ELECTROCHEMICAL ANODIZATION METHOD TOWRDS MULTI-LEG TiO_2 NANOTUBES FOR PEC APPLICATIONS

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Abstract

Nanostructuring and morphological engineering are the two important aspects of the control of the performance of functional materials. In the present work, we report on the fabrication of high aspect discrete TiO_2 nanotubes possessing two or multi-legs *via* electrochemical anodization of titanium foil. The effect of applied voltage and anodization time with appropriate optimization of electrolyte containing (NH_4) HF_2 in diethylene glycol-based electrolyte were investigated. Scanning electron microscopy was employed to examine the morphology of the synthesized TiO_2 nanotubes. We observed that prolonged anodization times from 2 hrs to 6 hours, results in the formation of dense and high aspect nanotubes with improved lengths compared to the sample synthesized with 2 hours of anodization time.

Keywords: TiO2, nanotubes, anodization, photoelectrochemistry

1. INTRODUCTION

Nanostructure materials have attracted enormous attention due to their interesting properties which differ from those of bulk materials. Among various types of ceramics, titanium dioxide as a significant inorganic functional material has extensively been investigated because of its useful chemical, optical and electronical properties. TiO_2 nanotubes with dictinct size and morphologies have been synthesized using different method such as hydrothermal method, template synthesis and anodization method [1]. Highly ordered and vertical TiO_2 nanotubes with controllable pore size and length can be obtained by anodization method for use in applications incluing dye-sentisized solar cells, photocatalysis, gas sensor, drug release systems and photoelectrochemical water splitting [2]. Synthesis of anodic hollow nanostructure of TiO_2 by anodizing titanium in chromic acid electrolyte solution was reported by Zwilling et al [2]. Gong et al. [3], reported the prepration of self-organized titanium nanotubes arrays by direct anodization of Ti foil in HF-H_2O electrolyte at room tempreture in which the length of the synthesized TiO_2 nanotubes were about 500 nm. Several anodization parameters have been considered, including potential, composition of electrolyte and time duration which can affect the morphology of nanotubes.

Shakar et al [4] obtained multi-leg TiO_2 nanotubes by a modified electrochemical bath solution consist of NH_4F and formamide and HF contining di-ehylene glycol (DEG) electrolytes. Such nanotubes possess wider diameter for the sake of joining together towards the top. It is well known that greater interface can be offerred proportionally by multi-legs TiO_2 nanotubes, which improves their photo-electrochemical ability than conventional TiO_2 nanotube array [5]. Furthermore, the graded refractive index presented by these nanotubes makes the effective scattering of light and thereby harnesses the available light appreciably.

In this present work, we report highly ordered, discrete (*i.e.* complately seperated and unconnected) multi-leg nanotubes with high aspect ratio which are effective candidates for light harvesting applications due to their branching nature, inter-tube spacing and wall thickness.

2. EXPERIMENTAL

The TiO_2 nanotubes were fabricated by the electrochemical anodisation method using Ti foil 0.25 mm thick (99.7 % purity, Sigma Aldrich) as an anode and Pt foil as a cathode. Prior to the anodisation the Ti foil was cleaned with low concentration HCl and subsequently ultrasonicated in acetone, isopropyl alcohol and de-ionised water, for 10 min each. The Ti foil was dried with nitrogen gas before mounting onto the anodisation set-up. The anodisation was carried out at 60. 80 and 100 V for 2, 4 and 6 h in an electrolyte mixture containing 96 ml DEG, 0.5 ml HF (48 % solution, Rankem) and 3.5 ml (1.5 M) NH_4F aqueous solution (see **Table 1**). After the anodization, the samples were rinsed thoroughly with isopropyl alcohol and deionised water and kept at room temperature for 1 h to dry. Subsequently, as-prepared samples were annealed at 400 °C for 2 h to achieve the anatase phase.

