

Titania-nanotube-array-based photovoltaic cells

H. Wang, C. T. Yip, K. Y. Cheung, A. B. Djurišić,^{a)} and M. H. Xie
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

Y. H. Leung and W. K. Chan
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

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Dye-sensitized solar cells based on perpendicular titania nanotube arrays were fabricated. Titania nanotube arrays were prepared by anodization of Ti foil. The cell performance as a function of nanotube length and anodization method was investigated. Short circuit current density and cell efficiency increased with the nanotube length. Device performance was also affected by anodization method, spacer layer thickness, and annealing conditions. With optimized device structure and titania annealing procedure, short circuit current density of 3.28 mA/cm² could be achieved under AM 1.5 simulated solar irradiation. © 2006 American Institute of Physics.

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Dye-sensitized solar cells (DSSCs) based on porous TiO₂ can reach an efficiency as high as 10%.¹ Therefore, considerable research effort has been devoted to the development of these types of solar cells. In addition to research on other types of metal oxides, such as ZnO,² SnO₂,³ Nb₂O₅,⁴ or SrTiO₃,⁴ considerable research has been devoted to the development of solar cells based on different morphologies of the oxide layer, such as ZnO nanowires⁵ or porous TiO₂ obtained from block copolymer templates.^{6,7} However, while ZnO nanowire arrays can be fabricated by a simple hydrothermal process, this is not the case for TiO₂. Hydrothermal or chemical synthesis methods typically result in freestanding titania nanotubes,^{8–10} which can be used to fabricate solar cells using similar techniques as in the case of TiO₂ powders. However, it has been shown that the use of nanotubes results in considerable improvement of the solar cell efficiency^{8–10} which was attributed to improved electron transport.⁹ It is expected that the electron transport would be further improved in perpendicular arrays of titania nanotubes, which can be fabricated by anodization of Ti foil.^{11–17}

Dye sensitization of the TiO₂ nanotubes has been investigated by measuring photocurrent in an electrochemical cell under illumination.^{14,15} However, achieved incident photon to charge carrier conversion efficiency (IPCE) values have been low, 3.3% for 2.5 μm long tubes¹⁴ and ~5% for flame annealed 4.4 μm long tubes.¹⁵ The performance of the nanotubes was strongly affected by annealing.¹⁵ It was also shown recently that performance of the nanotubes can be considerably improved with TiCl₄ treatment.¹⁷ We investigated influence of anodization method and the tube length on the performance of nanotube based dye-sensitized solar cells. Under the 1.5 AM illumination, the power conversion of dye-sensitized solar cell increased from 0.1% to 0.62% as the length of nanotube increased from 220 nm to 2 μm, and the short circuit current density of 3.28 mA/cm² was obtained for optimized annealing conditions.

The Ti foils (99.7%, 0.250 mm), KF (99.0%), sodium bisulfate monohydrate (99%), sodium citrate dihydrate (99%), and hydrofluoric acid (concentration of 40%) were purchased from Aldrich. The *cis*-bis(isothiocyanato)

bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II) (N3 dye), the electrolyte iodolyte PMI-50, platinum coated transparent electrodes, and sealing materials SX1170-25 (25 μm thick) and SX1170-60 (60 μm thick) were purchased from Solaronix. The Ti foils were anodized in different electrolytes to obtain nanotube arrays with different lengths. When electrolyte is 0.5 vol % HF in de-ionized water, anodization carried out for ~2 h at 15 V results in tube lengths from ~180 to 250 nm.¹⁶ In order to fabricate longer nanotubes (1 and 2 μm), the electrolyte consisted of a mixture of KF (0.1M), sodium citrate tribasic dehydrate (0.2M), sodium bisulfate monohydrate (1.0M), and sodium hydroxide in de-ionized water. Sodium bisulfate monohydrate and sodium hydroxide were used to adjust the pH value of the solution (in the range of 2–4) prior to addition of KF. The anodization was performed at 25 V for 24 or 48 h. The samples were then rinsed in de-ionized water and annealed at 450 °C (heating/cooling rate of 1 °C/min) for 3 h in air or ammonia [flow rate of 115 SCCM, (SCCM denotes cubic centimeter per minute at STP) pressure of ~160 torr].

