# Fabrication of Titanium Dioxide Nanotubes and their Photovoltaic Performance for Dye-sensitized Solar Cells

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TiO<sub>2</sub> nanotubes (TNTs) were prepared by the electrochemical anodization method using titanium thin films deposited on indium tin oxide (ITO) substrates by the DC magnetron sputtering technique. The effect of voltage (20 - 40 V) and amount of ammonium fluoride (NH<sub>4</sub>F) (0.4 - 1.4 wt%) were investigated. The fabricated TNTs were characterized by field emission scanning electron microscopy (FE-SEM), X-Ray Diffraction (XRD), X-ray Photoemission spectroscopy (XPS), and Fourier-Transformed Infrared Spectrophotometry (FT-IR) techniques. XRD pattern data exhibited anatase phase when TNTs were annealed at 400°C for 3 h. The XPS results revealed complement of Ti, O, F, Sn, In and C. The FT-IR spectrum exhibited the characteristic bands of the TiO<sub>2</sub> which indicate the Ti-O stretching mode. The average diameter and length of TNTs depend on ammonium fluoride, water and voltage and the optimal conditions were found to be 0.8 wt% ammonium fluoride, and voltage at 30 V. The obtained TNTs have an averaged diameter of 38 nm and length of 763 nm. For dye-sensitized solar cells (DSSCs) application, ruthenium complex (N719) was used as a sensitizer in this work. The energy conversion efficiency ( $\eta$ ) of TNTs was also evaluated.

**Keywords:** TiO<sub>2</sub> nanotubes, Electrochemical anodization method, Dye-sensitized solar cell, N719 ruthenium-based dye, Photovoltaic performance

## **1. INTRODUCTION**

The search for alternative renewable energy sources has been a field which receives a great deal of attention owing to two main reasons: the depletion of fossil fuels in the earth crust and the severe

environmental problems resulting from their combustion. Hence, it is necessary to search for alternative energy that is clean, renewable, cheap, safe and a viable alternative to fossil fuels [1]. Among the alternatives, solar energy is a promising candidate because of its sustainability and environmental friendliness. Therefore, photovoltaic cells are crucial in the conversion of solar energy to electrical energy [2]. Historically, dye-sensitized solar cells (DSSCs), developed by O'Regan and Gratzel in 1991, belong to the third generation [3] and can be considered to be a promising alternative because of their low manufacturing cost, non-toxicity and reasonable high conversion efficiency. In spite of these advantages, the DSSCs possess a number of drawbacks including the recombination reactions of the photo induced electron-hole pairs which cause the suppression of the photoelectric conversion efficiency (PEC) [4,5,6,7].

In DSSCs, the photoanode component has a significant influence on the device efficiency. Its properties, such as light scattering and harvesting dye adsorption, electron injection and collection, can deviate the photovoltaic device characteristics. Metal oxides are usually used as the photoanodes of DSSCs. Among them, titanium dioxide (TiO<sub>2</sub>) is a favorable material due to its unique structural and photoelectric properties as well as nontoxicity, biocompatibility and low cost. Moreover, TiO<sub>2</sub> nanostructures possess such excellent properties suitable for various applications such as photocatalysis, sensing, self-cleaning coating, and photovoltaic devices [8,9]. Anatase phase TiO<sub>2</sub> is predicted to exhibit excellent performance in photovoltaic devices because of its active surface chemistry, high electron mobility, and large band gap energy [10]. In order to improve the PEC of the DSSCs, the photoanodes properties, such as high specific surface area, fast electron transport, and outstanding light-scattering, must be taken into consideration. However, it is not always possible to combine all these factors in the same assembled materials. To overcome this problem, multilayer structures containing TiO<sub>2</sub> nanoparticles as the active layer as well as TiO<sub>2</sub> nanostructures with light scattering capability such as hierarchical flowers, rod like, microspheres, and nanotubes [11-14] have been investigated. Moreover, one dimensional (1D) nanostructures, TiO<sub>2</sub> nanotubes (TNTs) have been reported to exhibit higher electron transport efficiency when employed in DSSCs. Therefore, TNTs have received a great deal of attention due to its various functional properties and its high potential. Although several processing methods have been used to prepare TNTs, such as hydrothermal synthesis, anodic aluminium oxide template synthesis, and electrochemical anodization [15-18] which appears to be particularly useful because of its low cost and simple fabrication.