Field emission scanning electron microscopy (Hitachi SU6600- Tokyo, Japan) was used to investigate the surface morphology of the prepared samples. X-ray diffraction (PANalytical, The Netherlands) was employed to analyze the crystalline structure of the synthesized TiO_2; the analyses were performed using a Co-Kα as radiation (40 Kv, 30 Ma, λ = 0.1789 nm) in the range of $10^{\circ} \leq 2\theta \leq 80^{\circ}$.

Table 1 Experimental conditions of TiO_2 nanostubes arrays synthesized by anodization method

Sample name	Anodization time (h)	Voltage (V)	Temprature (°C)
NT1	2	60	Room Tempreture
NT2	4	60	35
NT3	6	60	35
NT4	2	80	35
NT5	4	80	35
NT6	6	80	35
NT7	2	100	35
NT8	4	100	35
NT9	6	100	35

3. RESULTS AND DISCISSION

Mohammadpour et al. [6] reported the synthesis of multi-leg TiO_2 nanotubes in HF containing DEG-based electrolyte at large anodization time (>40 h) and high voltage (120V). **Figure 1**. shows cross sectionals and top view images of synthesized TiO_2 nanotubes via anodization method at 60 V for 2, 4 and 6 h. SEM image of sample NT1 with using lower distilled water (**Figure 1a**) indicates a not compact structure. However, with increasing the temperature of solution up to 35 °C, and decreasing distilled water to 3.5 ml in the solution the results show a clearly seperated nanotubes with approximately 1 µm long and pore diameter of ~200 nm (sample NT2, **Figure 1b**). Prolonging the anodization time to 4 and 6 h (**Figure 1c** and **1d** respectively), could be used to increase the length of synthesized TiO_2 nanotubes up to 4 µm, while the tubes‘ diameter remains the same of approximately 220 nm. Further observation indicated that more dense nanotubes can be clearly seen in **Figure 1d** comparing to that in **Figure 1c**. It can be concluded that an increase in the anodization time can decrease the distance between the synthesized nanotubes.

A furture increase of the anodization voltage to 80 V for 2 h decreased the compression of multi-leg nanotube arrays with the same electrolyte solution (**Figure 2a**) comparing to the sample at 60 V for 2h (**Figure 1b**). However, by incresing the anodization time to 4 and 6 h, more nanotubes arrays can be observed (**Figures 2b** and **2c**). Moreover, from the SEM images, the diameter and the length of the nanotubes for the NT7 sample

(sample with 6 h anodization time at 80 V) were about 400 nm and 4-4.5 μm, respectively. In order to corroborate the TiO_2 nanotube arrays dispersion, SEM image of the sample NT7 with low magnification were depicted in **Figure 2d**.

