate which is not transparent to light.

3. RESULTS AND DISCUSSION

Morphology of anodic TiO_2 nanotube arrays can be adjusted by tuning synthesis conditions such as voltages, electrolyte composition and anodization time. Figure 2 displays smooth-walled nanotubes and bamboo-type nanotubes synthesized by anodizing Ti in EG electrolytes containing 0.3 wt % NH_4F and 5 vol % H_2O under CV and AV conditions, respectively. CV anodization at 60 V for 1 h leads to formation of ordered TiO_2 nanotubes with smooth walls, as shown in parts a and b of Figure 2. They are hollow inside with an open entrance on the top showing an average pore diameter $\sim 150 \text{ nm}$ (part a of Figure S1 of the Supporting Information). As can be seen from part a of Figure 2, the whole nanotube array is perpendicular to the Ti substrate, with a thickness of $\sim 8.0 \mu\text{m}$. In contrast to CV conditions, AV anodization processes produce bamboo-type TiO_2 nanotubes with rough walls, as shown in parts c and d of Figure 2 (BT-4), e and f (BT-2), and g and h (BT-1) with AV pulse duration times of 4, 2, and 1 min, respectively. BT-4 is formed under an AV condition with a sequence of 4 min at 60 V and 4 min at 10 V for 20 cycles as shown in parts c and d of Figure 2. The total time of this anodization sequence is 160 min; the resultant bamboo-type nanotube array (BT-4) has a thickness of $8 \mu\text{m}$ and the spacing between neighboring bamboo ridges is 400 nm . These bamboo-type TiO_2 nanotubes have clear top surfaces and open entrances, easy for infiltration of dye and redox electrolytes (parts b, c, and d of Figure S1 of the Supporting Information).

Parts e and f of Figure 2 present SEM images of BT-2 sample using AV condition with a sequence of 2 min at 60 V and 2 min at 10 V for 40 cycles. In comparison with BT-4 in parts c and d of Figure 2, the length of BT-2 nanotubes remains $8 \mu\text{m}$ as shown in part e of Figure 2, but the spacing between two neighboring bamboo ridges is decreased to 200 nm as can be seen from part f of Figure 2. In other words, ridge density is doubled in BT-2 compared to BT-4. To further increase surface area of bamboo-type nanotube arrays by increasing ridge density, the AV pulse duration time is further reduced to 1 min and number of AV cycles is increased to 80 yielding BT-1 sample as shown in parts g and h of Figure 2. The nanotube length stays at $8 \mu\text{m}$ (part g of Figure 2), but the spacing between neighboring bamboo ridges is further reduced to 100 nm (part h of Figure 2). Comparing the cross-section SEM images of BT-4, BT-2, and BT-1 in parts d, f, and h of Figure 2, ridge spacing of bamboo-type nanotubes decreases linearly with AV pulse duration time, whereas the nanotube length is the

Figure 2. SEM images of bamboo-type and smooth-walled TiO_2 nanotube arrays of $8.0 \mu\text{m}$ thickness. The tubes were synthesized in EG electrolytes containing 0.3 wt % NH_4F and 5 vol % H_2O under different anodization sequence of (a, b) smooth-walled: 60 V for 60 min; (c, d) bamboo-type-4: 60 V for 4 min, 10 V for 4 min, and 20 cycles; (e, f) bamboo-type-2: 60 V for 2 min, 10 V for 2 min and, 40 cycles; (g, h) bamboo-type-1: 60 V for 1 min, 10 V for 1 min, and 80 cycles.

same as the total high-voltage anodization time is the same. Our other work shows that a proper low-voltage duration time is required for ridge formation, whereas ridge spacing is dependent on the time of high-voltage step (D. S. Guan, P. Hymel, and Y. Wang, manuscript submitted). Because the ridge spacing relies on the high-voltage period, it can be seen that the total length of bamboo-type nanotubes is decided by the whole time of high-voltage steps. Therefore, morphology control of bamboo-type TiO_2 nanotube arrays can be achieved by simply adjusting AV pulse duration time and cycle numbers. Nanotube arrays with larger surface area can be obtained by using a shorter pulse duration for denser ridges and more cycle numbers for longer tubes for maximizing energy conversion efficiency of DSSCs.