In the present work, the TNTs were fabricated using the electrochemical anodization method. The synthesized TNTs samples were characterized by various physical techniques such as X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), X-ray Photoemission spectroscopy (XPS) and Fourier-transformed Infrared Spectroscopy (FT-IR). The energy conversion efficiency in DSSCs was investigated. We also used the synthesized TNTs as a photoanode material for the fabrication of dye sensitized solar cell with N719 dye as a sensitizer.

#### 2. EXPERIMENTAL

## 2.1 Materials

Conducting indium tin oxide (ITO) coated glass substrates  $(10\Omega/cm^2)$  were received from Solaronix SA, Switzerland. The analytical grade chemical reagents used in the experiment are polyethylene glycol (Fisher), ammonium fluoride (Merck), lithium iodide (Sigma Aldrich), iodine (Carlo Erba), 4 - tert-butylpyridine (Sigma Aldrich) and the sensitizing dye bis(tetrabutylammonium) – cis di(thiocyanato) - N, N - bis(4-carboxylato – 4 - carboxylic acid - 2, 2 bipyridine) ruthenium(II) (or N719 dye, Dyesol, Switzerland). All the chemicals were used without further purification.

#### 2.2 Fabrication of TiO<sub>2</sub> nanotubes

TNTs were prepared using the electrochemical anodization method. Titanium films were deposited onto ITO substrates  $(1.50 \times 2.50 \text{ cm}^2 \text{ in size} \text{ with a thickness of } 1.00 \ \mu\text{m})$  using the DC magnetron sputtering technique. An electrolyte solution of ethylene glycol with 0.8 wt% NH<sub>4</sub>F and 2 wt% deionized (DI) water was used to the TNTs fabrication similar to a previous work [19]. The sputtered Ti films were used as an anode and platinum (Pt) films as a cathode. The distance between the two electrodes was 3.00 cm. As illustrated in Figure 1, Anodization was performed at 30 V using a power supply (M10-QS1001 MCP lab electronics, China) and an operating time of 35 min. After anodization, the as-prepared TNTs were rinsed in DI water and dried in N<sub>2</sub> gas. The as-prepared TNTs were calcined at 400 °C for 3 h to improve the anatase crystalline structure of the TiO<sub>2</sub>.



Figure 1. Synthetic route of TNTs via the anodization process.

#### 2.3 Characterizations

The surface morphologies were studied using field emission scanning electron microscopy (FE-SEM, TESCAN model MIRA3). The crystalline phase of the as-prepared TNTs was determined by X-ray diffraction (XRD) technique using a Rigaku MiniFlex II X-Ray diffractometer with CuK<sub> $\alpha$ </sub> radiation (1.5406 Å) from 20° to 80° (20-scan). Fourier-transformed infrared (FT-IR) spectra were obtained by a Perkin Elmer Spectrum Bx spectrophotometer in the range of 400-4000 cm<sup>-1</sup> using the attenuated total reflectance (ATR) technique. The chemical compositions of the as-prepared TNTs were measured using X-ray Photoelectron Spectrometer (XPS, Kratos Analytical Ltd. AXIS Ultra DLD). The power conversion efficiencies of the DSSCs were measured under a simulated solar light source with standard testing conditions-AM1.5, 100 mW/cm<sup>2</sup>, 25°C- in a Wacom solar simulator.

