Preparation, characterization, and application of titanium nano-tube array in dye-sensitized solar cells

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Abstract

The vertically orientated TiO\textsubscript{2} nanotube array (TNA) decorated with TiO\textsubscript{2} nano-particles was successfully fabricated by electrochemically anodizing titanium (Ti) foils followed by Ti-precursor post-treatment and annealing process. The TNA morphology characterized by SEM and TEM was found to be filled with TiO\textsubscript{2} nano-particles interior and exterior of the TiO\textsubscript{2} nano-tubes after titanium (IV) \textit{n}-butoxide (TnB) treatment, whereas TiO\textsubscript{2} nano-particles were only found inside of TiO\textsubscript{2} nano-tubes upon titanium tetrachloride (TiCl\textsubscript{4}) treatment. The efficiency in TNA-based DSSCs was improved by both TnB and TiCl\textsubscript{4} treatment presumably due to the increase of dye adsorption.

Keywords: TiO\textsubscript{2}, titanium tetrachloride, titanium (IV) \textit{n}-butoxide, nano-tube, anodization, DSSCs

Introduction

Since O’Regan and Grätzel reported highly efficient TiO\textsubscript{2}-based dye-sensitized solar cells (DSSCs) in 1991, many attempts have been made to sensitize titanium dioxide (TiO\textsubscript{2}) nano-scale films. TiO\textsubscript{2} nano-particulate films are typically preferred as they provide a high surface area for dye adsorption, leading to high photocurrent conversion efficiency. Due to the three-dimensional transport path, TiO\textsubscript{2} nano-particulate films brought higher electron recombination and met larger grain boundary among interconnected nano-particles. In this research, we have fabricated vertically orientated one-dimensional nano-structure TiO\textsubscript{2} nano-tube array (TNA) by electrochemical anodization. The TNA-based DSSCs were expected to have a better performance than the nano-particulate-based DSSCs due to the better electron transportation and recombination property. However, due to the less surface area of TiO\textsubscript{2} nano-tube array, the efficiency of TNA-based DSSCs is still lower than that of TiO\textsubscript{2} nano-particle-based DSSCs. Post-treatment of TNA by Ti precursors to form a TiO\textsubscript{2} nano-particulate layers on TNA became a strategy which could increase the TiO\textsubscript{2} surface area for more dye adsorption. This research showed that the DSSCs fabricated by TNA after post-treatment by titanium tetrachloride (TiCl\textsubscript{4}) and TiO\textsubscript{2} nano-tubes after titanium (IV) \textit{n}-butoxide (TnB) raised up the photocurrent conversion efficiency.

DSSCs have aroused intense interest over the past few years because they have been demonstrated to be able to achieve high solar-to-electric energy conversion efficiency with low-cost manufacture process and materials. In DSSCs, the photoelectrodes are made of porous semiconductor layers chemisorbed with an organic sensitizer. When DSSCs are illuminated with sun light, the photoelectron of the sensitizer is ejected into the semiconductor films and sent to the external circuit. The redox pairs in the electrolyte transport the holes from the oxidized dye molecules to the counter electrode to complete the electric cycle [1]. TiO\textsubscript{2} is one of the most promising semiconductor materials in preparing the photoanodes for DSSCs due to its wide band gap characteristics and unique photoelectric properties [2]. TiO\textsubscript{2} nano-particulate films are preferred as they provide a high surface area for dye adsorption, leading to high photocurrent conversion efficiency. The electron-collecting TiO\textsubscript{2} layer in DSSCs is typically 10 to 15 μm thick with a three-dimensional network of interconnected nano-particles. However, TiO\textsubscript{2} nano-crystalline films
acquire long electron transport path and larger grain boundary between nano-particles [3,4]. This would hinder the electron collection efficiency and limit the performance of DSSCs. It was proposed that one-dimensional TNA aligned perpendicular to photoanode substrate could enhance the electron transportation and, thus, lower the possibility of electron recombination with redox electrolytes, leading to the higher photo-to-electron conversion efficiency [3-5]. The TNA has been first prepared by Zwilling et al. using the electrochemical anodization method [6]. The TNA morphology, including tube length, hole diameter, and wall thickness, can be systematically controlled by varying the anodization parameters, such as anodization potential, electrolyte, and pH value [7,8]. Zhu et al. had investigated the dynamics of electron transport and recombination properties of the oriented TiO2 nano-tube structure in DSSCs by frequency-resolved modulated photocurrent/photovoltage spectroscopies and found the higher charge-collection efficiency and slower electron recombination in the TiO2 nano-tube-based DSSCs than the TiO2 nano-particle-based counterparts [3]. One of the reasons for improving the performance of the DSSCs is considered to be due to the increase of the amount of the dye adsorbed onto the TiO2 surface of photoelectrodes in DSSCs. In order to increase the surface area of TiO2 electrodes, post-treatment of TNA to form an extra layer of TiO2 nano-particles has been applied [9-11]. In this work, we compared the effect of post-treatment of anodic TNA by different Ti-precursors on the TNA morphology and the resulting DSSCs performance.