The controllable formation of bamboo ridges via AV oxidation is related to the growth behaviors of anodic TiO_2 nanotube arrays under CV conditions. Once a constant voltage is applied, three fundamentally different morphologies of an

Figure 3. Schematic showing growth of bamboo-type TiO_2 nanotubes via anodic oxidation: (a) pH gradient profile in nanotubes during their steady growth at 1st high voltage step, (b) less steep pH gradient and pore formation at the 1st low voltage step, (c) formation of a ridge between the 1st section and 2nd section of nanotubes at the 2nd high voltage step, (d) pore formation at the 2nd low voltage step, (e) ridge formation between the 2nd section and 3rd section of nanotubes at the 3rd high voltage step.

oxide film emerge successively on Ti substrate. At the beginning, a compact oxide layer is formed; later, pits and pores originate in the compact layer and turn it into a porous structure; finally, these pores are separated by interpore cavities, eventually yielding an ordered tubular layer. Three chemical reactions occur simultaneously to complete such morphological evolution: (1) Field-assisted oxidation of titanium: water decomposes near the metal and produce O^{2-} and H^+ ions; the O^{2-} ions then migrate across an electrolyte–oxide interface to oxidize Ti. The reactions are described as:

(2) Field-assisted dissolution of titanium oxides: due to the electric field, Ti–O bond undergoes polarization and is weakened promoting dissolution of the oxides. (3) Chemical dissolution of titanium oxides: therefore, Ti^{4+} cations become soluble hexafluorotitanium complexes $[\text{TiF}_6]^{2-}$ that enter the electrolyte, whereas the free O^{2-} anions travel to the oxide–metal interface and react with metal. The reaction is described as:

After the anodization starts, pH and ion diffusion gradients are quickly established inside the tubular layer, which finally allows stable growth of TiO_2 nanotubes under a high voltage (part a of Figure 3). In this situation, water decomposes at the bottom of tubes and cavities (eqn1) and produces H^+ ions there. Some H^+ ions diffuse outward to cause a stable pH gradient, whereas others participate in the dissolution of surrounding oxides together with F^- ions from outside.²⁵ The substrate is continuously oxidized (eq 2) and the barrier layer at the bottom keeps moving toward the substrate resulting in steady growth of single-layer TiO_2 nanotubes.

Once this system is altered quickly to a lower voltage, fewer H^+ ions are yielded and fewer F^- ions diffuse to reach the tube bottom. Hence, pH gradient or ion concentration profiles are gradually adjusted to less steep gradients until compatible with the low-voltage condition (part b of Figure 3). Fewer H^+ ions make dissolution of oxides slower yielding a thicker barrier layer at the tube bottom or cavity bottom. After a short time, tiny pores originate in the barrier layer, which can be considered as the first stage of tube formation as introduced above. At this moment, a fast step back to the high voltage (60 V) will restart the growth of tubes and cavities toward the metal, and pores formed at low voltage are eaten by the regrown large tubes. The thick barrier layer under the tubes and cavities continued to be dissolved and pushed toward the substrate, but the part between two neighboring tubes survives and remains on the tube walls to form ridges yielding bamboo-

type nanotubes with two sections in the vertical direction (part c of Figure 3). Likewise, when this system is switched to the low voltage again, the pH gradient profile inside bamboo-type tubes tends to be less steep, and a second pore formation occurs at the base of these tubes, followed by origination of a second ridge between the second and third tube sections (parts d and e of Figure 3). In an anodization process consisting of multiple alternating high-voltage and low-voltage steps, such ridge formation event is repeated and the length of TiO_2 nanotubes with multiple sections is increased accordingly.

In addition to modifying the sidewall morphology, the length of bamboo-type TiO_2 nanotubes can also be tuned to grow ultralong nanotubes to further enhance surface area. Simply increasing the number of anodization cycles or time of anodization sequence does not necessarily lead to longer nanotubes due to dissolution of oxides in electrolyte. For example, an anodization sequence with 1 min at 60 V and 1 min at 10 V for 160 cycles (total time = 320 min, doubled time compared to anodization in part g of Figure 2) yields bamboo-type TiO_2 nanotube arrays with a thickness of 7 μm (part a of Figure 4), which is even shorter than 8 μm long BT-1

Figure 4. SEM images of bamboo-type nanotube arrays synthesized (a, b) in EG electrolytes containing 0.3 wt % NH_4F and 5 vol % H_2O under the anodization sequence of 60 V for 1 min, 10 V for 1 min, and 160 cycles; (c, d) in EG electrolytes containing 0.3 wt % NH_4F and 2 vol % H_2O under the anodize sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles.