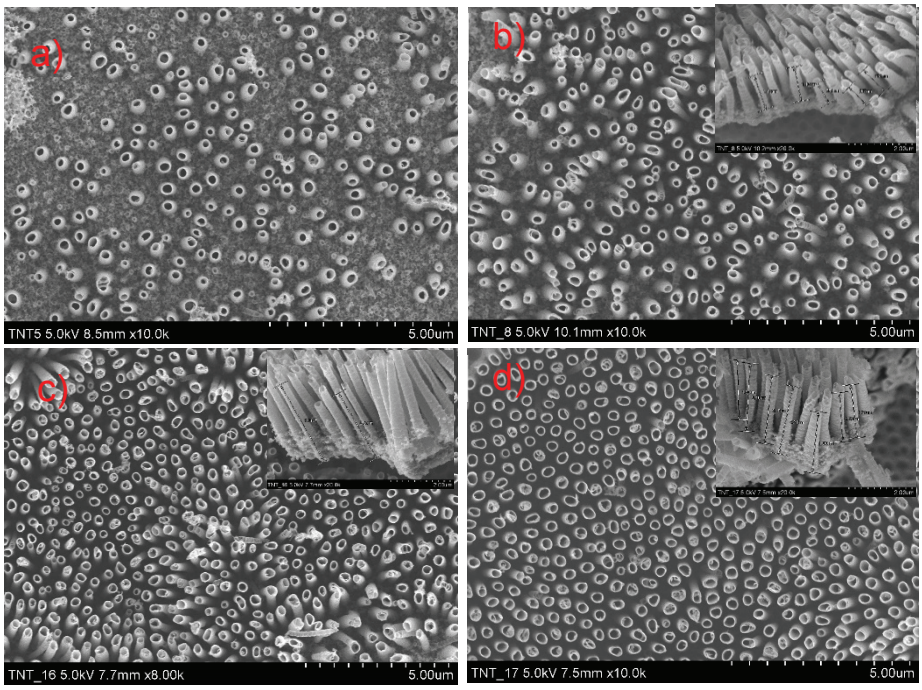

Figure 1 SEM images of the synthesized TiO_2 nanotubes arrays at 60 V for a) 2 h with 4 ml of distilled water, b) 2h with 3.5 ml of distilled water, c) 4 h and d) 6 h.

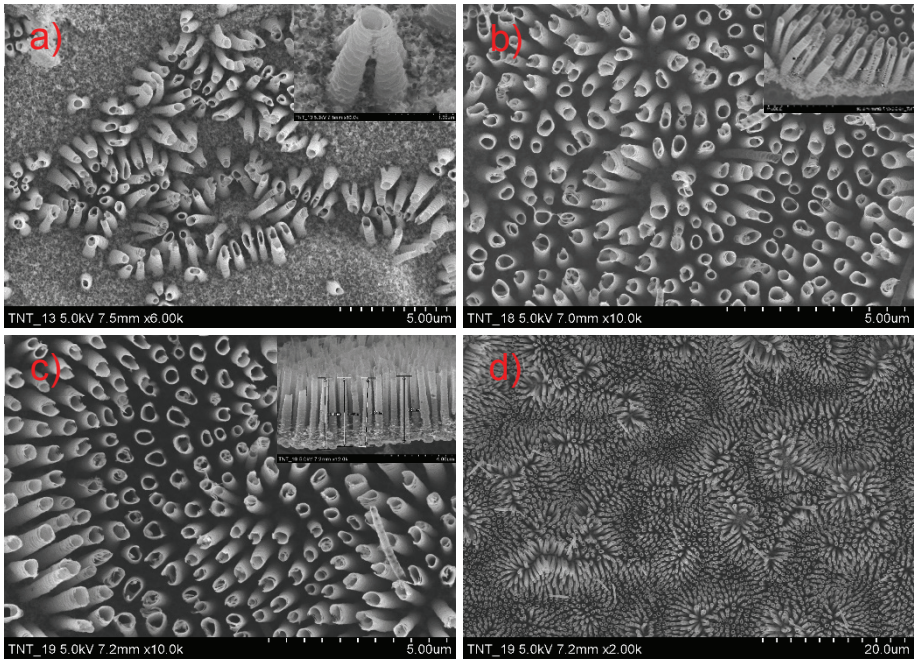

Figure 2 SEM images of the synthesized TiO_2 nanostubes arrays at 80 V for a) 2 h, b) 4h, c) and d) 6 h with different magnifications

The SEM images in **Figure 3a, 3b and 3d** confirm that prolonging the anodization time at 100 V for 2, 4 and 6 h respectively, results in considerable change in the obtained TiO_2 nanotube arrays density. Furthermore,

by increasing the voltage under same conditions, the formation of a sponage oxide layer is observed, showing only little self-organized ordering of TiO_2 nanotubes.