#### 2.4 Energy conversion experiment

To evaluate the performance of the dye on TNTs, photoanodes cells were fabricated. Dye sensitization was carried out by immersing the as-prepared photoanode films into 0.5 mM N719 ruthenium dye at ambient temperature for 24 h, which were then washed with isopropyl alcohol to remove excess dye and subsequently dried. The DSSCs were assembled in a typical sandwich-type cell by placing a platinum counter electrode side-by-side with the N719-sensitized TNTs electrode separated by a layer of films as a spacer. The active areas of the cells are about 0.25 cm<sup>2</sup>. The electrolyte was prepared with 0.5 M lithium iodide and 0.05 M iodine and 0.5 M 4-tert-butylpyridine in acetonitrile. The electrolyte was injected into the middle of the cell from the edge, which then spread into the inner space of the cell by capillary force, and the cell was tested immediately.

The photovoltaic test of the DSSCs was performed by measuring the J-V (current density-voltage) curves. The power conversion efficiencies of the DSSCs were determined under a simulated solar light source with standard testing conditions AM1.5, 100 mW/cm<sup>2</sup>, 25°C in a Wacom solar simulator.

It is well known that the photo conversion efficiency ( $\eta$ ) of DSSCs depends on the short-circuit photocurrent density ( $J_{SC}$ ), the open-circuit photo voltage ( $V_{OC}$ ), the cell fill factor (FF) and the incident light intensity [20]. The performance of DSSCs was calculated based on their FF and photo conversion efficiency ( $\eta$ ):

$$FF = \frac{V_{max}J_{max}}{V_{ocJsc}}$$
(1)  

$$\eta = \frac{V_{ocJsc}FF}{P_{in}} \times 100$$
(2)

where  $V_{max}$  is the maximum voltage,  $J_{max}$  the maximum current,  $V_{OC}$  is the open-circuit voltage (V),  $J_{SC}$  is the short-circuit current density (mA/cm<sup>2</sup>), and  $P_{in}$  is the incident light power (W/m<sup>2</sup>).

#### **3. RESULTS AND DISCUSSION**

## 3.1 Microstructure and optical properties

The formation of TNTs has been described in previous work [19]. Firstly, the TiO<sub>2</sub> films growth took place at the surface of the metal due to the interaction of the metal with  $O_2^-$  or  $OH^-$  ions. Then, chemical dissolution of the oxide by F<sup>-</sup> took place to produce  $[TiF_6]^{2-}$  complex ions by fluoride ions [21,22,23]. The tube formation growth continued when F<sup>-</sup> ions attack TiO<sub>2</sub> inside the pores [24].

The morphologies of the as-prepared TNTs were evaluated by FE-SEM technique as illustrated in Figures 2 and 3. As shown in the figure, regular and highly ordered nanotube arrays surface was obtained using the anodization method. The diameters and lengths of as-prepared TNTs from different anodization voltages and ammonium fluoride concentrations are shown in Table 1 and Table 2, respectively.



Figure 2. FE-SEM images of as-prepared TNTs obtained at different anodization voltages.

Table 1. A	Averaged	diameters and le	engths of a	s-prepare	d TNTs	obtained at	different	anodization	voltages

Condition	Diameter (nm)	Length (nm)
20 V	$42.1 \pm 7.6$	$393.4 \pm 32.1$
30 V	$48.2 \pm 5.1$	$848.8\pm19.9$
40 V	$55.9 \pm 7.0$	$979.8 \pm 13.8$

Figure 2 shows FE-SEM images of TNTs arrays on Ti films fabricated by anodization voltages of 20 V, 30 V and 40 V, which reveal a regularly arranged pore structure of the TNTs. The diameter of these pores gradually increased with increasing applied anodization voltage. Depending on the anodization voltage, pore diameters of the resulting nanotube arrays ranged from 40 nm to 60 nm.

The effect of fluoride concentration of the electrolyte on the morphology of the grown  $TiO_2$  was investigated by changing this parameter from 0.4 wt% to 1.4 wt%. As can be seen from the FE-SEM images in Figure 3, at low concentrations of fluoride, the porous structure as in Figure 3a was obtained. Increased fluoride concentrations led to TNTs structure with thinner walls. At high fluoride concentrations, the diameter of TNTs increased to 51 nm at 2.5wt% (a certain fluoride concentration) due to the increase rate of dissolution at the top and the bottom tube [24,25].