The morphology was examined by scanning electron microscopy (SEM, Leo 1530) and transmission electron microscopy (TEM, Philips Tecnai-20 and JEOL 2010F). The composition was studied using x-ray photoelectron spectroscopy (XPS, PAL 102) and energy dispersive x-ray spectroscopy (EDX) in TEM. XPS was performed before and after sputtering to remove surface contamination. For solar cell

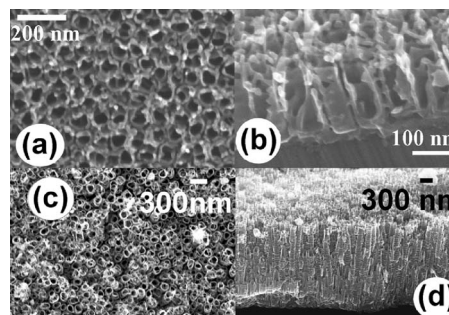


FIG. 1. SEM images of titania nanotubes with different tube lengths: (a) and (b) 220 nm, HF electrolyte and (c) and (d) 2 μm, KF electrolyte. Left panel represents top view, while right panel shows side view.

^{a)}Electronic mail: dalek@hkusua.hku.hk

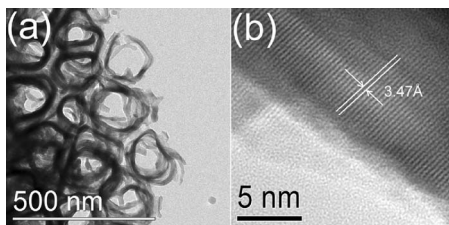


FIG. 2. (a) TEM and (b) high resolution TEM images of 1 μm TiO_2 nanotubes annealed in ammonia.

fabrication, the annealed samples were soaked in N3 dye solution (20 mg N3 in 100 ml ethanol) for 2 h at 80 °C and then 15 h without heating, followed by rinsing in pure ethanol to remove nonchemisorbed N3. Platinum coated glass was used as a counter electrode, and the electrolyte was infiltrated in vacuum oven (3×10^{-3} torr) overnight and then in high vacuum chamber ($\sim 10^{-5}$ torr) for 30 min. Spacer layers of 25 and 60 μm were used to separate the electrodes, and the cells were sealed at 100 °C according to instructions from the supplier. The device area was 0.785 cm^2 . The current-voltage characteristics were measured using a Keithley 2400 source meter. For white light efficiency measurements (at 100 mW/cm^2), Oriel 66002 solar light simulator with AM 1.5 filter was used. All the measurements were performed in air.

Figure 1 shows representative SEM images of nanotubes obtained by the following two anodization procedures. For 1 and 2 μm nanotubes obtained from KF based electrolyte, the tube inner diameter was 110 ± 10 nm and the thickness of tube wall was 20 ± 5 nm, in agreement with the literature.¹⁵ Tubes obtained from HF based electrolyte have a wall thickness of 10 ± 3 nm and an inner diameter of 50 ± 5 nm. Thus, the tubes fabricated with HF electrolyte have smaller diameters and thinner walls, in addition to shorter length compared to those fabricated with KF based electrolyte. The addition of other chemicals to KF containing electrolyte to stabilize the pH value and maintain it close to neutral one results in the formation of longer tubes^{12,13,15} due to slow chemical etching rate of TiO_2 . Apart from differences in size and consequently more fragile tubes made with HF based electrolyte (thinner walls), no other significant differences in tube morphologies were observed for two types of electrolytes.