**Experimental details**

**Preparation, modification, and characterization of anodic TNA**

Titanium foils with thickness of 0.25 mm (99.5% purity; Alfa Aesar, Ward Hill, MA, USA) were used for anodic growth of TNA. Titanium foils were first polished by sonication in chemical polishing solvent which contained nitric acid, ammonia fluoride, urea, ethanol, and hydrogen peroxide in 12:5:5:3:12 v/v ratio and rinsed subsequently with deionized (DI) water, acetone, and methanol. The anodization reaction was carried out in a two-electrode electrochemical cell with polished Ti foil (2 × 2.5 cm²) which served as the anode-working electrode and Pt foil (thickness 0.025 mm; Alfa Aesar) as the counter electrode. The separation between Ti electrode and Pt electrode was about 3.5 cm. The anodization electrolyte contains 0.3 wt% NH4F and 2 vol% H2O in ethylene glycol solution. The anodization was operated under a constant potential of 60 V at low temperature of 15°C with magnetic stirring. The reaction period controlled the thickness of TiO2 nano-tube arrays. Typically the TNA samples with tube length of approximately 15 μm were obtained after 2 h of anodization process. It is evident that increasing the TNA length leads to the increase of short-circuit photocurrent density due to the higher surface area available for dye adsorption. The TNA foils were then carefully washed with deionized water to remove the surface residual electrolyte in the nano-tube arrays. Such prepared TNA samples were then annealed at 450°C for 3 h with a heating rate of 1°C/min in order to transform the TNA from amorphous to anatase crystalline phase.

Figure 1 summarizes the procedures for post-treatment of annealed TNA. The TiCl4-treated TNA (TNA-TiCl4) was prepared from annealed TNA which was soaked in 0.2 M TiCl4 solution (in ethanol) at 60°C for 30 min followed by heat treatment at 450°C for 30 min. The TnB-treated TNA (TNA-TnB) was prepared as follows: titanium (IV) n-butoxide (Ti(O-Bu)4, TnB) (ACROS Organics, New Jersey, USA) was mixed with 2 M CH3COOH (pH = 2.5) at room temperature under magnetic stirring for approximately 5 days until a homogeneous sol solution was obtained. The TiO2 sol and the annealed TNA were both transferred to a teflon-lined autoclave to perform the hydrothermal treatment at 200°C for 5 h. The Ti foil was then removed from the autoclave, rinsed with DI water, and heated at 450°C for 30 min to form TNA-TnB.

The surface morphology and crystal phase of TNA, TNA-TiCl4, and TNA-TnB were investigated by scanning electron microscopy (SEM) (SM6500F, JEOL Ltd., Akishima, Tokyo, Japan) and X-ray diffraction (XRD) (PANalytical X’Pert PRO, Almelo, The Netherlands), respectively. The results were confirmed by high-resolution transmission electron microscopy (Hitachi H-7100, Hitachi Ltd., Chiyoda, Tokyo, Japan).

**Dye-sensitized solar cell assembly and performance measurement**

To fabricate DSSCs devices, three kinds of TNAs including TNA, TNA-TiCl4, and TNA-TnB, served as photoanodes, were combined with a transparent Pt counter electrode (cathode). The TNA samples were sensitized by dye molecules (3 × 10⁻⁴ M, N719 in a mixed solvent of acetonitrile and tertbutyl alcohol (volume ratio = 1:1)) for 24 h. The amount of dye adsorbed on TNA electrodes was determined by desorbing the N719 from TNAs surfaces into a solution of 0.1 M NaOH. The concentration of the adsorbed N719 was analyzed by UV-visible spectrophotometer (V-630, JASCO Corp., Easton, MD, USA). The Pt cathode was made by a ‘two-step dip coating’ process developed by Wei et al. [12]. We have first prepared the poly-N-vinyl-2-pyrrolidone (PVP)-capped Pt nano-particles by dissolving PVP (M.W. = 8000) and H2PtCl6 (Pt precursor)
into deionized water at room temperature and well stirred until a light-yellow solution was obtained. A NaBH₄ solution was then added drop by drop to the H₂PtCl₆-PVP solution, and the solution quickly turned into a black color, indicating the formation of Pt nano-particles (Pt-PVP solution).