Figure 3. SEM images of as-prepared TNTs obtained at different ammonium fluoride concentrations.

**Table 2**. Averaged diameters and lengths of as-prepared TNTs obtained at different ammonium fluoride concentrations.

Condition	Diameter (nm)	Length (nm)
0.4% wtNH <sub>4</sub> F	$37.4 \pm 4.5$	$961.5 \pm 14.3$
0.8% wtNH <sub>4</sub> F	$48.2 \pm 5.1$	$848.8 \pm 19.9$
1.2% wtNH <sub>4</sub> F	$51.0 \pm 4.5$	$818.5\pm17.1$
1.4% wtNH4F	$49.2\pm4.2$	575.1 ± 22.4

The as-prepared TNTs arrays were amorphous. They must be converted into anatase phase for the application of DSSCs. The thermal annealing is a convenient way to obtain crystalline formation of the anodized TNTs arrays with the well-ordered tubular structure retained [26,27]. The XRD diffraction patterns of the as-prepared TNTs films are shown in Figure 4. It can be seen that all diffraction peaks of TNTs corresponded to the anatase phase (JCPDS 21-1272) [28]. The predominant anatase face of (101) was detected for the calcined TNTs sample while the non-calcined TNTs sample was amorphous phase.



Figure 4. XRD patterns of the as-prepared TNTs before and after calcination.



Figure 5. FT-IR spectra of the as-prepared TNTs before and after calcination.

The surface chemical composition was measured with Fourier-transformed Infrared Spectroscopy (FT-IR) as shown in Figure 5. Both as-prepared TNTs and calcined TNTs films revealed vibration bands of the Ti-O bond (400-800 cm<sup>-1</sup>) [28]. The as-prepared TNTs films showed the more intense band of adsorbed H<sub>2</sub>O (stretching mode at 3000-3600 cm<sup>-1</sup> [28] and bending mode at 1640 cm<sup>-1</sup> [28]) than the calcined TNTs films. The characteristic bands of TiO<sub>2</sub> (Ti-O band and –OH group) were found for both samples. The residual ethylene glycol molecules absorbed on the surface of TNTs films (-CH<sub>2</sub> (band v as-CH<sub>2</sub> at 2927 cm<sup>-1</sup>, v s-CH<sub>2</sub> at 2856 cm<sup>-1</sup>) and C-O (band at 1304 cm<sup>-1</sup>), C-C bond (band at 1304 cm<sup>-1</sup>) [29] was an indication of some adsorbed damaged ethylene glycol molecules after calcination.

The surface probe technique was used to determine the surface chemical state and composition of the materials. As depicted in the survey XPS spectrum in Figure 6, the elemental composition on the surface of the composite, both TNTs samples were found to contain Ti, O, F and C elements. The obtained elements existed on the surface of as-prepared TNTs measured from XPS technique were shown in Table 3. Peaks at 464.05 and 458.35 eV in Figure 6b are the characteristic peaks corresponding to Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> binding energies characteristics of the abundance of Ti<sup>4+</sup> on the surface of both TNTs samples [30]. A sharp peak observed at binding energies of 685.30 eV can be assigned to F1s confirming the presence of [TiF<sub>6</sub>]<sup>2-</sup> complex on the surface of the TNTs samples [31]. The non-calcined TNTs sample exhibited high F contents and the calcined TNTs samples showed low F contents due to the decomposition of [TiF<sub>6</sub>]<sup>2-</sup> complex during the calcination. The peak at 285-287 eV indicated the presence of ethylene glycol molecules adsorbed on the surface of the TNTs sample. The C1s peak was detected at 285 eV which was attributed to the Ti-C-O bonds, the C-OH found at 286.57 eV and C=O bond appeared at 288.88 eV of the residual ethylene glycol molecules adsorbed onto the surface of TNTs surface of TNTs surface of TNTs surfaces, which was confirmed by FT-IR technique.

