



Enhanced physical properties of the anodic TiO₂ nanotubes via proper anodization time

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Abstract

Vertically aligned titanium dioxide (TiO₂) nanotubes were synthesized by electrochemical anodic oxidation in an electrolyte solution containing 0.45 wt% ammonium fluoride (NH₄F) and 2 vol% deionized water at constant potential (70 V) for various anodization time at the room temperature. The influence of the anodization time on the morphology and optical properties of the anodic TiO₂ nanotubes have been studied. Field emission scanning electron microscopy results revealed that the anodic TiO₂ nanotube morphology extremely depends on the anodization time. It was observed that by increasing anodization time, length of the anodic TiO₂ nanotubes increased and nanotubes destroyed at the top of the tubes. After a long time of anodization process (9 h), nanotubes completely destroyed. Photoluminescence measurements showed that the anodic TiO₂ nanotube band gap energy depends on the anodic TiO₂ nanotube morphology. The anodic TiO₂ nanotubes without any damage had a minimum band gap energy (2.9 eV).

Keywords TiO₂ nanotube · Anodization time · Morphology · Band gap

Introduction

In the past decades, TiO₂ nanotubes have been widely investigated due to their high interest in various applications like biomedical fields [1], photovoltaic cells [2], photocatalysts [3, 4], solar cells [5–7] and electrochromic devices [8]. These possible applications are due to the advantages of not-toxicity, thermal and chemical stabilities, high photocatalytic activity [9–13] and high surface area of the TiO₂ nanotubes [14, 15]. TiO₂ nanotubes could be fabricated using numerous physical or chemical methods including sol–gel [16], electrochemical anodization [17], template [18], hydrothermal [19, 20], micro-wave irradiation [21], alkaline [22] and sonoelectrochemical [23] methods.

Among these methods, electrochemical anodization is the prominent approach to prepare TiO₂ nanotubes. Self-

organized TiO₂ nanotubes grown by an electrochemical anodization method have attracted scientific interests because these nanotubes can directly synthesize on the titanium (Ti) surface, used directly as a back-contact electrode [24]. This method also is a simple, effective, low cost especially with great ability of controlling growth parameters (potential, PH, the chemistry of electrolyte solution and time) [10, 25, 26]. The chemical and physical properties of the anodic TiO₂ nanotubes are dependent on their growth conditions [27], so by changing growth parameters like anodization time, applied potential and electrolyte composition, morphological structure of the anodic TiO₂ nanotubes can be modified [28] and optimum anodic TiO₂ nanotubes can be obtained. For example, among the growth parameters, anodization potential is the key factor controlling the diameter of the nanotubes [29].

The aim of this work is to investigate effect of the anodization time on the morphology and physical properties of anodic TiO₂ nanotubes using FESEM, XRD and PL analyses and find the optimum anodization time.

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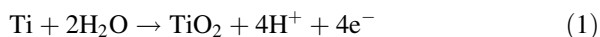
Experimental

Anodic TiO₂ nanotubes were grown using the anodization method. Prior to anodizing, titanium foils (99.6% purity, 0.25 mm thick, Sigma-Aldrich) were mechanically ground with different silicon carbide paper grades and ultrasonically cleaned by acetone, deionized water (DI) and ethanol, respectively, for 20 min. The anodization process was carried out in a two-electrode system, comprised of Ti as anode and platinum as cathode with distance of 1 cm from each other, at a constant potential of 70 V and various anodization time (20 min–9 h) at room temperature. The electrolyte contained 100 ml ethylene glycol (99.5%, Merck), 2 vol% DI water and 0.45 wt% NH₄F (98%, Merck). After anodization, as-prepared anodic TiO₂ nanotubes were immersed in methanol for few minutes and dried in air. In order to improve crystal structure and physical properties of the as-grown TiO₂ nanotubes, they annealed at 400 °C for 1 h in air (heating/cooling rate 10 °C/min). The current density was measured during the anodization process. Anodic TiO₂ nanotube morphology was characterized via field emission scanning electron microscope (FESEM, JEOL, 7610f). The structural and optical properties of the anodic TiO₂ nanotubes were evaluated by X-ray diffraction (XRD) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) and photoluminescence (PL) spectra using a PL module using an excitation laser with 380 nm wavelength (helium–cadmium laser) associated with a spectrophotometer (FL0906M003, Cary Eclipse).

