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Formation of High Aspect Ratio TiO_2 Nanotube Arrays by Anodization of Ti Foil in Organic Solution

(Penghasilan Susunan Nanotiub TiO_2 Bernisbah Aspek Tinggi melalui Proses Penganodan Kerajang Ti dalam Larutan Organik)

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ABSTRACT

Titanium oxide (TiO_2) nanotubes were successfully formed by anodization of pure titanium foil in a standard two-electrode bath consisting of ethylene glycol solution containing 5 wt% NH_4F. The pH of the solution was ~ 7 and the anodization voltage was 60 V. It was observed that such anodization condition results in ordered arrays of TiO_2 nanotubes with smooth surface and a very high aspect ratio. It was observed that a minimum of 1 wt % water addition was required to form well ordered TiO_2 nanotubes with length of approximately 18.5 µm. As-anodized sample, the self-organized TiO_2 nanotubes have amorphous structure and annealing at 500°C of the nanotubes promote formation of anatase and rutile phase. Photocatalytic activity of well ordered TiO_2 nanotubes with two different lengths was evaluated by measuring the degradation of methyl orange (MO). The elaboration of this observation is described in detail in this paper.

Keywords: Anodization; ethylene glycol; phase transformation; TiO_2 nanotubes

ABSTRAK

Nanotiub titanium dioksida (TiO_2) berjaya dihasilkan melalui penganodan kerajang titanium tulen dalam takungan 2-elektrod piawai dengan elekrolit larutan etilena glikol yang mengandungi 5% berat NH_4F. pH larutan ialah ~ 7 dan voltan penganodan ialah 60 V. Didapati bahawa keadaan penganodan mempengaruhi susunan nanotiub TiO_2, permukaan dinding lebih licin dengan nisbah aspek yang lebih tinggi. Didapati tambahan minimum 1% berat air diperlukan untuk menghasilkan nanotiub TiO_2 yang tersusun dengan teratur dan panjang kira-kira 18.5 µm. Sampel yang dianod menghasilkan nanotiub TiO_2 tersusun sendiri yang mengandungi struktur amorfus dan penyepuhlindapan nanotiub pada 500°C menggalakkan pembentukan fasa anatas dan rutil. Aktiviti foto-pemangkin bagi nanotiub TiO_2 yang tersusun dengan panjang yang berbeza ditentukan dengan mengukur degradasi metil oren (MO). Penerangan lanjut mengenai pemerhatian ini diterangkan secara terperinci di dalam kertas ini.

Kata kunci: Etilena glikol; penganodan; nanotiub TiO_2; transformasi fasa

INTRODUCTION

Over the past several years, preparation of TiO_2 nanotubes by the anodization process has caught the attention of the scientific community due to its one-dimensional nature, ease of handling, and simple preparation. TiO_2 nanotubes can be considered as an important material which is widely utilized in many engineering application such as photoelectrochemical hydrogen generation (Mor et al. 2007; Shankar et al. 2007), solar cells, gas sensing (Paulose et al. 2006a) and biomedical applications (Park et al. 2007; Popat et al. 2007). Synthesis of TiO_2 nanotubes is typically carried out in an acidified aqueous solution containing a fluoride salt with pH less than 4. These nanotubes typically have diameters in the range of 60–100 nm and have length varying from 400 to 700 nm (Mor et al. 2006a, 2006b). According to Paulose et al. (2006b), the length of the nanotubes can be improved by using any organic solvent or mixture of organic solvent because it reduces the dissolution rate of the oxide layer. Therefore in this work, we investigate the formation of TiO_2 nanotubes in ethylene glycol with and without addition of water. In addition, the photocatalytic activity of the TiO_2 nanotubes have been investigated and presented.

