



# Aggregated TiO<sub>2</sub> nanotubes with high field emission properties



Bohr-Ran Huang\*, Jun-Cheng Lin, Tzu-Ching Lin, Yu-Jyun Chen

Graduate Institute of Electro-Optical Engineering and Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, ROC

## ARTICLE INFO

### Article history:

Received 11 December 2013  
Received in revised form 12 May 2014  
Accepted 12 May 2014  
Available online 20 May 2014

### Keywords:

Field emission  
TiO<sub>2</sub> nanotubes  
Electrochemical anodization

## ABSTRACT

A facile approach is developed to easily fabricate field emission (FE) cathodes based on TiO<sub>2</sub> nanotubes with different geometrical structures at low temperature. Planar TiO<sub>2</sub> nanotubes (P-TNTs) are first synthesized using the electrochemical anodization process with applied voltages of 20–50 V for 1 h at room temperature followed by thermal oxidation at 280 °C for 2 h under atmosphere ambient. P-TNTs can be transformed into aggregated TiO<sub>2</sub> nanotubes (A-TNTs) after H<sub>2</sub>O<sub>2</sub> post-treatment for 1 h at room temperature. FESEM, XRD, and Raman spectroscopy were used to analyze the surface morphology, crystallinity, and chemical binding, respectively. The A-TNTs fabricated with the applied voltages of 30–50 V cathodes possess higher levels of FE properties (lower turn-on electric field and higher current density) than the other cathodes due to their greater number of emission sites and decrement of the screening effect. The A-TNT with an applied voltage of 40 V cathode exhibits the lowest turn-on electric field (4.87 V/μm, 1 μA/cm<sup>2</sup>) and the highest enhancement factor β (1486). These superior properties indicate that the A-TNTs are promising field cathodes for future FE applications.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

TiO<sub>2</sub> is a wide band gap (3.1–3.2 eV) semiconductor material that has been extensively studied and applied for use in dye-sensitized solar cells [1], photocatalysis [2], gas sensors [3], and field emission (FE) devices [4] due to its unique chemical stability, high photocatalytic activity, and nontoxicity. One-dimensional (1-D) TiO<sub>2</sub> nanostructures exhibit high aspect ratio, small radii of curvature, good electrical, thermal and chemical stability, which means that they could be a good candidate for use in FE applications. The 1-D TiO<sub>2</sub> nanostructures can be prepared by many approaches such as the hydrothermal method [5], chemical vapor deposition [6], and electrochemical anodization [7]. Compared with other methods, electrochemical anodization is a simple and cost-effective approach to synthesize various highly ordered 1-D TiO<sub>2</sub> nanostructures including nanorods, nanowires, and nanotubes. The characteristics and potential applications of these structures have also been extensively studied. Moreover, the structure of nanotubes has been found to provide superior performance to those of

nanorods and nanowires in many important fields of nanotechnology research [8–10].

Generally, TiO<sub>2</sub> nanotubes (TNTs) are prepared by electrochemical anodization, which have poor FE properties (high turn-on electric field and low current density) due to the well-aligned structure. Several improvements of FE properties in TNT structure fabricated have been reported previously in the literature. Chen et al. [11] indicate that semiconducting TNTs are transformed into semimetallic TNTs by annealing at 750 °C, with the turn-on electric field ( $E_{on}$ ) being significantly improved from 25.6 to 3 V/μm. Wang et al. [12] and Zhu et al. [13] report that carbon-doped TNTs and hydrogenated TNTs can be obtained by heat treatment of as-fabricated TNTs at 550 °C, with  $E_{on}$  being reduced from 21.9 to 5 V/μm and 32.75 to 4.12 V/μm, respectively. Chen et al. [14] also demonstrate a decrease in  $E_{on}$  from 11.4 to 3 V/μm as a result of the deposition of diamond-like carbon on TNTs. Compared to the above high temperature and complicated procedure, this study presents a facile and simple technique to change the morphology of TNTs at room temperature. Furthermore, this study focuses on the effect of H<sub>2</sub>O<sub>2</sub> post-treatment on the morphology and arrangement dependence of TNTs for improving the FE properties.

## 2. Experimental

Prior to the fabrication of the planar TiO<sub>2</sub> nanotubes (P-TNTs), the Ti foils (99.6% purity, 0.2 mm thickness) were cleaned by

\* Corresponding author at: 43, Sec. 4, Keelung Road, Taipei 106, Taiwan, ROC. Tel.: +886 2 2730 3273; fax: +886 2 2737 6424.

