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The effects of fluoride-based electrolyte concentrations on the morphology of self-organized titania nanotubes

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This paper presents growth of titania nanotubes by electrochemical oxidation (anodizing) approach of titanium foil in fluoride-based ion electrolyte. The ammonium fluoride (NH_4F) concentration was varied from 0.6 to 1.5 wt.% and its effects on the morphology of titania nanotubes were investigated. The inner diameters were affected by the concentration of electrolyte, it was observed that arrays of titania nanotubes with pores diameter ranging from 15 to 115 nm can be prepared by using NH_4F electrolyte. The study showed that the titania nanotube arrays formed by anodization were more uniformly arranged at low concentration fluoride-based electrolyte. In addition, from field emission scanning electron microscope (FESEM), a very interesting structure, i.e. small pores formed in bigger pore, was observed.

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1. Introduction

Recently, nanoscale structures of TiO_2 have attracted interesting scientific and technological attention due to their potential applications in various fields. For examples, nanoscale structures of TiO_2 are used in photocatalysts [1], dye sensitized solar cells [2], hydrogen sensor [3, 4] and water splitting [5]. Xiaobo Chen reported that the TiO_2 nanotube arrays photoanodes could generate H_2 by H_2O photoelectrolysis with a photoconversion efficiency of 12.25% [5]. Much effort has been focused on the synthesis of titania nanotube arrays prepared by nano-imprint, sol-gel coating, or electrochemical oxidation. In the anodization process, TiO_2 nanotubes are formed by anodization of titanium foil in suitable electrolyte conditions [6-10].

In this work, the morphologies of TiO_2 nanotube arrays fabricated by various electrolyte concentrations were investigated. TiO_2 nanotubes on titanium foil have been successfully fabricated by using ammonium fluoride (NH_4F) dissolved in a mixture of deionized water (DI) with glycerol to increase the smoothness of nanotube walls.

2. Experimental details

Ti foils (99.7% purity, Strem Chemicals) with 8.0 cm^2 surface area and thickness of 0.127 mm were polished to a mirror quality smooth finish using silicon carbide sandpaper of successively finer grits (600, 1200) and degreased ultrasonically in DI for 5 minutes followed by rinsing with ethanol and dried in nitrogen stream. After drying, the samples were anodized in NH_4F (0.6-1.5 wt.%) with mixture of glycerol and DI. The anodization was performed in a two-electrode configuration bath with Ti foil as the anode and the platinum rod as the counter electrode. The electrolyte solution was generally not stirred during anodization. The electrolyte was maintained at room temperature. The anodization voltage was fixed at 20V and duration of anodizing was 60 minutes. The distance between anode and cathode was kept at 3.5cm. The samples generated by 0.6, 0.8, 1.1 and 1.5 wt.% were denoted as S1, S2, S3 and S4, respectively.

After anodization, the samples were cleaned again ultrasonically in DI and then rinsed with ethanol and dried in nitrogen stream. The effects of different electrolyte concentrations on the surface morphologies of TiO_2 nanotubes were analyzed by field emission scanning electron microscope (FE-SEM, Leo Supra 50VP) with an accelerating voltage of 15kV.

3. Results and discussion

Titania nanotubes formation mechanism has been well established and basically it could be summarized as [11, 12] : (1) Oxidation of Ti metal to form TiO_2; (2) formation of pit on the oxide layer; (3) growth of pits into pores; (4) oxidation and field-assisted dissolution of the metallic part between the pores; (5) nanotubes were formed.

In this work, the effects of electrolyte concentrations on the formation of TiO_2 nanotubes were investigated. When titanium samples were anodized in NH_4F solution, structures of the anodized titanium samples changed remarkably along with the changing of electrolyte concentrations. Fig. 1 shows the low magnification FE-SEM images of the top view TiO_2 nanotube arrays, which were generated under different concentrations of electrolyte, i.e. 0.6 wt.%, 0.8 wt.%, 1.1 wt.%, and 1.5 wt.%, anodized at 20V for 60 min. Among the samples, the nanotubes are most orderly formed in S1 as shown in Fig. 1(a). In contrast, the nanotubes in higher concentration were observed to be relatively less orderly formed, i.e. S4, as shown in Fig. 1(d).