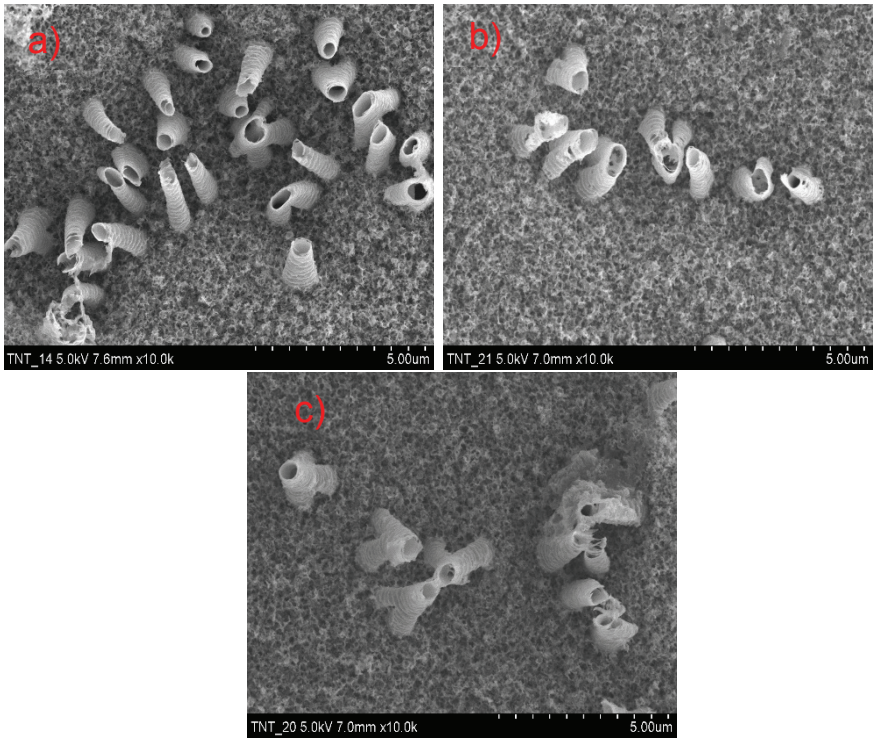

Figure 3 SEM images of the synthesized TiO_2 nanostubes arrays at 100 V for a) 2 h, b) 4h, and c) 6 h

X-Ray diffractions (XRD) were used to demonstrate phase structure of the synthesized TiO_2 nanotubes after calcination at 400 ˚C for a 2 h in air. XRD patterns of calcined NT2 indicate anatase phase (see **Figure 4**).