FTO glass (8Ω/sq., Solaronix SA, Aubonne VD, Switzerland) was pretreated by 1% ML-371 aqueous solution at room temperature for 1 min in order to increase adhesion between the PVP-capped Pt nano-particles and FTO surface. The ML-371-modified FTO substrate was then dipped into the Pt-PVP solution for 5 min and rinsed with deionized water followed by heat-treatment at 450°C for 1°C/min for 30 min to remove completely the organic component and complete the preparation of counter electrode.

To assemble the DSSCs, the liquid electrolyte of 0.1 M lithium iodide, 0.05 M iodine (I₂), 0.5 M 4-tert-butylpyridine, 0.5 M 1,2-Dimethyl-3-propylimidazolium iodide in acetonitrile was applied to the above-prepared Pt electrode which was then placed over the N719-coated TNAs electrodes. The edges of the cells sealed with a hot-melt film (Surlyn, 125 μm) and the electrolyte (I⁺/I⁻ redox couple) were injected into the space. The active cell area studied in this work is 0.25 cm² (0.5 cm × 0.5 cm). The photoelectrochemical performance of the resultant solar cells were measured by back illuminated through the Pt counter electrode due to the non-penetration of light through the photoanode Ti metal substrate.

The current (I)-voltage (V) characteristics were performed using a digital source meter (Keithley model...
with the TNA-based DSSCs devices under one-sun AM 1.5 irradiation from a solar simulator (300 W Xe light and filters, Oriel Instruments, Irvine, CA, USA) on a 0.25 cm² sample area.

Results and discussion
Formation and characterization of anodic titanium oxide nano-tube arrays
TiO₂ electrode is one of the major concerns in DSSCs application. Since the TiO₂ phase, morphology, and surface area of TiO₂ films will affect the dye adsorption, electron transport, and electrolyte diffusion in the cell as well as the DSSCs performance. In this work, we have devised two kinds of Ti-precursor solutions to fabricate TiO₂ nano-particles decorated TNA on Ti substrates which can serve as photoanodes for DSSCs device. During the optimization stage of anodization process, the important roles of the anodization condition, including the thickness of Ti-foil (0.05-0.25 mm), temperature (15-30°C), anodization potential (20-60 V), reaction period (10 min-24 h), and various kinds of F-containing electrolytes (HF, KF, and NH₄F) in controlling the thickness (length of TiO₂ nano-tubes), homogeneity, and morphology of TNA were revealed. The data presented below were obtained with NH₄F/H2O/ethylene glycol electrolyte solution after anodization procedure at 15°C for 2 h. Figure 2 shows a typical current-time plot recorded during the constant potential anodization process. Within the first few seconds, the current dropped drastically to a local minimum indicating the oxidation of Ti-foil to form surface pits acting as nucleation sites for tube formation [13]. Upon increasing the pit density, the current increased to a maximum where the pit density reached saturation. After further anodization, the current gradually decreased due to the continuously lengthen of TiO₂ nano-tubes. Such anodization behavior is commonly observed in the self-organized pore formation process [14] in which the competition between TiO₂ oxide layer formation and dissolution of titanium progressed concurrently. Finally, the formation of vertically oriented TNA was achieved. The initially grown TNA was gray, which turned to yellow color after annealing at 450°C for 3 h.

Figure 3a shows the SEM images of the untreated TNA formed by anodizing a titanium foil with two types of magnification: 10,000× (top view) and 50,000× (side view, inset). The SEM image of lower magnification of TNA (Figure 3a) shows high porosity character of anodic TiO₂ films with some nano-scale cracks. The higher magnification image of TNA (inset of Figure 3a) shows the self-organized TiO₂ nano-tubes aligned densely with hexagonal close-packed arrangement. The inner diameters of these TiO₂ nano-tubes based on SEM images are in the range of 100-120 nm, and the wall thickness is approximately 10 nm. The thickness of TNA corresponding to the length of TiO₂ nano-tubes is about 15 μm obtained from the SEM cross section analysis shown in Figure 4. It is consistent with other research works that high-aspect-ratio TiO₂ nano-tubes can be fabricated with rapid growth rate by anodization [4,9,15].