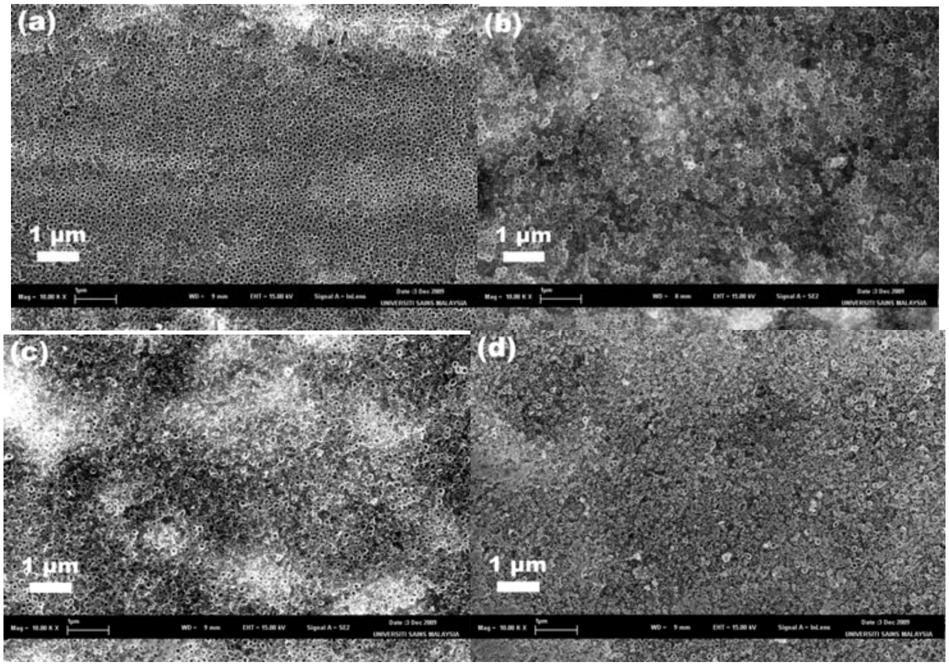

Fig. 1. FE-SEM images of TiO_2 nanotubes formed under various NH_4F concentrations fixed at 20V for 60 min: (a) S1, (b) S2, (c) S3 and (d) S4.

Based on the FE-SEM images in Fig. 1, an analysis on the pore size of titania nanotubes has been carried out. A large population of nanotubes for each sample have been taken to analyze the inner diameter distribution of nanotubes. Fig. 2 shows the inner diameter distribution of nanotubes formed under different NH_4F concentrations. From the statistical data, inner diameter could be affected by concentration of electrolyte. The peaks of inner diameter of sample S1, S2, S3 and S4 were found to be 65, 45, 35 and 45nm, respectively. Fig. 2 shows that the peaks of the inner diameters gradually shifted to smaller values and reached the smallest peak value at 35nm for sample S3. The subsequent increase of electrolyte concentration would not further reduce the inner diameter peak value.