nanotubes in part g of Figure 2. During the anodization oxidation process, the nanotube length typically increases with anodization duration time at the beginning of anodization. However, after the nanotube length reaches to a critical value, the longer nanotube limits the diffusion of ionic species to the metal/oxide interface, and chemical dissolution begins to dominate the anodization kinetics, resulting in decrease of nanotube length. Moreover, water content in electrolyte has significant effect on the tube length as well as the ridge spacing in bamboo-type nanotubes. So far we use EG electrolytes containing 0.3 wt % NH_4F and 5 vol % water. Reducing water content to 2 vol % and using the same anodization sequence for growing BT-1 earlier in part g of Figure 2 yields bamboo-type TiO_2 nanotube arrays (BT-L) as long as 16.5 μm (part c of Figure 4), which is significantly longer than BT-1 (8 μm). However, ridge spacing is increased to 230 nm, larger than 100

nm for BT-1 in part h of Figure 2. Less water in electrolyte allows formation of thinner barrier layers at the substrate because the donation of oxygen becomes difficult (eq 1 and 2) and results in a reduced tendency to form oxide.^{40,41} Ionic transport across the barrier layer is enhanced, and thus the motion of this layer toward the substrate is accelerated yielding faster growth of nanotubes. Meanwhile, as water content decreases, few H^+ ions are produced and diffusion of electrolyte species is slowed down, which makes difficult for origination of bamboo ridges, as evidenced by weakened and less clear ridges shown in the SEM image of part d of Figure 4.

The as-prepared anodic TiO_2 nanotubes are amorphous and they are heated at high temperature to convert to anatase phase for applications in DSSCs. Figure 5 shows XRD patterns of

Figure 5. XRD diffraction patterns of bamboo-type TiO_2 nanotubes produced by anodization sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles in EG electrolyte containing 0.3 wt % NH_4F and 5 vol % H_2O (a) As-prepared TiO_2 nanotube; (b) anatase TiO_2 nanotube formed after annealing at 450 $^{\circ}\text{C}$.

bamboo-type TiO_2 nanotubes (BT-1) produced by an anodization sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles in EG electrolyte containing 0.3 wt % NH_4F and 5 vol % H_2O . The XRD pattern of as-prepared bamboo-type nanotubes only has diffraction peaks of Ti indicating that the as-prepared bamboo-type nanotubes are amorphous. After heat treatment in air at 450 $^{\circ}\text{C}$ for 2 h, the TiO_2 nanotubes are converted into crystalline forms. The emergence of (101) and (200) peaks of metastable anatase suggested the transformation of amorphous TiO_2 to anatase TiO_2 .

High-concentration TiCl_4 treatment is carried in this work to improve short circuit current for DSSC applications. It has been reported in literature that TiCl_4 treatment can enhance dye absorption on the surface, improve the electron transport properties in nanocrystalline TiO_2 films, and increase the charge separation efficiency.^{42–44} After being treated in TiCl_4 aqueous solution, TiO_2 nanotube arrays are sensitized by N719 dye, and are integrated into DSSCs. Figure 6 presents J – V curves of DSSCs based on 8 μm long smooth-walled TiO_2 nanotubes (SW), 8 μm long bamboo-type nanotube arrays with different ridge spacing (100 nm, 200 nm, 400 nm) (BT-1, BT-2, BT-4), and 16.5 μm long bamboo-type nanotubes with a ridge spacing of 230 nm (BT-L). Photovoltaic characteristics of these DSSCs such as short-circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and efficiency (η) are summarized in Table 1. It is evident that all the bamboo-type nanotube arrays (BT-4, BT-2, and BT-1) show higher short circuit currents than smooth-walled nanotube array (SW) of the same length because the bamboo ridges on sidewalls enhance the

Figure 6. J – V characteristics of DSSCs using different TiO_2 nanotube arrays. (SW: smooth-walled nanotube synthesized at 60 V for 60 min; BT-4: bamboo-type nanotube synthesized at 60 V for 4 min, 10 V for 4 min, and 20 cycles; BT-2: bamboo-type nanotube synthesized at 60 V for 2 min, 10 V for 2 min and, 40 cycles; BT-1: bamboo-type nanotube synthesized at 60 V for 1 min, 10 V for 1 min and, 80 cycles; BT-L: bamboo-type nanotube synthesized in the electrolyte containing 2 vol % H_2O at 60 V for 1 min, 10 V for 1 min, and 80 cycles.

Table 1. Photovoltaic Characteristics of Dye-Sensitized Solar Cells Shown in Figure 6

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF ^a	η^b (%)	tube length (μm)
SW	6.96	0.85	0.66	3.90	8.0
BT-4	7.91	0.83	0.60	3.94	8.0
BT-2	9.44	0.78	0.60	4.42	8.0
BT-1	11.60	0.81	0.60	5.64	8.0
BT-L	13.95	0.87	0.56	6.80	16.5

^aFill-factor (FF) = $((P_{\text{max}})/(I_{\text{sc}} \times V_{\text{oc}}))$. ^bPower conversion efficiency (η) = $((I_{\text{sc}}(\text{mA}/\text{cm}^2) \times V_{\text{oc}}(\text{V}) \times \text{FF})/(100(\text{mW}/\text{cm}^2))) \times 100(\%)$.

surface area of nanotube arrays for dye chemisorption. Among the three bamboo-type nanotube arrays with the same length of 8 μm , BT-1 with highest ridge density delivers the highest energy conversion efficiency (5.64%) compared to BT-2 and BT-4, exhibiting V_{oc} of 0.81 V, J_{sc} of 11.60 mA/cm^2 , FF of 0.60 (Table 1), which represents a 44.6% increase in cell efficiency compared to SW. Similarly, DSSC based on BT-2 with higher ridge density shows better performance than DSSC based on BT-4. These results indicate that bamboo-type TiO_2 nanotube arrays (same length) with higher ridge density enhance DSSC performance more due to larger surface area.