EXPERIMENTAL PROCEDURE

Ti foils (0.127 mm thickness, 99.6% purity) were purchased from STREM Chemicals. Anodization was performed in a standard two-electrode bath with Ti as the working electrode and platinum as the counter electrode. Prior to anodization, Ti foils were degreased by sonicating in acetone followed by rinsing with deionised water, and then drying using nitrogen stream. After drying, the foil was exposed to electrolyte which consists of ethylene glycol with 5 wt% NH_4F. The anodization voltage was kept constant 60 V and the anodization temperature was fixed to room temperature 25°C. The resulting TiO_2 structures were then rinsed and subsequently annealed at 500°C

in argon for 2 h. It was anticipated that the formation of the crystalline phase will enhance the photodegradation activity.

Photocatalytic degradation studies were performed by dipping 2 pieces of 3 cm^2 Ti foil in 200 mL of 30 ppm MO in a custom-made photoreactor consisting of a quartz glass. The sample was left in the reactor for 30 min in dark environment to achieve the adsorption/desorption equilibrium. It was then photoirradiated at room temperature by using TUV 8 W UV-C Germicidal light. Solution (5 mL) was withdrawn for every 1 h from the quartz tube to monitor the degradation of methyl orange after irradiation. The concentration of the degradated MO was determined using UV spectrometer

Results and Discussions

Formation of TiO_2 nanotubes

Figure 1 shows the illustrative top view and cross-sectional image of the TiO_2 nanotube arrays which were grown by potentioastatic anodization of Ti foil at 60 V in ethylene glycol. As shown in Figures 1a and 1b the use of 100% ethylene glycol allows the formation of well aligned nanotubes with average tube diameter 80 nm and 2.8 μm lengths, respectively. The rate of formation was 83.3 nm/min.

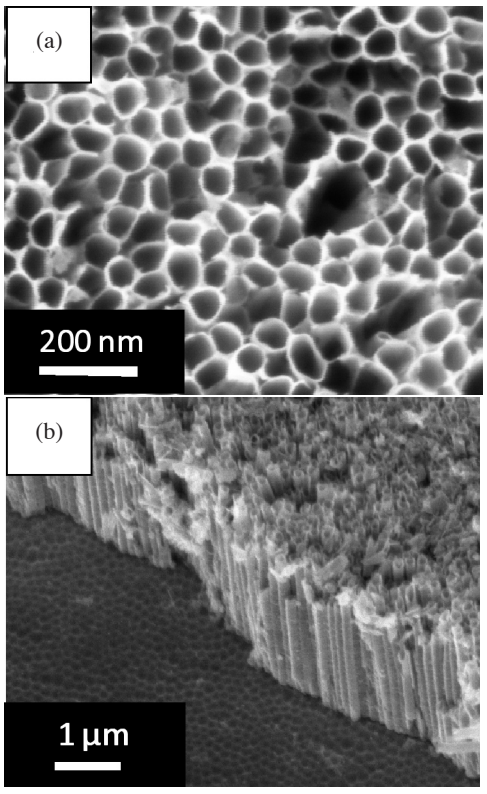

FIGURE 1. FESEM micrograph of the TiO_2 nanotubes produced in ethylene glycol with 5 wt% fluoride without water (a) top view and (b) cross section of a fractured sample

When anodization was continued in the same electrolyte with addition of water, a significant difference in length of the nanotubes could be noted. When the water content was approximately 1 wt%, the length of the tubes was 18.5 μm (Figures 2a and 2b). It is worth to note that, the formation rate of the tubes as high as 308.3 nm/min was achieved in this work using conventional mixing. This rate was much better than the highest growth rate achieved by Paulose et al. (2006b). The above results clearly indicate that water content facilitate the formation of long nanotubes and this is probably because water acts as source of H^+ and O^{2-} ions for local acidification and oxide formation. The use of water has also resulted in the formation of smooth and ridges free nanotubes (insert in Figure 2b) with high aspect ratio, 23.