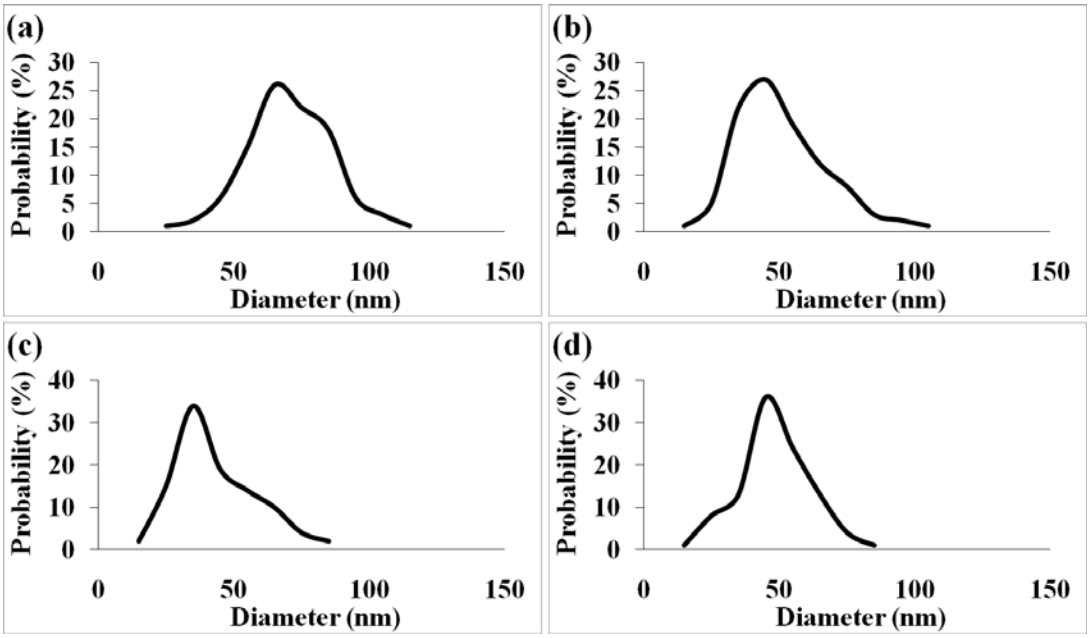

Fig. 2. Inner diameters distribution curve of TiO_2 nanotubes formed in various NH_4F concentrations under 20 V for 60 min.: (a) 0.6 wt.%; (b) 0.8 wt.%; (c) 1.1 wt.%, and (d) 1.5 wt.%.

Table 1 shows the energy dispersive X-ray (EDX) analysis result of the samples under different electrolyte concentrations. EDX analysis data confirmed the elements exist in nanotubes including titanium, oxygen and fluorine. The atomic percentage ratio of titanium to oxygen in S1, S2, S3 and S4 was determined to be 0.61, 0.68, 0.68 and 0.61, respectively. The presence of small amount of fluorine was due to the use of fluoride-based electrolyte, and its atomic percentage slightly increased with the electrolyte concentration. On the other hand, the atomic percentage of titanium and oxygen were found to be relatively constant with electrolyte concentrations. This showed that the change of electrolyte concentrations would not significantly affect the compositions of the Titania nanotubes.

Table 1. EDX analysis data of four titania nanotubes samples under different electrolyte concentrations.

Element	Atomic percentage, %			
	S1 (0.6 wt. %)	S2 (0.8 wt. %)	S3 (1.1 wt.%)	S4 (1.5 wt. %)
Titanium	35.27	37.37	37.12	34.92
Oxygen	57.54	55.22	54.83	56.91
Fluorine	7.19	7.42	8.05	8.17

Fig. 3 shows a higher magnification of FE-SEM image for S3 sample. A careful examination on the S3 surface morphology revealed a very interesting structure formed in this sample. Inset in Fig. 3 illustrates the enlargement of this structure found at location (i). The inset clearly shows that a few small pores were present within the bigger pores. These structures were hardly found at tatania nanotube samples synthesized at lower electrolyte concentrations, i.e. 0.6. and 0.8 wt%. To the best of our knowledge, this kind of structure has not been observed and reported in the literature. The underlying microscopic growth model which describes the presence of small pores in bigger pores is still not well understood. Intensive work is underway to further investigate the growth mechanism of this newly discovered structure.

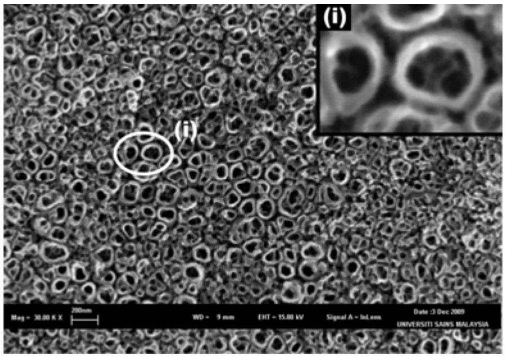

Fig. 3. The presence of small pores within larger pore on S3. Inset shows the enlargement of nanotubes at locations (i).

4. Conclusions

In summary, we have used FE-SEM to characterize the TiO_2 nanotubes samples synthesized under different fluoride-based electrolyte concentrations. Among the samples, the nanotubes were most orderly formed in 0.6 wt.% electrolyte. In contrast, the nanotubes synthesized at higher concentrations were observed to be less orderly formed. The peaks of inner diameter at concentration of 0.6, 0.8, 1.1 and 1.5 wt.% were found to be 65, 45, 35 and 45nm, respectively. The peaks shifted to smaller values and reached the smallest peak value at 1.1 wt.%. The subsequent increase of electrolyte would not further reduce the inner diameter peak value. Apart from that, a very interesting structure was observed in which small pores were found within the larger pores.

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