

Comparison of photocatalytic and photoelectrochemical behavior of TiO₂ nanotubes prepared by different organic electrolyte

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Titania (TiO₂) nanotubes with different surface morphologies were successfully synthesized by anodization process in glycerol and ethylene glycol electrolytes. The morphology of TiO₂ nanotubes was observed via FESEM and the crystal structure was studied by XRD analysis. It was found that different morphologies of TiO₂ nanotubes show an evident influence on photocatalytic and photoelectrochemical behavior. From the results obtained, the high aspect ratio TiO₂ nanotubes with small intertube spacing, which were synthesized from ethylene glycol electrolyte demonstrated better photocatalytic and photoelectrochemical behavior compared to low aspect ratio TiO₂ nanotubes with large intertube spacing, which were synthesized from glycerol electrolyte. The elaboration of this observation is described in detail in this paper.

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1. Introduction

TiO₂ has attracted great attention owing to its excellent characteristic such as great capacity for oxidation, wide band gap, non-toxicity, low cost and long term stability [1-5]. Due to its wide range of characteristics, TiO₂ photocatalyst is applied to the field of environmental clean-up including deodorization, antibacterial protection, anti-fouling protection, water treatment, gas emission treatment, dye-sensitized solar cells, hydrogen generation by water photoelectrolysis, gas sensors and so on [5-8]. Studies have indicated that for these applications, well-arranged TiO₂ nanotubes are of great importance due to their one-dimensional (1D) nature, ease of handling and simple preparation [8-10]. Therefore, in recent year, considerable efforts have been focused on new technique for synthesizing TiO₂ with unique nano architecture especially highly ordered nanotube arrays. The advantages of nanotubes over thin film are higher surface area, consume less material to form the structure and less cost [10-12].

The photocatalytic and photoelectrochemical behavior of a TiO₂ is largely controlled by (i) the light absorption properties, (ii) reduction and oxidation rates on the surface by the electron and hole, and (iii) the electron-hole recombination rate [13-15]. The high aspect ratio of TiO₂ nanotubes have high surface area structure including the inner-cavity and outer surface compared to the low aspect ratio of TiO₂ nanotube [16-20]. Therefore, in this work, we investigate the effect of the geometry of the TiO₂ nanotubes, which were synthesized from two different organic electrolytes (glycerol and ethylene glycol). In addition, the photocatalytic and photoelectrochemical

behavior of TiO₂ nanotubes were investigated and were presented in the following sections.

2. Experimental

2.1 Preparation of TiO₂ nanotube arrays

High purity (99.6% purity with 0.1 mm thickness) titanium (Ti) foils were used in this study. The Ti foils were purchased from Strem Chemicals. Prior to anodization, Ti foils were cut into dimension of 4 cm × 1 cm and were degreased by sonication in ethanol for 30 minutes. The foils were then rinsed in deionized water and were dried in nitrogen stream. Anodization was performed in a two-electrode configuration bath with Ti foil as the anode and platinum electrode as the counter electrode. The experiment was done by adopting optimum condition for TiO₂ nanotube formation [21-22]. Two different electrolytes were used to anodize Ti, one was glycerol (85 wt% of glycerol and 15 wt% of water) containing 5 wt% of NH₄F with applied potential of 30V, and another one was ethylene glycol (100 wt% of ethylene glycol) containing 5 wt% NH₄F and 5 wt% H₂O₂ with applied potential of 60 V. The anodization process was conducted for 60 minutes. After anodization was completed, the anodized foil was rinsed in DI water and was annealed at 400°C in argon atmosphere for 4 hours.

2.2 Characterization of TiO₂ nanotubes

Morphology of the anodized Ti foils was viewed via field emission scanning electron microscopy (FESEM, Zeiss SUPRA 35VP) at a working distance of

approximately 1 mm. To obtain the thickness of the anodic oxide formed, cross-sectional measurements were conducted on mechanically bent samples, wherein a partial lift-off of the anodic layer occurred. Phase determination of the anodic layer was determined via XRD (Philips, PW 1729) operating at 45 kV and 40 mV.

2.3 Photocatalytic degradation testing

Photocatalytic degradation studies were performed by dipping 4.0 cm² of Ti foil in 100 ml of 30 ppm methyl orange (MO) in a custom-made photoreactor consisting of a quartz glass. A blank sample (without TiO₂ nanotubes) was also prepared in order to eliminate the effect of light towards the degradation of MO. The samples were left in a reactor for 30 minutes in dark environment to achieve adsorption and desorption equilibrium. Then, samples were photo-irradiated at room temperature using TUV 18W-C Germicidal light. 5 ml of MO solution was withdrawn from the quartz tube for every one hour to monitor the degradation of MO after irradiation. The concentration of the degraded MO was determined using UV spectrometer.