Among all the TiO_2 nanotube arrays, BT-L (16.5 μm long, ridge spacing of 230 nm) shows the highest DSSC efficiency of 6.80% owing to its doubled length. Obviously, the significantly increased nanotube length leads to the enhanced short circuit current (13.95 mA/cm^2), which contributes to the high DSSC efficiency. Efficiency of DSSC based on BT-L is almost twice the highest cell efficiency (3.43%) from DSSCs based on bamboo-type TiO_2 nanotubes reported in literature to date.³⁸ However, it is noted that J_{sc} does not increase linearly with the length of nanotubes. This phenomenon is consistent with others' work on anodic TiO_2 nanotube arrays. For example, Li et al. fabricated various smooth-walled TiO_2 nanotube arrays with the increasing thickness of 10, 17, and 22 μm , which exhibited the increasing but nonlinear J_{sc} of 3.16, 3.85, and 4.29 mA/cm^2 and efficiencies of 1.08%, 1.25%, and 1.39%, respectively.²⁹ Likewise, Kim et al. reported synthesis of TiO_2

nanotube arrays with 10, 20, and 30 μm in length and corresponding nonlinearly increasing J_{sc} of 7.77, 9.62, and 10.40 mA/cm^2 and efficiency of 2.33%, 2.88%, and 2.87%.³⁰ It has been discovered that the inner diameter of nanotubes is decreasing from the tube entrance to tube bottom, due to continuous dissolution of formed tube walls, yielding a V-like hollow structure.⁴⁵ Accordingly, the intertube cavities tend to be narrower at the bottom where the roots of nanotubes are closely contacted. The narrowing gaps make it difficult to achieve full filling of dye solution or redox electrolytes resulting in an undesired loss of outer surface area especially in long TiO_2 nanotube arrays. This limitation is probably responsible for a fact that DSSCs based on ultralong TiO_2 nanotubes with a length of several hundreds of micrometers do not show much improved J_{sc} .³² However, if the surface area of long nanotubes is fully utilized by dye loading and electrolyte infiltration, a linear increase in J_{sc} with the tube length could be observed. For example, Gao et al. synthesized vertically aligned TiO_2 nanotubes with identical diameters but with lengths varying from 10 to 20 μm , by using long ZnO nanowires as templates.⁴⁶ Gaps between these long nanotubes are wide enough for complete dye absorption and electrolyte infiltration, and thus the related J_{sc} increases linearly from 6.5 to 12.2 mA/cm^2 when the nanotube length is doubled.

4. CONCLUSIONS

We employ a facile anodic oxidation method to synthesize bamboo-type TiO_2 nanotube arrays with controllable ridge density and tube length by applying alternating voltage sequence, for enhanced efficiencies of dye-sensitized solar cells (DSSCs). Synthesis in this work involves nonhazardous electrolyte and is much more efficient than those reported in literature. Using less than one-third of the anodization time and half of the voltage that were reported in literature yields bamboo-type TiO_2 nanotubes with comparable tube length and ridge density. Formation mechanism for these bamboo-type TiO_2 nanotube arrays is also discussed. Wall morphology and length of these nanotubes can be manipulated by tuning high-voltage anodization time and electrolyte composition, which can be used to improve and maximize efficiency of DSSCs. For instance, DSSC based on 8 μm long bamboo-type TiO_2 nanotubes with ridge spacing of 100 nm exhibits a significantly improved efficiency of 5.64% due to the enhanced surface area and light scattering provided by the bamboo ridges, whereas DSSC based on smooth-walled nanotubes of the same length shows an efficiency of 3.90%. In addition, ultralong (16.5 μm) bamboo-type TiO_2 nanotube array can be fabricated by decreasing water content in electrolyte, to further increase surface area and improve DSSC efficiency to 6.80%. Such facile synthesis and morphology control of bamboo-type TiO_2 nanotube arrays allow for optimizations of nanotubes for maximized efficiency of DSSCs and will advance the DSSC technology.

■ ASSOCIATED CONTENT

Supporting Information

Top-view SEM images of TiO_2 nanotubes prepared via constant-voltage or alternating-voltage anodization conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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