As can be seen in Figure 6, the  $O^{2-}$  species of obtained TNTs before and after calcination gave four deconvoluted peaks related to the lattice oxygen in TiO<sub>2</sub> (at approximately 529.9 eV) and chemisorbed oxygen (peak at 530.7 eV was assigned to the surface oxygen defects of TNTs) [34] and another peak related to the oxygenated species at higher binding energy site centered at ~532.7 eV corresponding to the oxidized hydrocarbons as the residual ethylene glycol molecules were adsorbed onto the surface of the TNTs [34,35,36,37].

Element	Non-calcined TNTs (%wt)	Ts (%wt) Calcined TNTs (%wt)		
Ti	40.13	33.22		
Ο	32.40	35.13		
F	5.68	1.44		
С	20.07	11.00		

**Table 3.** Elements observed on the surface of as-prepared TNTs using the XPS technique.



Figure 6. XPS spectra of as-prepared TNTs a) non-calcined TNTs and b) calcined TNTs.

#### 3.2 Energy conversion efficiency

Current-voltage characteristics have been analyzed to understand the behavior of the as-prepared TNTs in the simulated solar spectrum. The J-V curve of the as-prepared TNTs solar cell sensitized by the N719 ruthenium-based dye is shown in Figure 7. The photovoltaic parameters of DSSCs with different TNTs are summarized in Table 4. The TNTs obtained from the condition of 1.2 wt% NH<sub>4</sub>F, 30 V showed an energy conversion efficiency of 0.40 % with the J<sub>sc</sub> value of 2.60 mA/cm<sup>2</sup>, V<sub>oc</sub> of 0.63 V and the FF of 0.24. Generally, the photocurrent density of DSSCs results from three major factors: (a) the number of photoexcited electrons, influenced by the capacity of dye molecules adsorption, (b) the rate of recombination at the interfaces, and (c) the redox property of  $I^-/I_3^-$  in the electrolyte. Moreover, since the TNTs could induce a large surface area resulting in an increase of dye molecules adsorption on the electrode surface; this TiO<sub>2</sub> photoanode could capture more photons to produce more photoexcited electrons. These photoexcited electrolyte interfaces [21,38]. The experimental results indicated the optimal condition were 1.2 wt% NH<sub>4</sub>F at 30 V. Hence, the obtained TNTs obtained the highest photo-to-electron conversion efficiency of 0.40 %.

_	Condition NH4F/voltage	$\mathbf{J}_{\mathbf{sc}} (\mathrm{mA} \;\mathrm{cm}^{-2})$	Voc (V)	FF	η (%)	_
	TNTs-0.4 %wt	1.05	0.60	0.25	0.17	
	TNTs-0.8 %wt	2.05	0.60	0.23	0.28	
	TNTs-1.2 %wt	2.60	0.63	0.24	0.40	
_	TNTs-1.4 %wt	1.81	0.60	0.27	0.29	_
	TNTs-20 V	0.98	0.59	0.20	0.12	
	TNTs-30 V	2.05	0.60	0.23	0.28	
	TNTs-40 V	1.94	0.60	0.23	0.27	

**Table 4.** DSSCs performance, short-circuit current density values (J<sub>sc</sub>), open-circuit voltages (V<sub>oc</sub>), and fill factors (FF) of prepared TNTs under different conditions.

\*Note: The conditions of 30 V and 0.8 wt% NH<sub>4</sub>F were the same. (The low DSSCs performance is due to the fact that we used an ITO substrate instead of an FTO substrate.)



**Figure 7.** Comparison of the J-V characteristics of DSSCs synthesized at different a) anodization voltages and b) NH<sub>4</sub>F concentrations.

A schematic representation of the mechanism of N719-sensitized TNTs electrode of the simplified setup of the current DSSCs is shown in Figure 8.



Figure 8. Mechanism of dye-sensitized TNTs solar cell.