2.4 Photoelectrochemical response testing

Photoelectrochemical behavior of the TiO₂ nanotubes were characterized using a three-electrode photoelectrochemical cell with TiO₂ nanotube arrays as the working photoelectrode, platinum rod as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. A solution of 1 M potassium hydroxide (KOH) with 1 wt% ethylene glycol was used as the electrolyte. All three electrodes were connected to a potentiostat (μ Autolab III). A 150 W xenon lamp (Zolix LSP-X150) with an intensity of 800 W/m² was used to produce a largely continuous and uniform spectrum; 100% of the light was transmitted by the quartz glass as the xenon lamp shone on the TiO₂ nanotube arrays (photoanode). The xenon lamp was switched on after the three electrodes were connected to the potentiostat. The corresponding photocurrent was measured during the voltage sweeping (5 mV/s).

3. Results and discussion

3.1 FESEM observation

Formation of TiO₂ nanotubes arrays on the surface of Ti depends on electrochemical etching and chemical dissolution. Therefore, it is predicted that the morphology of TiO₂ nanotubes will be affected since the interaction between electrochemical etching and chemical dissolution is different in glycerol and ethylene glycol. Fig. 1 shows the illustrative top view and cross-sectional image of TiO₂ nanotubes produced by potentiostatic anodization of Ti foil in glycerol containing 5 wt% of NH₄F. The anodized Ti has complete porous structure with well aligned nanotubes arrays. The average length of the nanotubes is 2 μ m and

the diameter of the nanotubes is 90 nm. The aspect ratio (tube length / tube diameter) of the TiO₂ nanotube sample is approximately 22. The pores are not exactly circular and ridges on the circumference of the nanotubes are obviously seen. The reason may be attributed to the existing water (15 wt %) in the glycerol have caused the pH burst and thus making the surface of the nanotubes serrated [23].

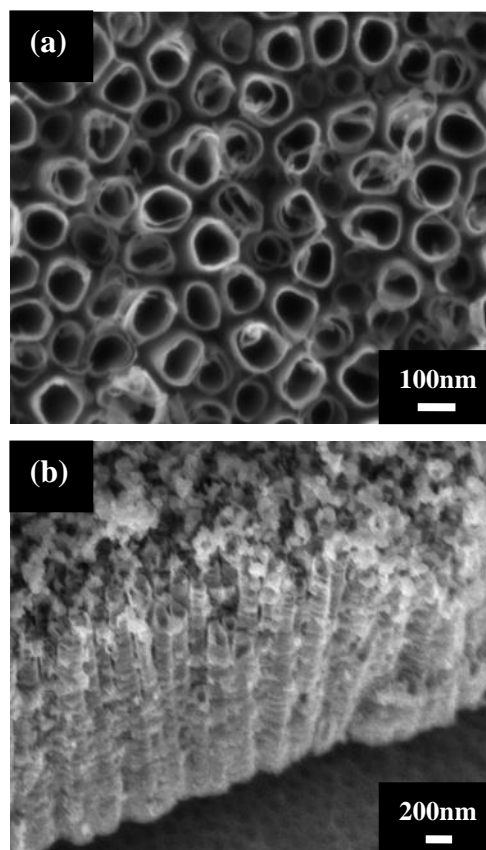


Fig. 1. FESEM images of TiO₂ nanotubes synthesized in glycerol containing 5 wt% NH₄F; (a) top view, and (b) cross section of TiO₂ nanotubes.

The ethylene glycol electrolyte was selected because it is expected that electrolyte with low viscosity, $\eta = 16$ cP at 25 °C (as compared to the glycerol with $\eta = 945$ cP) may result in formation of longer nanotubes. Furthermore, the absence of water in pure ethylene glycol is also expected to reduce the pH burst and thus allowing the formation of smooth nanotubes. Similar structure of TiO₂ nanotubes was obtained in ethylene glycol; however, the wall is smoother as compared to the FESEM images in Fig. 1. The tubes were arranged in very tight bundles but were not connected with each other. The average length of the tubes is 8 μ m and the diameter of the tubes is 100 nm. The aspect ratio (tube length / tube diameter) of this TiO₂ nanotube sample is approximately 80. This smooth wall and small gap between adjacent tubes in the TiO₂ nanotube arrays hinder unwanted materials from entering and introducing imperfections into the array.