The structure and composition of the nanotubes were examined using TEM and EDX. TEM revealed that the walls of the tube have a lattice spacing of 3.47 Å (consistent with

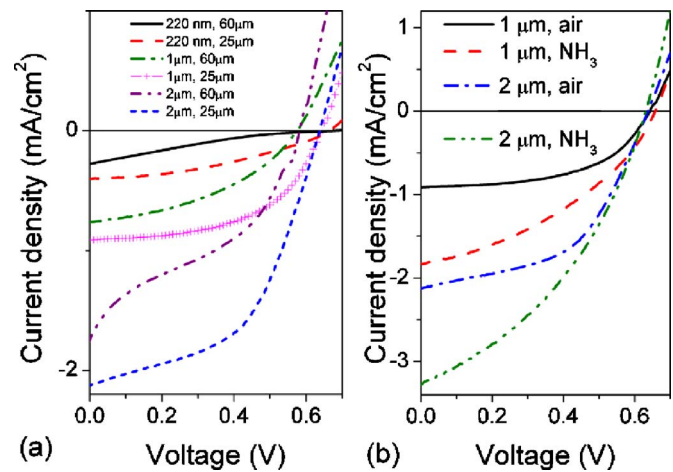


FIG. 3. (Color online) (a) Current-voltage characteristics under AM 1.5 illumination for different lengths of titania tubes (220 nm, 1 μm , and 2 μm) and different spacer layers (25 and 60 μm). (b) Comparison of current-voltage characteristics under AM 1.5 illumination for cells consisting of 1 and 2 μm long TiO_2 tube arrays annealed in air and NH_3 .

[101] direction in anatase TiO_2), as shown in Fig. 2. Solar cells were fabricated based on arrays obtained with KF and HF electrolytes. The cell performances for different nanotube lengths and different thickness of the spacer layer are summarized in Table I, while Fig. 3(a) shows the I - V curves of the devices. The short circuit current density increases as the tube length increases. Higher quantity of the dye can be adsorbed on longer tubes, leading to improved photon absorption and carrier generation with increased tube length.¹⁷ It can also be observed that the spacer layer thickness significantly affects the device performance. Thicker spacer layer for all nanotube lengths results in reduced short circuit current density and reduced fill factor. Since the electrolyte thickness was found to affect the series resistance of DSSCs,¹⁸ thicker spacer layer would result in longer distance to platinum electrode, and hence larger series resistance and poorer device performance. Since the device performance is dependent on the distance between the electrodes, large electrode distance is likely responsible for low values of photocurrent in electrochemical cells.^{14,15} With the spacer layer of 25 μm , combined with improved impregnation and infiltration techniques, device performance can be improved and short circuit current density of 2.12 mA/cm^2 for 2 μm long nanotubes annealed in air can be achieved. To further improve device performance, annealing in NH_3 has been performed. It has been shown that nitrogen doping increases the

TABLE I. The performance parameters of the dye-sensitized solar cells with different TiO_2 tube lengths under AM 1.5 illumination. The 220 nm tubes were fabricated using HF electrolyte, while the 1 and 2 μm tubes were fabricated using KF electrolyte.

TiO_2 length (nm)	Spacer thickness (μm)	V_{oc} (V)	I_{sc} (mA/cm^2)	FF	η (%)
220	25	0.67 ± 0.02	0.40 ± 0.05	0.39 ± 0.03	0.10 ± 0.02
220	60	0.69 ± 0.01	0.28 ± 0.02	0.18 ± 0.01	0.03 ± 0.003
1000	25	0.65 ± 0.01	0.92 ± 0.05	0.53 ± 0.06	0.32 ± 0.05
1000	60	0.58 ± 0.01	0.77 ± 0.04	0.41 ± 0.01	0.18 ± 0.01
1000, NH_3	25	0.66 ± 0.01	1.83 ± 0.25	0.39 ± 0.02	0.47 ± 0.04
2000	25	0.64 ± 0.01	2.12 ± 0.02	0.51 ± 0.08	0.69 ± 0.09
2000	60	0.58 ± 0.02	1.75 ± 0.03	0.35 ± 0.06	0.36 ± 0.07
2000, NH_3	25	0.64 ± 0.01	3.28 ± 0.06	0.38 ± 0.09	0.80 ± 0.19

efficiency of DSSCs due to increased absorption of doped titania in the visible range and increased quantity of the adsorbed dye,¹⁹ and that nitrogen can be effectively incorporated by calcinations of titania in ammonia atmosphere.²⁰ Short circuit current densities increased for both 1 and 2 μm tube devices, and I_{sc} of 3.28 mA/cm² is obtained for 2 μm nanotubes. On the other hand, fill factor is somewhat reduced for ammonia annealed cell, in agreement with previous work,¹⁹ but the overall efficiency is still higher due to considerable increase in the short circuit current density.