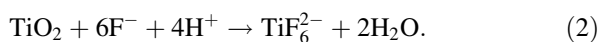
Results and discussion

Study of the formation mechanism of the TiO₂ nanotubes has been of interest for the researchers that among all the theories two important theories including oxygen bubble [30] and field-assistant are challenging [31–33]. Field-assistant theory about TiO₂ nanotubes growth is based on 3 significant processes [34]:

1. oxidation by field-assistant at the metal/oxide interface, given by Eq. (1):



2. dissolution by field-assistant at the oxide/electrolyte interface at the bottom of the nanotubes.
3. chemical etching at the top of the nanotubes. Chemical interactions of these two last cases is given by Eq. (2):



The collective effects of them will decide the final morphologies of the TiO₂ nanotubes. Figure 1 shows the current density–time curves obtained during anodization process. Regardless of the anodization time, the curves show approximately same behavior. At the first stage, the sharp drop in the current density is due to the oxide layer formation on the Ti surface [35], which decreases the conduction resulting in sharp drop in the current density. At the second stage, current density is increased, indicating the pore formation. At the next stage, current density is decreased and remains constant. At this stage, oxide growth rate in the oxide/metal interface and oxide dissolution rate at the electrolyte/nanotube bottom are in equilibrium [35]. See inset of Fig. 1, which shows the current density–time curve for the 9 h anodization time in detail; at the last stage after 7 h, the curve is slightly increased and again remains constant. It may due to the temperature increment of the solution during the anodization process, which is occurred after a long time of anodization process and could increase conductivity of the solution.

The influence of anodization time on the anodic TiO₂ nanotube morphologies is shown in Fig. 2. The anodization process at the different anodization time but 9 h resulted in vertically oriented TiO₂ nanotube arrays. Differences were observed between the anodic TiO₂ nanotube morphologies grown at the different anodization time. By increasing anodization time from 20 min to 3 h, an increase in nanotube length from 7.5 to 34 μm was observed. Length of the TiO₂ nanotube grown for 1 h reached to about 22 μm without any significant collapse of the nanotubes. The top of the anodic TiO₂ nanotubes for the 3 h, as shown in Fig. 1c, was destroyed. The significant collapse of the anodic TiO₂ nanotubes for 3 h is due to the nanotube top dissolution by fluoride ions [36, 37]. The 9 h anodization

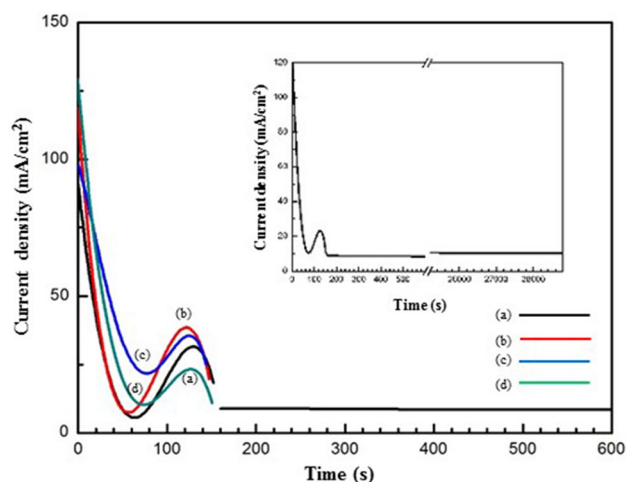


Fig. 1 Anodization current density–time curves obtained for TiO₂ nanotubes grown at different anodization time; (a) 20 min, (b) 1 h, (c) 3 h and (d) 9 h

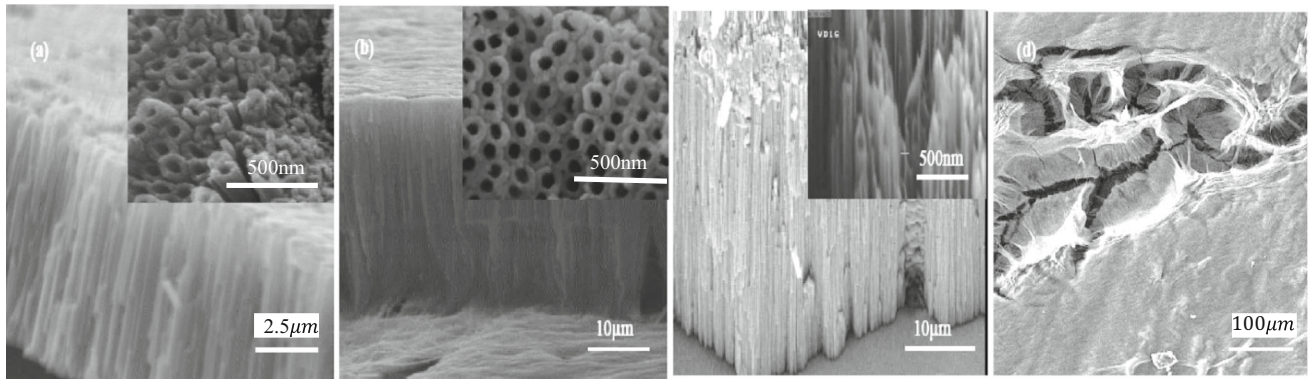


Fig. 2 FESEM images of TiO₂ nanotubes grown at different anodization time; (a) 20 min, (b) 1 h, (c) 3 h and (d) 9 h

time resulted in destroying the nanotubes and forming the nanograss (Fig. 1d). Nanograss structures form when the growth rate of the nanotubes at the oxide/metal interface is smaller than the chemical dissolution rate at the tubes top/electrolyte interface. In other words, chemical dissolution rate at the tubes top/electrolyte interface is higher than at tubes bottom [38].