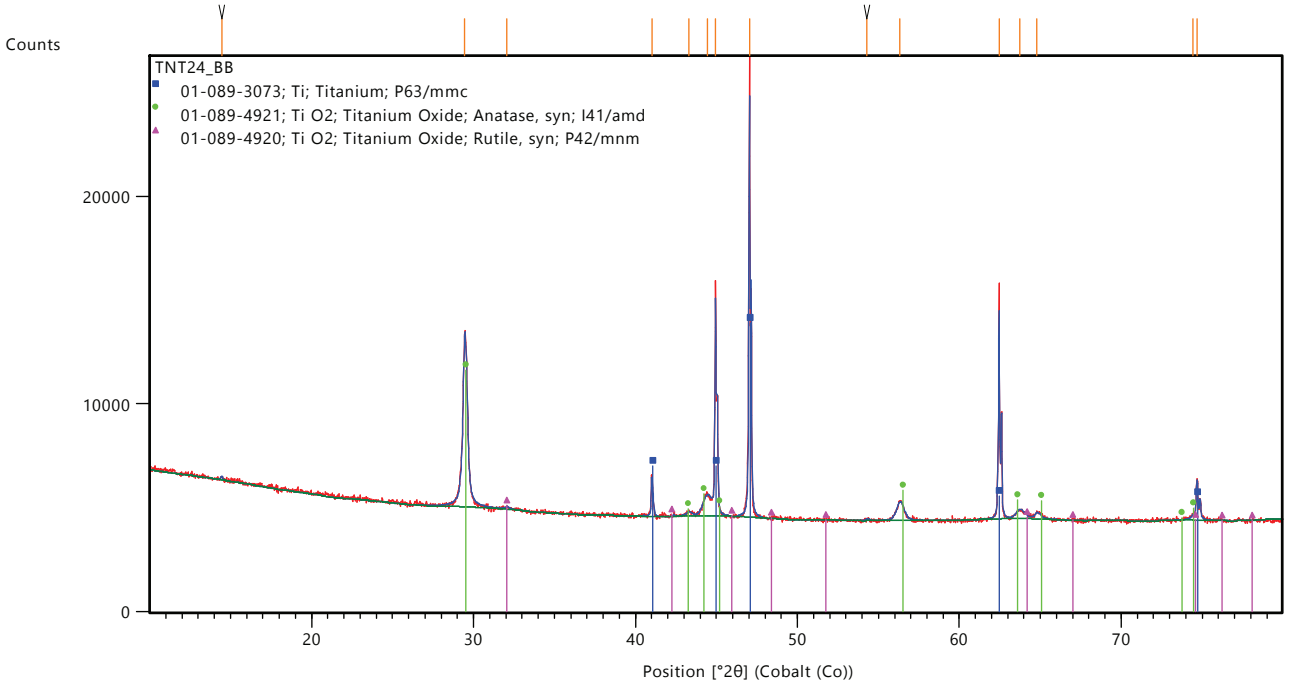

Figure 4 XRD patterns of sample NT2

4. CONCLUSION

In conclusion, we report on synthesis of discrete multi-leg TiO_2 arrays using the electrochemical anodization method in diethylene glycol (DEG) containing fluoride ions. An increase in the anodization time from 2 up to 6 h leads to synthesis longer nanotubes and at anodization potential of 80 V for 6 h, the longest nanotubes with wider diameter were obtained. These multi-leg nanotubes are suitable for enhanced light harvesting, leading to higher photocurrents in photoelectrochemical water splitting experiments.

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REFERENCES

[1] KMENT, Stepan, RIBONI, Francesca, PAUSOVA, Sarka, WANG, Lei, WANG, Lingyun, HAN, Hyungkyu, HUBICKA, Zdenek, KRYSA, JOSE, SCHMUKI, Patrik, ZBORIL, Radek. Photoanodes based on TiO_2 and α-Fe_2O_3 for solar water splitting-superior role of 1D nanoarchitectures and of combined heterostructures. *Chemical Society Reviews*. 2017, vol. 46, pp. 3716-3769

[2] TAHMASEBPUOR, Roghayeh, BABALUO, Aliakbar, SHAHROUZI, Javad Rahbar, TAHMASEPOOR, Maryam and SHAHREZAEI, Mahdi. Theoretical and experimental studies on the anodic oxidation process for synthesis of self-ordering TiO_2 nanotubes: effect of TiO_2 nanotube lengths on photocatalytic activity. *Journal of environmental chemical engineering*. 2017, vol. 5, pp. 1227-1237.

[3] GONG, Dawei, GRIMES, Craig, VARGHESE, Oomman C, HU, Wenchong, SINGH, R.S, CHEN, Zhi, DICKEY, Elizabeth C. Titanium oxide nanotube arrays prepared by anodic oxidation. *Journal of material research*, 2011, Vol. 16, no.12, pp. 3331-3334.

[4] RAMBABU, Yalavarthi, JAISWAL, Manu, ROY, Somnath. Enhanced photoelectrochemical performance of multi-leg TiO_2 nanotubes through efficient light harvesting. *Journal of Physic D: Applied Physics*. 2015. vol. 48, pp. 1-9.

[5] BODA, Muzaffar Ahma, AFSHAR SHAH and Mohammad. Nhancd phoo-electrochemical potential of Fe_2O_3 by nanotube arra wit multiple legs. *Journal of material science*, 2018, vol. 29, pp. 4569-4601.

[6] MOHAMMADPOUR, Arash, WAGHMARE, Prashant, MITRA, Sushanta and SHANKAR, Karthik. Anodic groeth of large -diameter multipodal TiO_2 nanotubs. *ACS Nano*, 2010, vol. 4, no. 12, pp. 7421-7430.