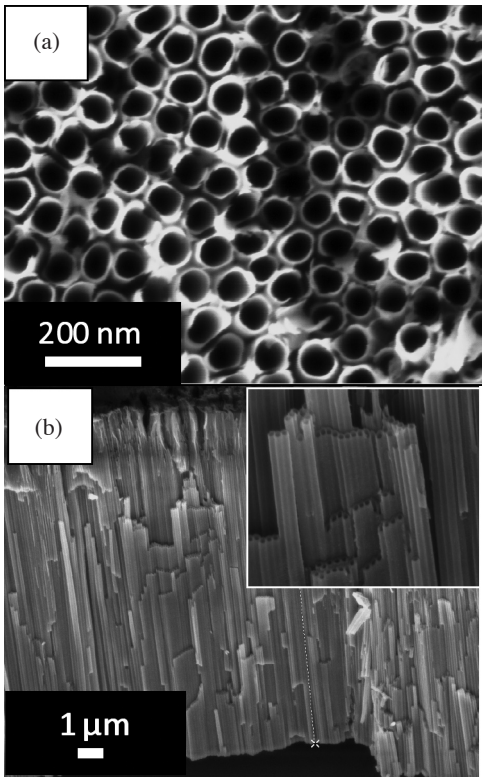

FIGURE 2. FESEM micrograph of the TiO_2 nanotubes produced in ethylene glycol with 5 wt% fluoride with 1 wt% of water (a) top view and (b) cross section of a fractured sample (the insert shows higher magnification of the fractured surface)

Effects of Heat Treatment

In order to investigate the effects of heat treatment on the crystal structure, the anodized sample prepared in ethylene glycol with and without water content was heat treated at 400°C and the crystalline structure was examined. It is anticipated that heat treating the nanotubes at 400°C will result in anatase phase and thus poses excellent photocatalytic activity (Sreekantan et al. 2009). The result in Figure 3 shows the crystal structure of titania depends on the annealing temperatures. The as-made sample (without

annealing) indicated that the titania have amorphous structure as only Ti- peaks were shown. However, sample annealed at 400°C showed Ti- peaks and anatase peaks. Figure 4 shows the EDX spectrum of the composition of the sample prepared in ethylene glycol and an average value of all elements in atomic and weight percentage. It is evident that content of carbon for sample anodized in ethylene glycol is 6.35 wt%. The content of carbon was similar (not shown) for sample prepared in ethylene glycol with 1 wt% water.

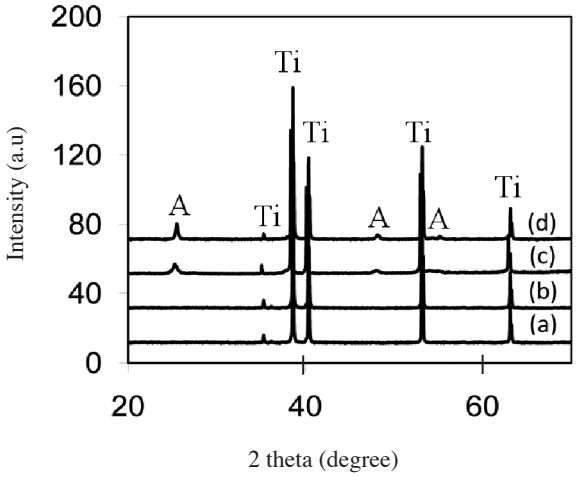

FIGURE 3. XRD pattern of TiO_2 nanotubes (a) anodized in ethylene glycol, (b) anodized in ethylene glycol with water, (c) anodized in ethylene glycol and annealed and (d) anodized in ethylene glycol with water and annealed (A: anatase, Ti: titanium metal)

