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REVIEW REPORT

Effects of various applied voltages on physical properties of TiO_2 nanotubes by anodization method

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Abstract Three steps anodization process is used to synthesize highly ordered and uniform multilayered titanium oxide (TiO_2) nanotubes and effect of different anodization voltages are studied on their physical properties such as structural, morphological and optical. The crystalized structure of the synthesized tubes is investigated by X-ray diffractometer analysis. To study the morphology of the tubes, field emission scanning electron microscopy is used, which showed that the wall thicknesses and the diameters of the tubes are affected by the different anodization voltages. Moreover, optical studies performed by diffuse reflection spectra suggested that band gap of the TiO_2 nanotubes are also changed by applying different anodization voltages. In this study using physical investigations, an optimum anodization voltage is obtained to synthesize the uniform crystalized TiO_2 nanotubes with suitable diameter, wall thickness and optical properties.

Keywords Anodization · TiO_2 · XRD · SEM

Introduction

Among various oxide semiconductor materials, Titanium dioxide (TiO_2) is attracted much attention due to its band gap, which is about 3 eV. Its wide band gap causes photoactivity effect in the UV range, good mechanical strength, non-toxicity, low cost and long-term photostability [1–4]. Different nanostructures of TiO_2 such as nanotubes [5], nanofibers [6], nanowires [7] and nanorods [8] have been investigated for its wide application in gas sensors [9, 10], biomedical application [11], hydrogen generation [12], battery electrode [13] and dye-sensitized solar cells [14–17] so far. TiO_2 nanoparticles were used in dye-sensitized solar cells as photoanode in 1991 by O'Regan and Gratzel [14]. Different approaches were suggested so far to improve dye cells efficiency like replacing TiO_2 nanoparticles with nanotubes since one dimensional TiO_2 nanotube arrays provide direct path for electrons and improves the electron transport velocity and also cause reduction of the charge recombination [18, 19]. TiO_2 nanotubes have been prepared by various methods such as sol–gel [20–22], liquid-phase deposition [23], hydrothermal [24–26] and electrochemical anodization processes [27, 28]. Amongst them, the electrochemical anodization of Titanium foil is producing compacted and oriented arrays and is known to be one of the most simple and low cost processes. On the other hand, one of the advantages of this process is morphological control of the TiO_2 nanotubes by changing anodization conditions like voltage and time of anodization, temperature and concentration composition of the electrolyte [29–31]. Since the morphological properties of the TiO_2 nanotubes such as diameter and wall thickness of tubes and arrays' length are so effective on their optical application hence it is important to synthesize the nanotubes by morphological controlled methods. At first Masuda and Fukuda suggested anodization process to grow alumina (Al_2O_3) nanostructures in 1995 [32] and then Zwilling et al. promoted this methods for synthesizing TiO_2 nano porous on Ti metal in electrolyte containing HF [33] and at last the TiO_2 nanotubes which had acceptable arrays' length were anodized by Schmuki et al.

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[34, 35]. However, the nanotubes, which are synthesized by anodization are not top open channel and the suggested solution is two step anodization process to produce highly ordered and open channel arrays of TiO_2 nanotube [36, 37]. In this method, the first anodized foils were ultra sonicated to remove the nanotubes and later second anodization steps can be performed. Therefore, the three step electrochemical anodization is known to be more concerned due to the possibility of producing vertically oriented and controllable dimension nanotube arrays. In this work we focus on the influence of the anodizing voltage on the morphological properties of the TiO_2 nanotubes grown by three steps anodization process. Furthermore, correlation between structural, morphological and optical properties are studied using X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM) and diffuse reflection spectra (DRS).

Experimental

Top open TiO_2 nanotubes are grown through a three step anodization process. Firstly the titanium foils (0.25 thickness, 99.9% pure Sigma Aldrich) were cut and they were polished by ultra sonication in ethanol, acetone and deionized water for 20 min, respectively, to remove a surface contamination and later were dried by N_2 stream. For the electrochemical anodizing setup, the two electrodes of a platinum foil (as cathode) and a titanium foil (as anode) were connected to the DC power supply in electrolyte solution. The distance between the anode and the cathode was adjusted about 2 cm. The electrolyte solution contained ethylene glycol ($C_2H_6O_2$), 0.3 wt% ammonium fluoride salt (NH_4F) and 2 v% deionized water (DI). Electrochemical setup and the anodizing parameters such as process temperature, concentration of electrolyte and anodizing time were kept same for all of the processes and different voltages of 35, 45 and 55 V were applied to study the effect of the applied voltage on the TiO_2 grown samples. The first step of the electrochemical process was anodizing Ti foil for 1 h. After that the TiO_2 nanotubes grown on the substrate were detached by ultra sonication in methanol to prepare hexagonal patterns on the Ti surface. Presence of this pattern is essential to grow compact and top open arrays at the next step. For the second step, the prepared Ti substrate was re-anodized at the same condition for 3 h and then ultrasonicated in methanol. This is followed by annealing the samples w in air ambient at 450 °C for 1 h with a heating ramp of 2.5 °C min^{-1}. In the last step the annealed samples were anodized for 1 h and dried by N_2 stream. The high resolution FESEM and XRD Cu Kα radiation ($\lambda = 1.5418$ Å) are used to observe morphological and structural properties of the TiO_2 nanotube films. Moreover, DRS were also obtained in 200–800 nm wavelength range to calculate the band gap energy of the samples.