E-mail addresses: [huangbr@mail.ntust.edu.tw](mailto:huangbr@mail.ntust.edu.tw) (B.-R. Huang), [d9902305@mail.ntust.edu.tw](mailto:d9902305@mail.ntust.edu.tw) (J.-C. Lin), [d9702308@mail.ntust.edu.tw](mailto:d9702308@mail.ntust.edu.tw) (T.-C. Lin), [m10002321@mail.ntust.edu.tw](mailto:m10002321@mail.ntust.edu.tw) (Y.-J. Chen).

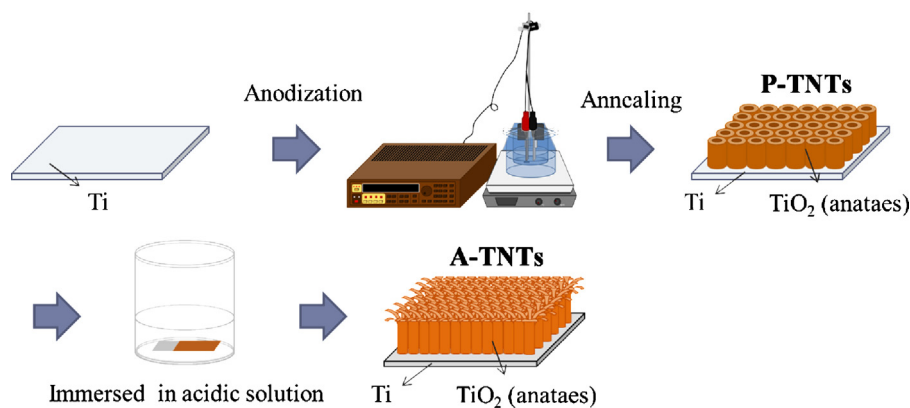


Fig. 1. Schematic diagrams of the fabrication process for P-TNTs and A-TNTs.

ultrasonication in acetone, isopropyl alcohol, and deionized water. The electrochemical anodization of Ti foils was performed in an ethylene glycol solution containing 0.5 wt.%  $\text{NH}_4\text{F}$  and 2.5 vol.% deionized water with magnetic agitation and a constant applied voltage of 20–50 V for 1 h at room temperature. Subsequent heating at 280 °C for 2 h under an ambient atmosphere was applied to achieve the crystallization of the P-TNTs. Then, the P-TNTs were immersed in  $\text{H}_2\text{O}_2$  solution for 1 h at room temperature to form aggregated  $\text{TiO}_2$  nanotubes (A-TNTs). A-TNTs were rinsed with deionized water and air-dried. Schematic diagrams of the fabrication process of P-TNTs and A-TNTs are shown in Fig. 1.

The surface morphology of the samples was observed using a field-emission scanning electron microscope (FESEM, JSM-6500F) with an acceleration voltage of 15 kV. The crystal structure of the samples was characterized by X-ray diffraction (XRD, D2 PHASER-X-ray Powder Diffraction, Bruker) using  $\text{CuK}\alpha 1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The bonding structure of the samples was characterized by Raman spectroscopy with an excitation wavelength of 514.5 nm. FE measurements of the samples were performed in an ultrahigh vacuum system with a base pressure of  $10^{-4}$  Pa at room temperature. The sample was used as the cathode and a copper plate served as the anode. The cathode surface was separated from the anode by a distance of 150  $\mu\text{m}$ . The applied voltage was in the range 0–1100 V that corresponds to an electric field range of 0–7.3 V/ $\mu\text{m}$ . The maximum voltage applied was limited by measurement setup.

### 3. Results and discussion

Fig. 2 shows FESEM images of the surface and cross-section morphology of the P-TNTs and A-TNTs are fabricated with applied voltages of 20–50 V, respectively. Fig. 2(a–d) presents the high density, high aspect-ratio, and vertically-aligned P-TNTs fabricated by electrochemical anodization. The P-TNTs are connected with each other and held perpendicular to the substrates, and all P-TNTs have a neat and uniform length. The average diameter of the P-TNTs fabricated with applied voltages of 20, 30, 40, and 50 V are 22, 53, 71, and 101 nm, and the respective average lengths are 1.4, 2.6, 3.9, and 4.1  $\mu\text{m}$ . This indicates that the diameter and length of the P-TNTs both increase as the applied voltage increases. However, the P-TNTs are then transformed into A-TNTs after the  $\text{H}_2\text{O}_2$  post-treatment at room temperature, as shown in Fig. 2(e–h). Sreekantan et al. [15] indicate that excessive  $\text{H}_2\text{O}_2$  is detrimental to the self-ordered nanotubular structure and produce chemical etching for TNTs. The A-TNTs present a bundled structure with rough morphology and very sharp edges, which is important for potential applications in FE devices. As the applied voltages with 50 V, the TNTs congregate homogeneously and connect with other TNTs to form the larger

bundled structure. These results demonstrate that the  $\text{H}_2\text{O}_2$  post-treatment technique is a critical approach for the formation of the A-TNT structure.