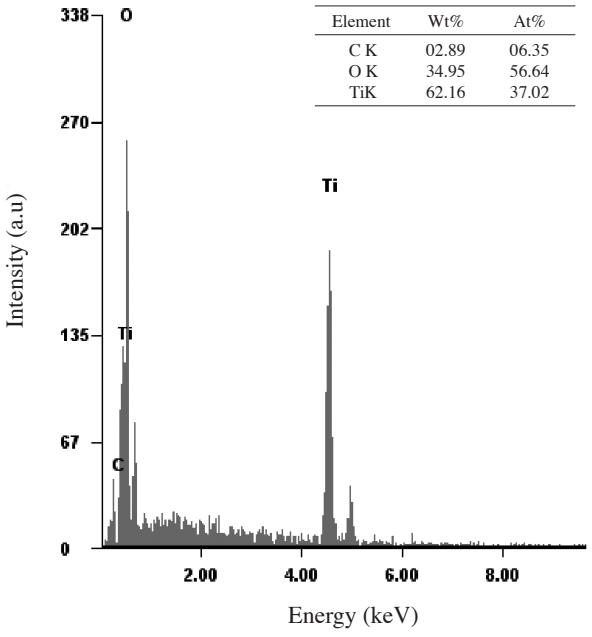

FIGURE 4. EDX spectrum of the sample anodized in ethylene glycol

PHOTOCATALYTIC ACTIVITY OF THE TIO_2 NANOTUBE ARRAYS

The photocatalytic activity of the TiO_2 nanotube was evaluated by photodegradation of methyl orange aqueous solution after UV irradiation for 5 h. In order to evaluate the effect of TiO_2 nanotube surface structure on its photocatalytic activity, the degradation of methyl orange in the presence of sample with two different tube lengths and annealed at 500°C was carried out and the result is shown in Figure 5. It can be noted that for the first 2 h of irradiation, nanotubes with 2.8 μm length exhibited almost similar degree of MO degradation with the longer nanotubes of 18.5 μm. After that, longer tubes showed relatively better degradation as compared to short tubes. It is generally believed that both the absorption of the incident photons and adsorption of MO by the TiO_2 nanotubes should increase with the increasing of tube length, which is beneficial to achieve a greater photocatalytic degradation rate. The fact that the photoactivity was not significantly enhanced with the longer nanotubes indicates a lot of room for improvement in this work. The insignificant improvement on MO degradation probably due to the small diameter of the nanotubes which limits the depth of incident photon penetration through the nanotubes and the diffusion of reactant inside long nanotubes required longer time due to the capillarity structure.

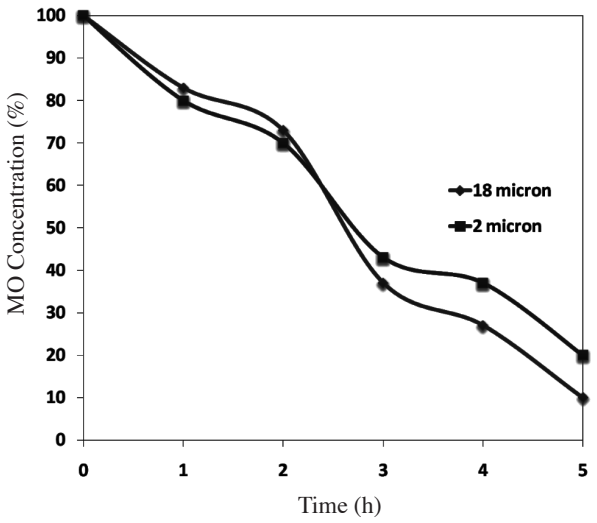

FIGURE 5. Photocatalytic activity of the nanotubes with different length

CONCLUSION

From the foregoing discussion, it can be concluded that ethylene glycol as a solvent, can be used to synthesize highly ordered TiO_2 nanotube arrays and incorporate carbon into TiO_2 nanotubes. The nanotubes length can be tuned by introducing limited amount of water. The present study also demonstrated that the photocatalytic activity was not significantly altered with tube length and might be

improved with increasing tube diameter to enhance light penetration and reactant diffusion.

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