In order to study the crystal phase, X-ray diffraction analysis had been conducted. Figure 3 shows the XRD patterns of the anodic TiO₂ nanotubes grown at 1 h condition. The presence of Ti peaks and anatase TiO₂ is observed. Other peaks such as rutile and brookite peaks were not detected, that is due to the annealing temperature. Similar results were observed for other samples grown at different anodization time (not included in Fig. 3).

Figure 4 presents the PL spectra of the TiO₂ nanotubes for different anodization time at 380 nm excitation wavelength. Peak of the all samples appeared within the visible range from 400 to 450 nm, so the samples have a narrow band gap energy. All samples' PL shapes are similar; however, peak locations and peak intensities are different.

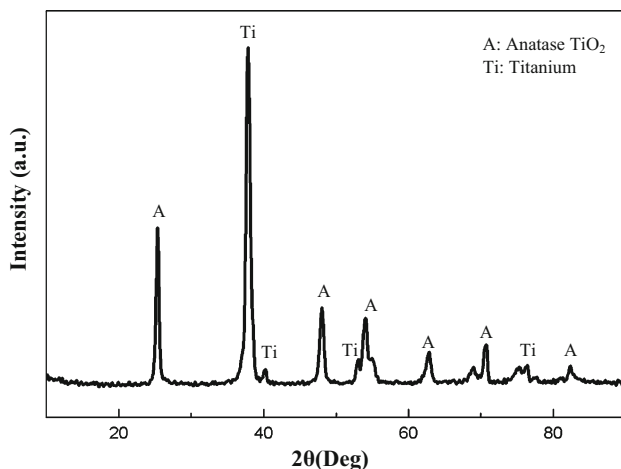


Fig. 3 XRD patterns of the TiO₂ nanotubes grown at 1 h anodization time

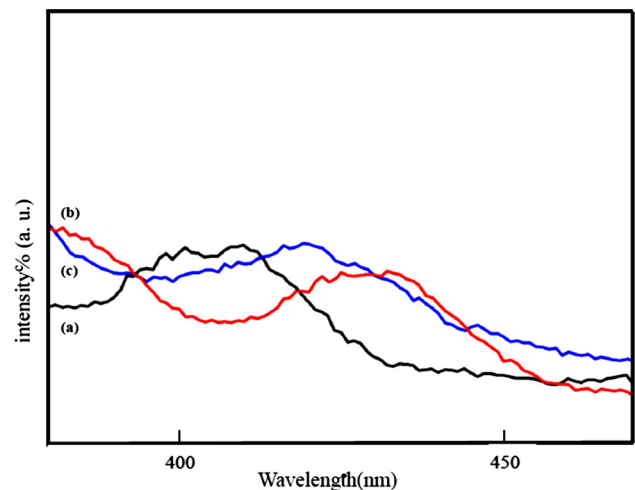


Fig. 4 PL spectra of the TiO₂ nanotubes grown at different anodization time; (a) 20 min, (b) 1 h and (c) 3 h

As it is known, PL intensity reflects the recombination rate of the electron–hole, that is lower PL intensity reflects a lower electron–hole recombination rate [39]. Maximum intensity of the PL peaks belongs to the TiO₂ nanotubes grown for 3 h, which could be due to the fact that it is significant damage compare to the other samples. Well-aligned TiO₂ nanotubes without any damage can enable a convenient and rapid pathway for charge transport, decreasing the carrier path length so as a consequence can reduce recombination losses and in the other words results in reduced number of the recombination centers [40]. However, in the damaged TiO₂ nanotubes the carrier path length can increase and as a result the number of recombination centers increases. So the PL peaks intensity of the damaged nanotubes can be higher than that of nanotubes without any damage. It is known that band gap energy of the anodic TiO₂ nanotubes decreases with increasing anodization time [40]; it could be due to tube length increase. Therefore, it is expected that the TiO₂ nanotubes grown for 3 h had the minimum band gap energy, but the

tubes grown for 1 h have the minimum band gap energy (about 2.9 eV). The redshift in the peak of TiO₂ nanotubes grown for 1 h as compared with the 3 h may be due to the tube wall thickness decrease of the nanotubes grown for 3 h compare to the 1 h, which is in good agreement with the previous work [41].

Conclusion

Anodic TiO₂ nanotubes were synthesized by anodization method at different anodization time. Influence of the anodization time on the TiO₂ nanotube physical properties was investigated. Anodization time significantly affected the morphology of the nanotubes. By increasing anodization time, length of the nanotubes increased. At 3 h anodization time, the anodic nanotubes were destroyed at the top of the tubes and nanotubes grown for 9 h completely destroyed. Morphology differences could change the value of the band gap energy which the nanotubes with the length of 22 μm and without any damage had a minimum band gap energy. Therefore, the morphology and optical properties of the TiO₂ nanotubes could be optimized by proper anodization time.

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