It is well known that the change of surface morphology is closely related to phase transformation and crystal growth [11]. Fig. 3 shows the XRD patterns of the P-TNTs and A-TNTs with various applied voltages, respectively. All samples are highly crystalline and exhibit obvious diffraction peaks at the 25.3° (101), 37.8° (004), and 47.2° (200) planes, which conform to the anatase crystalline structure of  $\text{TiO}_2$ . No diffraction peaks from any other impurities are detected. All these results evidence that cylindrical tubular TNTs are successfully prepared [16]. The full width at half maximum (FWHM) of the diffraction peak at the 25.3° of P-TNTs fabricated with applied voltages of 20, 30, 40, and 50 V are 0.41, 0.4, 0.31, and 0.34  $\text{cm}^{-1}$ , and the respective values of A-TNTs are 0.4, 0.38, 0.32, and 0.33  $\text{cm}^{-1}$ .

Fig. 4 shows the Raman spectra of the P-TNTs and A-TNTs fabricated with various applied voltages, respectively. All curves are similar and exhibit four peaks at 143, 394, 515, and 638  $\text{cm}^{-1}$ , and these peaks are characteristic of the anatase  $\text{TiO}_2$  crystal. The peak at around 143  $\text{cm}^{-1}$  presents a low-frequency O–Ti–O bending vibration and the peak at around 394  $\text{cm}^{-1}$  corresponds to the anatase  $\text{TiO}_2$ . The Ti–O stretching-type vibrations are respectively located at 515  $\text{cm}^{-1}$  and 638  $\text{cm}^{-1}$  [17,4]. The FWHM of the characteristic peak at 143  $\text{cm}^{-1}$  of P-TNTs fabricated with applied voltages of 20, 30, 40, and 50 V are 15.47, 15.04, 13.73, and 14.07  $\text{cm}^{-1}$ , and the respective values of A-TNTs are 15.14, 14.55, 13.85, and 14.51  $\text{cm}^{-1}$ . The above results indicate that  $\text{H}_2\text{O}_2$  post-treatment causes a dramatic change in the surface morphology but does not significantly affect the TNTs. Moreover, it is also found that the samples of P-TNTs and A-TNTs fabricated with an applied voltage of 40 V have higher crystallinity and chemical binding than those fabricated in the other conditions.

FE properties are usually described in terms of parameters defined by the Fowler–Nordheim (F–N) theory. Fig. 5 shows the current density–electric field (J–E) plot and the corresponding F–N plot for A-TNT cathodes. According to the F–N equation, the emission current density  $J = (\alpha A (\beta E)^2) / \phi \exp(-(\beta \phi^{3/2} / \beta E))$ , where  $J$  is the FE current density ( $\text{A}/\text{cm}^2$ ),  $E$  is the applied electric field ( $\text{V}/\mu\text{m}$ ),  $A$  and  $B$  are constants,  $\alpha$  is the effective emission area,  $\beta$  is the enhancement factor, and  $\phi$  is the work function of 4.4 eV for  $\text{TiO}_2$  [18]. The values of  $E_{\text{on}}$  at a current density of 1  $\mu\text{A}/\text{cm}^2$  of the A-TNTs fabricated with applied voltages of 30, 40, and 50 V are 5.4, 4.87, and 5 V/ $\mu\text{m}$ , respectively. The field enhancement factors of the A-TNTs fabricated with applied voltages of 30, 40, and 50 V are 1373, 1486, and 1386, and the corresponding effective emission areas are  $1.55 \times 10^{-12}$ ,  $3.45 \times 10^{-12}$ , and  $2.87 \times 10^{-12}$   $\text{cm}^2$ , respectively.

Download English Version:

<https://daneshyari.com/en/article/5361357>

Download Persian Version:

<https://daneshyari.com/article/5361357>

[Daneshyari.com](https://daneshyari.com)