Results and discussion

Figure 1a–c show SEM images of the samples which are anodized using three different voltages of 35, 45 and 55 V. As we can see top open nanotubes with different diameters and wall thicknesses are synthesized. The applied voltage produce electric field between anode and cathode to absorb more fluoride ions, on the other hand more fluoride ions promote etching process. Hence the fluoride ions are etching surface of the Ti foils and produced pours on its surface and reduced the thickness of oxide layer. When more fluoride ions are absorbed through bottom of pours, make them deeper and produce tubes. The tubes grown at 55 V are more uniform, compact and identical in their diameters and wall thickness than the other samples. However, the samples prepared at 35 and 45 V do not show compact and uniform arrays, which result in increasing the tube center to center distance. The non-uniformity is more observable in case of the sample prepared at the lower applied voltage of 35 V. It is known that the applied voltage is one of the most important parameters on nanotubes morphology and by increasing the anodizing voltage, tubes diameters can be increased due to the improved chemical etching through the more florid ion arrived to the Ti substrate [28]. The TiO_2 nanotubes diameters and wall thickness depend on anodizing voltage as follows [38]:

$$d(\text{nm}) = k\text{V} \tag{1a}$$

$$w(\text{nm}) = h\text{V} \tag{1b}$$

where, w, d and V are wall thickness, diameters and applied voltage, respectively. Moreover k and h are nanotubes' diameters growth coefficient and wall thickness growth coefficient with anodizing voltage. According to Table 1 k and h coefficients are estimated about 1.2 (nm V^{-1}) and 0.13 (nm V^{-1}), respectively. The ratio of surface area occupied by pores to the whole surface area is defined by porosity, P, from SEM images. The porosity of the nanostructures may improve the absorption of the incident photon in comparison with the flat surface. Porosities of the TiO_2 nanotubes can be calculated using following equation [36]:

$$P = \left(1 - 2\pi\frac{dw + w^2}{\sqrt{3}I^2}\right) \times 100\% \tag{2}$$

where, d, w and I are inner pore diameters, wall thickness and center–center distance between nanotubes, respectively.

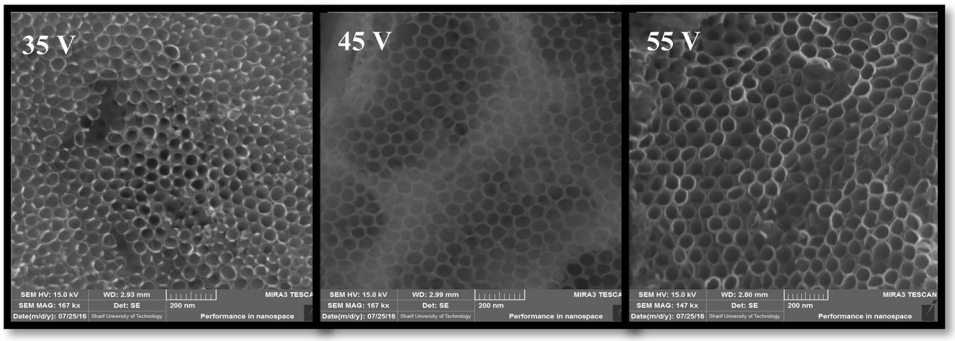

Fig. 1 SEM images of TiO_2 nanotube samples anodized at different applied voltages of **a** 35, **b** 45 and **c** 55 V in (2 v%) DI and (0.3 wt%) NH_4F electrolyte solution and annealed at 450 °C in air

Table 1 Diameter, wall thickness, porosity and roughness factor calculated from SEM images for the samples anodized at 35, 45 and 55 V

Sample (V)	Diameters (nm)	Wall thickness (nm)	Porosity (%)	Roughness factor $(\mu m)^{-1}$
35	50	4.8	73.1	110.2
45	57	6	71.1	96
55	65.7	8.2	67.3	79.5