Figure 3b, c shows the top-view SEM images of the decorated TNAAs after post-treatment by TiCl₄ and TnB solution, respectively, with the corresponding side view images with higher magnification as shown in the inset.
of Figure 3b, c. The length of TiO₂ nano-tubes remains the same after different post-treatment. For both TiCl₄ and TnB treated TNAs samples (denoted as TNA-TiCl₄ and TNA-TnB), additional materials can be observed on the top of TNAs and inside the TiO₂ nano-tubes. Yet, outside the TnB-treated TNA, the TiO₂ nano-tubes

Figure 3 SEM images of top view of (a) TNA, (b) TNA-TiCl₄, and (c) TNA-TnB. The inset images are the side view of (a) TNA, (b) TNA-TiCl₄, and (c) TNA-TnB. TNA, TiO₂ nano-tube array; TNA-TnB, TiO₂ nano-tubes after titanium (IV) n-butoxide treatment; TNA-TiCl₄, TiO₂ nano-tubes after titanium tetrachloride treatment.
were apparently coated with an extra layer of TiO$_2$ nano-particles. Transmission electron microscope (TEM) experiments had been performed on TNA-TiCl$_4$ and TNA-TnB samples detached from the Ti foil and dispersed on a copper grid. The bulk crystallites were observed (Figure 5a) inside TiO$_2$ nano-tubes in the case of TiCl$_4$-treated TNA sample. In TnB-treated TNA, bulk crystallites were observed both inside and outside the nano-tubes as shown in Figure 5b. The average inner diameter of TiO$_2$ nano-tubes in TNA-TiCl$_4$ and TNA-TnB after different post-treatment was about 85-120 nm based on TEM analysis which is consistent with SEM results.

XRD was used to confirm the crystalline phase of TiO$_2$ nano-structure. Figure 6 shows the XRD patterns of (a) as-prepared TNA, (b) annealed-TNA, (c) TiCl$_4$-treated TNA, and (d) TnB-treated TNA. The as-prepared TNA (before annealing) were amorphous (Figure 6a). Upon annealing to 450°C, the sharp anatase diffraction peaks appeared (Figure 6b) with crystal domain of approximately 20 nm. After post-treatment by TiCl$_4$ and TnB, the XRD patterns remain the same for both TNA-TiCl$_4$ and TNA-TnB, suggesting that the TiO$_2$ crystalline phase was not affected by post-treatment. The slight increase of TiO$_2$ crystal domain to 22 nm (for TNA-TiCl$_4$) and 29 nm (for TNA-TnB) was due to the two times annealing at 450°C for post-treated TNAs samples.

**Application of anodic TNA electrodes to DSSCs and photoelectrochemical performance study**

The above-prepared TiO$_2$ nano-tube arrays (TNA, TNA-TiCl$_4$, and TNA-TnB) were used to fabricate the DSSCs for photoelectrochemical performance study. The results obtained from I-V curve measurements for N719-sensitized DSSCs under simulated AM 1.5 illumination is shown in Figure 7. The thickness of TNAs layers on Ti foil was fixed at approximately 15 μm. Table 1 lists the TNAs thickness, the amount of dye adsorbed on TNAs layers (N719$_{ads}$), and photoelectric data of the DSSCs in Figure 7 including the open circuit voltage, the short-circuit photocurrent density ($J_{sc}$), the fill factor, and the photocurrent conversion efficiency ($\eta$). It is apparent that by post-treatment of the TNA, the performance of DSSCs was notably enhanced. The device based on the untreated TNA has shown the lowest $J_{sc}$ (3.84 mA/cm$^2$) and $\eta$ (1.38%). This is due to the low surface area of the untreated TNA which uptakes less amount of dye molecules (0.092 μmole/cm$^2$). Higher efficiency and current density of DSSCs device might be attributed to the higher amount of adsorbed N719 and the fast electron transportation on TiO$_2$ electrodes. As shown in Table 1, TnB treatment assisted the higher dye adsorption amount, raised from 0.092 to 0.116 μmole/cm$^2$ (approximately 26% increase of N719$_{ads}$), and $J_{sc}$ also raised from 3.84 to 5.97 mA/cm$^2$ (approximately 55% increase of $J_{sc}$). Both results lead to the efficiency improvement from 1.38% to 2.40% (approximately 74% increase of $\eta$). The significant increase of dye adsorption is due to the increased surface area from the decorated TiO$_2$ nano-particles on TNA, as clearly seen from the SEM images (Figure 3c). TEM images (Figure 5b) also vindicated the presence of bulk TiO$_2$ crystallites inside and outside the TNA. The further increase