It can also be observed that the cells with nanotubes prepared from HF based electrolyte exhibit smaller fill factor than those prepared from KF based electrolyte for the same spacer layer thickness. One possible reason for the observed difference is different electron transport for the titania tubes obtained by two anodization procedures. It has been shown that the anodization method required to produce long nanotubes results in incorporation of sodium (~ 5 at. %) and fluorine (~ 2 at. % at the surface, 0.2 at. % in the interior) impurities due to the presence of sodium and fluorine in the electrolyte solution.¹⁵ To investigate in detail the differences between the nanotubes prepared under different conditions, XPS measurements have been performed. Wide range scan revealed that the samples contain only C, O, Ti, and N, in agreement with EDX results. No sodium or fluorine impurities previously observed in titania nanotubes¹⁵ were found. Narrow range scans of relevant peaks have been performed for all samples, before and after sputtering (10 nm) to remove surface contamination. After sputtering, only the sample annealed in NH₃ exhibited N peak, confirming incorporation of nitrogen inside the tubes, but the nitrogen concentration is low. Sputtering also caused broadening of the Ti and O peaks, indicating sputtering induced damage (point defects and surface states) which caused broader distribution of binding energies. Thus, detailed analysis of sample compositions was performed by fitting the oxygen and titanium peaks before sputtering. The composition was determined from the fitted peak areas taking sensitivity factors into account. Oxygen peak could be fitted with two peaks, O₁ (530.8–530.9 eV) and O₂ (531.7–531.9 eV) corresponding to two different oxidation states of oxygen, in agreement with previous work.²¹ In the case of Ti peak, three peaks are necessary in the 2*p*_{3/2} region, one at 459.7 eV corresponding to Ti⁴⁺ in anatase/rutile titania,^{21,22} one peak at 460.8 eV, and one small contribution at lower energy (~ 457.7 eV) which can be attributed to Ti³⁺ 2*p*_{2/3} contribution. From the peak areas, we can obtain that O₁/O₂=2.29 for HF, 2.42 for KF, air annealing, and 1.99 for KF, NH₃ annealing. O₁/Ti ratios are 1.80 for HF and KF, NH₃ annealed samples and 2.02 for KF, air annealed samples. There are also small differences in Ti³⁺/Ti⁴⁺ ratios, which may affect adsorption of the dye molecules,²² but in all samples Ti³⁺/Ti⁴⁺ ratio is small. Therefore, the main difference between the samples is in O₁/Ti ratio, which is lower for the HF and KF, NH₃ annealed samples compared to samples prepared with KF electrolyte annealed in air. Overall O/Ti and O₁/O₂ ratios are also higher for sample annealed in air. This indicates that stoichiometry and defects significantly affect the charge transport, and that lower O₁/Ti ratio results in higher short

circuit current density, but somewhat lower fill factor.

To summarize, the DSSCs based on titania nanotube arrays were fabricated for different lengths of titania nanotubes. While the short circuit current density was mainly determined by the nanotube length, the anodization method and/or composition of the electrolyte during anodization, as well as annealing environment, affected the fill factor of the devices. For annealing in ammonia, the increase in the short circuit current density results in overall improved efficiency in spite of the decrease in fill factor, with the short circuit current density of 3.28 mA/cm² and power conversion efficiency of 0.80%. Further improvements could likely be obtained with further optimization of annealing conditions and device structure, as well as increased amount of adsorbed dye, either via fabricating longer tubes or by TiCl₄ treatment.

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