3.2 X-ray diffraction (XRD) analysis

The corresponding XRD pattern for TiO₂ nanotubes synthesized from glycerol and ethylene glycol electrolytes are shown in Fig. 3. The XRD pattern shows the presence of anatase phase with improved degree of crystallinity after annealing at 400°C in argon atmosphere. From the results obtained, the TiO₂ nanotubes synthesized from ethylene glycol electrolyte containing 5 wt% NH₄F and 5

wt% H₂O₂ showed more prominent anatase phase as compared to the TiO₂ nanotubes synthesized from glycerol electrolyte containing 5 wt% NH₄F. The obvious anatase peaks can be detected at 25.5°, 38.5°, 48°, 54.5°, and 55.5° corresponding to (101), (004), (200), (105), and (211) plane of the anatase TiO₂ with ICDD number of 00-021-1272.

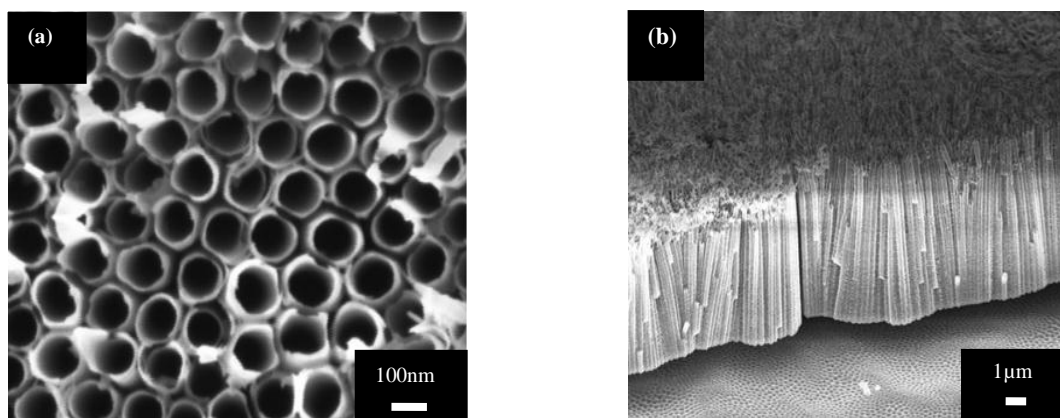


Fig. 2. FESEM images of TiO₂ nanotubes synthesized in ethylene glycol containing 5 wt% of NH₄F and 5 wt% H₂O₂, (a) top view, and (b) cross section of TiO₂ nanotubes.

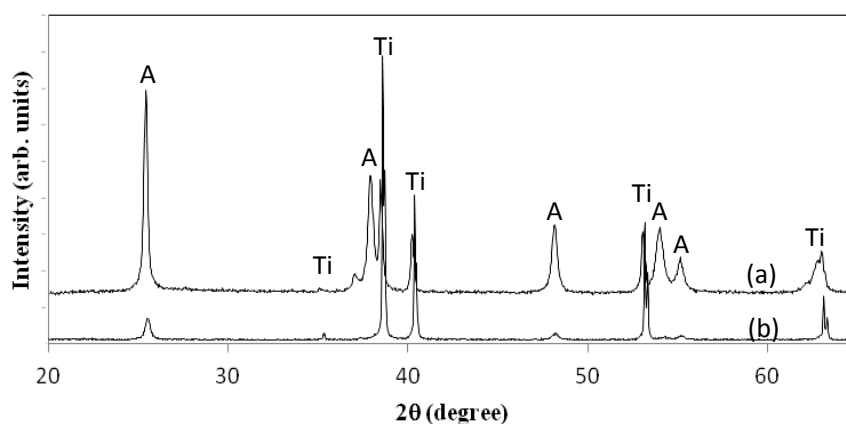


Fig. 3. XRD pattern of the TiO₂ nanotubes produced in electrolyte, (a) ethylene glycol containing 5 wt% NH₄F and 5 wt% H₂O₂, and (b) glycerol containing 5 wt% NH₄F (A= Anatase, Ti= Titanium).