Moreover surface roughness is the ratio of total area to the projected area [38]. This factor is essential to handle nanotubes application such as dye absorbing for dye-sensitized solar cells and gas sensor. Following formula is used to calculate R_f from SEM images and the results are given in Table 1:

$$R_f = \frac{4\pi}{\sqrt{3}} \frac{(d+w)}{I^2}. \quad (3)$$

The calculated results for P are 73.1, 71.1 and 67.3% in case of samples 35, 45 and 55 V, respectively. The calculated amount of P for sample 55 is in good agreement with previously reported data on the TiO_2 nanotubes [37]. Furthermore, increasing the anodizing voltage is caused to reduce roughness factor of sample. TiO_2 optical properties such as photoelectron chemical and photo catalysis are known to depend on their phase crystallites and moreover these are so important for their application [39, 40]. XRD pattern of the TiO_2 nanotubes synthesized at various anodizing voltage are 35, 45 and 55 V are given in Fig. 2. All the three samples are annealed in air ambient at 450 °C, before XRD measurement to form polycrystalline structures. Different phase crystallites like anatase, rutile and brokite are reported for TiO_2 films by previous groups [39, 40]. As it can be seen XRD pattern of the samples grown at 35 and 45 V show mixed crystalline crystal phases of anatase and rutile with (210) and (212) planes. The sample synthesized at 55 V shows anatase as a dominant phase and two peaks corresponding to the (200) and (105) planes. It is observable that all the three samples show a peak that is centered at about 25.3° which is a characteristic peak of TiO_2 (anatase, 00-001-0562). This

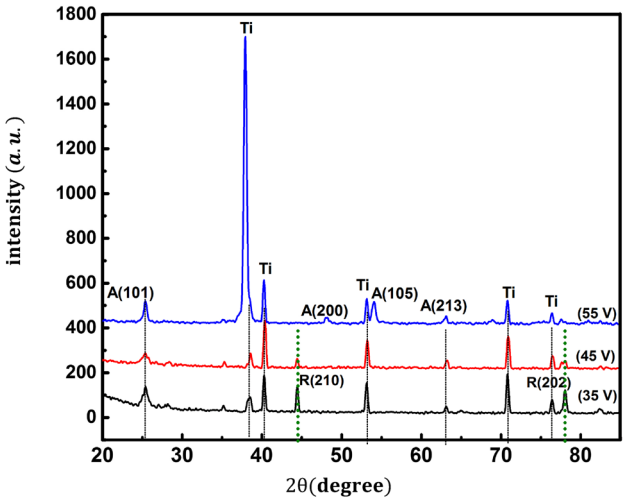

Fig. 2 XRD spectra for the anodized samples at different applied voltages of 35, 45 and 55 V anodized in (2 v%) DI and (0.3 wt%) NH_4F electrolyte solution and annealed at 450 °C in air

peak corresponds to the (101) preferential growth orientation plane of TiO_2. So if anodizing voltage is increased, the anatase peak intensity will also be improved. This increasing may be caused by the formation of thicker and denser nanotube films on the substrate. The size of the anatase crystal is calculated using the Deby–Scherrer relation as follows:

$$\beta = \frac{k\lambda}{D\cos\theta}, \quad (4)$$

where β is full width half maximum of TiO_2 peak for reflections (101) corresponding to $2\theta = 25.1°$, D is crystallite size, K is a constant (close to 0.94), λ is the

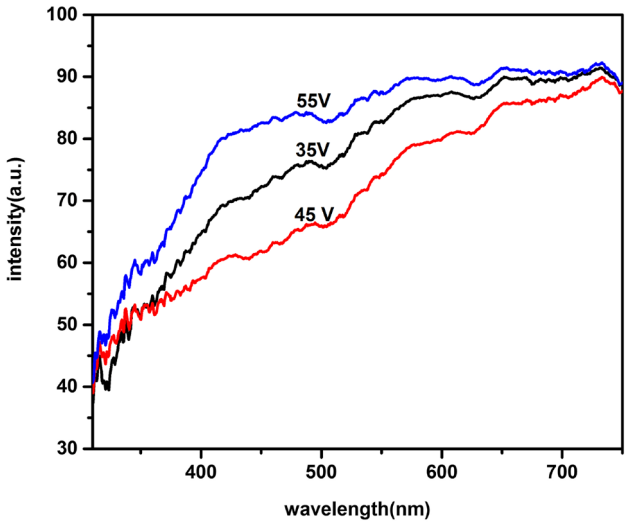

Fig. 3 Diffuse reflectance spectra versus wavelength for the samples prepared at applied voltages of 35, 45 and 55 V anodized in (2 v%) DI and (0.3 wt%) NH_4F electrolyte solution and annealed at 450 °C in air (*inset image* shows fringes in 250–340 nm range wavelength)