It consists of three main components: a dye-sensitized TNTs photoanode, an electrolyte with a redox couple and a conductive counter electrode. In the general process, the N719 dye molecules are excited by photon leading to the excitation of the electrons from the valence band to the conduction band. These excited electrons are then transferred to the conduction band of TiO<sub>2</sub> at the interface. The dye molecules then lose their electrons and are oxidized. The oxidized dye molecules are subsequently reduced by the electrolyte  $\Gamma$ , which makes the dye molecules circulated. The  $\Gamma$  ion is oxidized to  $I_3^-$  and then diffuses to the counter electrode surface to receive the electrons from the external circuit. Finally, the  $I_3^-$  ion is restored to  $\Gamma$  ion [39,40]. As a result, more electrons are transported to ITO glass. It should be noted that the higher surface area of TNTs structure facilitates fast transport of electrons from TiO<sub>2</sub> to ITO resulting in the enhancement of the performance for DSSCs.

TNTs	Method	Dye	DSSCs	η (%)	Reference
length				-	
(µm)					
0.76	Electrochemical	N719	ITO/TNTs/N719/Pt	0.40	Current
	anodization method				work
	(NH <sub>4</sub> F+ethylene glycol,				
	30 V, 35 min, Ti films				
	using the DC				
	magnetron sputtering				
	technique as precursor)				
3.30	Anodization method	N719	Pt /N719/TNT/Ti	0.65	[41]
	(NaF+ethylene glycol,				
	60 V, 60 min, Ti foil as				
	precursor)				
1.60	Anodization method	N719	FTO/TNTs/N719/Pt	0.38	[42]
	(NH <sub>4</sub> F+ethylene glycol,				
	15 V, 5 h, Ti foil as				
	precursor)				
3.00	Anodization method	porphyrin	FTO/TNTs/porphyrin/	0.55	[43]
	(NaF+ethylene glycol,	(GD2)	Pt		
	60 V, 1 h, Ti foil as				
	precursor)				
2.00	Anodization method	natural dye	FTO/TNTs/natural	0.23	[44]
	(NH <sub>4</sub> F+ethylene glycol,	(Tradescantia	dye/Pt		
	60 V, 2 h, Ti foil as	zebrina)			
	precursor)				

**Table 5.** Comparison of photovoltaic performances using different TNTs arrays by AM 1.5 solar simulator (100 mW cm<sup>-2</sup>).

Photovoltaic performance of TNTs photoanode materials, as shown in Table 5, were dependent on several factors including the TNTs length (film thickness), anodization condition, type of DSSC electrolyte, dye loading, electrode, and light scattering effect. However, TNTs from our work could be used as a photoanode with enhanced DSSCs performance.

## 4. CONCLUSIONS

In summary, we have successfully fabricated the self-organized TNTs arrays with diameter of 38 nm and length of 763 nm in electrolytes consisting of water, ethylene glycol, and ammonium fluoride via the anodization method. We have found that the ordered nanotubes can be formed directly with the voltage applied in the electrolyte, and concentration of the fluoride electrolyte. The success of the present work is based on the effects of both the anodization voltage and the ammonium fluoride concentration on the formation of TNTs arrays. In addition, we have converted all the as-prepared amorphous TNTs arrays into the anatase phase by annealing at high temperatures. Investigation of the obtained TNTs to achieve the best photoelectrochemical performances of DSSCs device was undertaken. The fabricated DSSCs exhibited a high energy conversion efficiency of 0.40% with a corresponding  $J_{sc}$  value of 2.60

 $mA/cm^2$ ,  $V_{oc}$  value of 0.63 V and the FF value of 0.24. These results indicate that the TNTs induce a large surface area to facilitate adsorption of the dye molecules onto the electrode surface, which improves the light absorbance and generates photoexcited electrons, thereby enhancing the DSSCs performance. Herein, the obtained TNTs films could be used as a photoanode to facilitate the effective utilization of the incident light with enhancement of the performance of DSSCs.

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