3.3 Photocatalytic activity of TiO₂ nanotubes

Photocatalytic activities of the TiO₂ nanotubes synthesized in two different electrolytes were evaluated in the photodegradation of MO solution after UV irradiation for 3h. In order to evaluate the effect of TiO₂ nanotubes surface morphology structure on its photocatalytic behavior, the photodegradation of MO in the presence of TiO₂ nanotubes with two different aspect ratio was conducted and the result is shown in Fig. 4. As seen in Fig. 4, the TiO₂ nanotubes produced in ethylene glycol exhibited better degree of MO degradation as compared to the TiO₂ nanotubes produced in glycerol. The

photocatalytic activity increases with higher aspect ratio nanotubes because larger surface area of nanotubes will lead to the better diffusion of reactant inside nanotubes [19, 23-24]. Besides this, the smoothness of the wall is responsible for the enhancement of the photocatalytic activity of TiO₂ nanotubes prepared in ethylene glycol. It is believed that the ridges on circumference of the nanotubes produced in glycerol can act as light scattering points which limit the light penetration towards the bottom of the nanotubes and thus resulting in poor degradations.

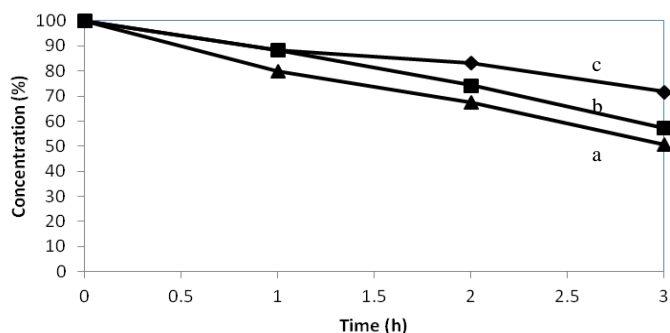


Fig. 4. Degradation of methyl orange with TiO₂ nanotubes produced in electrolyte, (a) ethylene glycol containing 5 wt% NH₄F and 5 wt% H₂O₂, (b) glycerol containing 5 wt% NH₄F, and (c) without TiO₂ nanotubes (blank sample).

3.4 Photoelectrochemical response of TiO₂ nanotubes

The higher photocurrent density of the higher aspect ratio TiO₂ nanotubes (synthesized from ethylene glycol electrolyte) is strongly dependent upon the availability of larger active surface area. The photoelectrochemical reaction for those samples is presented in photocurrent density-voltage (*I-V* curve) as seen in Fig.5. The larger active surface area of longer tubes have better photon absorption, thus more photo-induced electrons were effectively generated from TiO₂ nanotube photoanode to counter electrode through the external circuit during light illumination [19-20, 22]. This statement is further confirmed by more negative values of photopotential for sample synthesized from ethylene glycol (-0.6 V) than sample synthesized from glycerol (-0.45V) as shown in Fig. 5. In addition, higher uniformity and smoother surface of nanotube arrays synthesized from the ethylene glycol can also improve the photocurrent density. The highly uniform morphology of TiO₂ nanotubes provides a high degree of photo-induced electrons mobility along the tube axis [25-26]. This condition resulted in better charge transfer properties in high uniformity smooth surface nanotubes as compared to the serrated surface nanotubes.

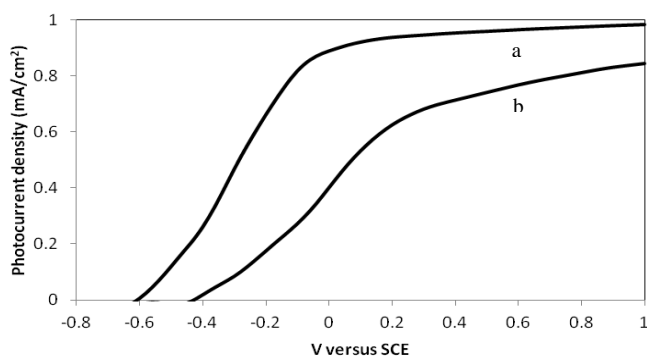


Fig. 5. The *I-V* characteristics of TiO₂ nanotubes produced in electrolyte, (a) ethylene glycol containing 5 wt% NH₄F and 5 wt% H₂O₂, and (b) glycerol containing 5 wt% NH₄F.

4. Conclusion

From the foregoing discussion, it can be concluded that organic electrolyte of ethylene glycol can be used to synthesize higher aspect ratio and uniformity of TiO₂ nanotubes. From the results obtained, higher aspect ratio TiO₂ nanotubes with smooth surface showed the better photocatalytic and photoelectrochemical behavior as compared to the low aspect ratio TiO₂ nanotubes with serrated surface. This is attributed to the better photon absorption to generate more charge carriers exhibited by the TiO₂ nanotubes of higher surface area, which enhances the photocatalytic and photoelectrochemical reaction rates. In addition, the smooth surface of nanotubes with small intertube spacing reduces electron scattering and recombination problem of charge carriers.

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