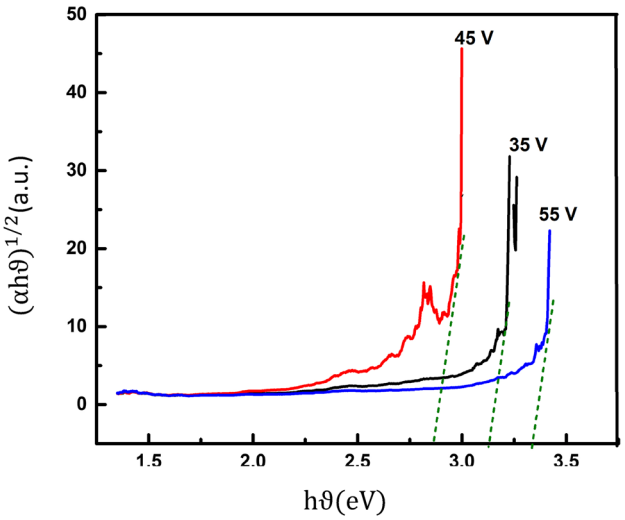

Fig. 4 Tauc plot, $\sqrt{\alpha h\vartheta}$ versus $h\vartheta$ for nanotubes grown in (2 v%) DI and (0.3 wt%) NH_4F electrolyte solution and annealed at 450 °C in air

wavelength of the X-rays (1.54 Å) and θ is the Bragg angle [38]. The estimated value of the crystallite size for the sample, which was anodized at 55 V was about 3.13 nm. With decreasing anodizing voltage from 55 to 35 V, the size of the anatase crystallites is increased to 4 nm. Presence of both the anatase and rutile phases in the samples grown at 35 and 45 V and rutile phase in the sample prepared at the higher voltage of 55 V can be explained by effect of the different anodization voltages on producing the tubes with different diameters and wall thickness which can cause various phase crystallites.

Figure 3 shows UV–Vis diffuse reflectance spectroscopy (DRS) of the samples grown at different applied voltages are recorded from 200 to 900 nm wavelengths. DRS is one of the most useful optical measurements and through its absorption spectrum, the electronic transitions of material can be investigated. As we can see the DRS show blue shifted and the strong absorption coefficient of the TiO_2 nanotubes in short wavelength range reduce the diffuse reflectance intensity in 300–400 nm wavelength [41]. Furthermore the DRS intensities are gradually increased in the wavelength range of 500–800 nm and the highest ones appear for the sample, which is anodized at 55 V. This maybe related to increasing of the TiO_2 nanotube thickness by increasing the anodization voltage.

Band gap energy can be also determined from butter equation [40] as follows:

$$\alpha h\vartheta = \beta(h\vartheta - E_g)^m \quad (5)$$

where α is an absorption coefficient, h is a plank constant, ϑ is a frequency, β is a proportionality constant and m is a parameter for semiconductor direct transition and this value can be considered as 2 [42]. By plotting the Tauc graph ($\sqrt{\alpha h\vartheta}$ versus $h\vartheta$), the band gap energies of the TiO_2 nanotubes can be evaluated with the extra plotting line to the x-axis from Fig. 4. The band gap energies of samples 35, 45 and 55 were found to be about 3.2, 2.8, 3.3 eV, respectively. The difference between the values of the band gap may arise from the different crystal phases [43, 44]. In other words, variation in band gap energy maybe related to the nanotubes morphology. Morphological properties such as nanotube ordering and grain size affect their optical properties. More compacted and highly oriented TiO_2 nanotube arrays cause to produce the small grains due to the stronger redox capacity by producing the photo-induced charges in the highly oriented TiO_2 nanotube arrays [45]. According to the XRD pattern diffraction and the SEM image, the sample which was anodized at 55 V have the smallest size of grain and the most ordered arrays and confirms higher band gap energy of the sample.

Conclusion

In this paper the effective approach, three step anodization process, proposed to develop highly ordered crystallized and top open channel TiO_2 nanotubes. The pore diameter, porosity and wall thickness of the TiO_2 nanotubes could be tuned by changing the anodization voltages. Moreover, it was observed that the anodization voltage has significant effect on band gap values. The optimum anodization voltage was found to be 55 V in our experiments using (2 v%) DI water and (0.3 wt%) NH_4F solution to grow

compact TiO_2 nanotubes with 67% porosity, which can be used as photoanode in dye-sensitized solar cells.

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