![Figure 4 SEM cross sectional view of annealed-TNA](http://www.nanoscalereslett.com/content/7/1/147)
of $J_{sc}$ as well as $\eta$ is attributed to the increase of TiO$_2$ crystallinity of TNA-TnB, as evidenced by XRD. The dye loading for TNA-TiCl$_4$ sample is lower compared to that of TNA-TnB because the TiO$_2$ nano-particles only subsist inside the nano-tubes. The slightly higher efficiency of TNA-TiCl$_4$-based DSSCs compared to the untreated TNA one is due to the better TiO$_2$ crystallinity after two times annealing process. Variation in the performance of different devices might be due to the variations in the TiO$_2$ tube length. Nevertheless, same trends were observed within each batch of device study.
Conclusions
The decorated TNAs were successfully fabricated by anodization method followed by titanium precursor post treatment. The morphology of TNA without post-treatment was observed from SEM and TEM images, typically approximately 15 μm length, approximately 100 nm diameter, and 10 nm wall thickness were achieved after 2 h reaction. TNA with titanium precursor treatment alters the morphology which was confirmed from the SEM and TEM images. In the case of TNA-TnB, TiO₂ nano-particles were filled interior and exterior of the TiO₂ nano-tubes, whereas TiO₂ nano-particles were filled only inside the TiO₂ nano-tubes in TNA-TiCl₄ upon TiCl₄ treatment. An XRD pattern clearly indicates

![Figure 6 XRD patterns of (a) as-prepared TNA, (b) annealed-TNA, (c) TiCl₄-treated TNA, and (d) TnB-treated TNA. XRD, X-ray diffraction; TNA, TiO₂ nano-tube array; TNA-TnB, TiO₂ nano-tubes after titanium (IV) n-butoxide treatment; TNA-TiCl₄, TiO₂ nano-tubes after titanium tetrachloride treatment; A, anatase diffraction peak.](image)

![Figure 7 Photocurrent-voltage characteristics of DSSCs made by TNA, TNA-TiCl₄, and TNA-TnB. TNA, TiO₂ nano-tube array; TNA-TnB, TiO₂ nano-tubes after titanium (IV) n-butoxide treatment; TNA-TiCl₄, TiO₂ nano-tubes after titanium tetrachloride treatment.](image)
that the TNA, TNA-TiCl₄, and TNA-TnB were pure anatase phase after annealing process at 450°C. The photocurrent conversion efficiency of TNA-based, TNA-TiCl₄-based, and TNA-TnB-based DSSCs was 1.38%, 1.61%, and 2.40%, respectively. The results showed that the DSSC efficiency in TNAs was enhanced by TiCl₄ and TnB precursor post-treatment, presumably due to the increase of dye adsorption. The higher solar efficiency in TnB-doped DSSCs is due to the formation of extra layer of TiO₂ nanoparticles on TNA, leading to the higher amount of dye adsorption as well as higher photocurrent.

### Abbreviations

D: deionize; DSSCs: dye-sensitized solar cells; TEM: transmission electron microscope; TiCl₄: titanium tetrachloride; TiO₂: titanium dioxide; TNA: anatase phase after annealing process at 450°C. The photocurrent conversion efficiency of TNA-based, TNA-TiCl₄-based, and TNA-TnB-based DSSCs was 1.38%, 1.61%, and 2.40%, respectively. The results showed that the DSSC efficiency in TNAs was enhanced by TiCl₄ and TnB precursor post-treatment, presumably due to the increase of dye adsorption. The higher solar efficiency in TnB-doped DSSCs is due to the formation of extra layer of TiO₂ nanoparticles on TNA, leading to the higher amount of dye adsorption as well as higher photocurrent.

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### Authors' contributions

The work presented here was performed in collaboration of all authors. SYH confirmed the results from the preliminary experiments and helped in writing the manuscript. CCC set up the anodization system and carried out the preliminary trials of anodization reaction. CS and WRL discussed the results and wrote the manuscript. SK and CYL proofread the manuscript and corrected the English. All authors read and approved the final manuscript.

### Competing interests

The authors declare that they have no competing interests.

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### Table 1 The I-V characteristics of TNA-based DSSCs

| Sample | N719ads μmole/cm² | Film thickness (nm) | Voc (V) | Jsc (mA/cm²) | FF |
|--------|-------------------|--------------------|--------|--------------|----|
| TNA    | 0.092             | 14                 | 0.68   | 3.84         | 0.53 1.38 |
| TNA-TiCl₄ | 0.096           | 15                 | 0.66   | 4.83         | 0.51 1.61 |
| TNA-TnB | 0.116            | 16                 | 0.66   | 5.97         | 0.61 2.40 |

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