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Effect of Charcoal as Cathode Material on the Morphology of Highly Ordered TiO_2 Nanotube Arrays

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Abstract: This work presents the potentiostatic anodization study of titania nanotube array films fabricated in fluoride-based Ethylene Glycol (EG) electrolyte. The study focuses on the effect of charcoal, the cathode material on the formation of titanium dioxide (TiO_2) nanotube arrays. Electrochemical anodisation using charcoal is found to be a better alternative to platinum, the commonly used cathode material. The variation in tube length, stability of the tube arrays on the Ti-substrate and the surface morphologies of the nanotube array samples at various anodization potentials are investigated and compared. The samples are characterized by Field Emission Scanning Electron Microscope (FESEM) and X-ray Diffraction (XRD). The results show that charcoal can be a cheap alternative to the costly platinum material for the fabrication of TiO_2 nanotube arrays.
Keywords : Titania nanotubes; Anodization; Surface morphology; cathode material.

Introduction and Experimental:

Tremendous research efforts have been made to fabricate TiO_2 nanotubes by anodization method. Gong et al. were the first to report the fabrication of uniform TiO_2 nanotube arrays by electrochemically anodizing Ti in hydrofluoric acid aqueous solution [1]. Since then various researches have been going on to develop nanotube arrays by anodization technique that allows good control over the pore size and the uniformity of the nanotubes at low cost. In anodic TiO_2 nanotube arrays, each individual tube is grown vertical to the Ti substrate, thereby providing larger surface areas and being an excellent module for use in optical and electronic devices such as gas sensors [2], dye sensitized solar cells [3], hydrogen generators [4], etc.

Herein we report the study on electrochemical anodization of high purity Ti in organic electrolytes, with the main focus being on the effects of cathode material on the formation of TiO_2 nanotube arrays. Although platinum is commonly used as the cathode material for anodization due to its high catalytic activity it may not provide the desired nanotube morphology [5]. Therefore, to develop an alternative to Pt cathode, we have chosen charcoal, a cheaper carbon product, as cathode material and investigated its effects on the morphology of the resulting TiO_2 nanotubes.

Experimental details:

Anodization was performed using a two-electrode cell with titanium foil as the working anode and platinum/charcoal as cathodes. Anodization was carried out for 3 h at two different voltages (30 & 60 V) at room temperature. Titanium foil (0.127 mm thick, 99.7%, Sigma-Aldrich) with a size of 1.5 × 1.5 cm^2 was used as anode. A platinum mesh (Sigma Aldrich) with a size of 2 × 2 cm^2 and a compressed charcoal road (1 cm diameter) with a required length were used as cathode materials. The samples were degreased prior to anodization by sonicating in methanol, acetone and distilled water for 15 min. each. The electrolyte is composed of ethylene glycol (EG, 99.5%, Merck), ammonium fluoride (0.35 wt. %) (NH_4F, 98%, Merck), deionized water (DI) (2 vol. %). The anodizing voltage was kept constant during each experiment with Keithley 2400 source meter. The size parameters of the TiO_2 nanotube arrays such as tube length and pore diameter were measured using the scale bar of FESEM images.

Results and Discussion:

Samples of nanotubes produced were subjected to annealing process at varying time and temperature in order to improve the crystallinity of the nanotubes. Figure 1 shows the XRD patterns of the as-synthesized and annealed nanotube arrays prepared using Pt (Fig 1.a) and charcoal (Fig 1.b) as cathode materials. The synthesized Ti nanotubes before annealing show the amorphous phase of the crystalline structure [6]. The sample after annealing showed anatase peaks and Ti-peaks. Ti-peaks were found again present because the information from the substrate was revealed. Fig. 1a is in close conformity with Fig. 1b, and it reveals that the anodized Ti films were transformed into crystallized phases as predominant anatase and some trace of titanium (JCPDS No 89-4921).

The highly ordered porous titania nanotube arrays were synthesized by anodization method with Pt and charcoal as cathode materials show highly ordered and vertically grown nanotube arrays on Ti substrate (Fig. 2). The pore size of the titania nanotubes prepared with Pt ranges from 80 to 102 nm, and the length of the nanotubes was found to vary from 6 µm to 116 µm at anodization voltages of 30 and 60 V respectively. Charcoal, the newly introduced cathode material, produced architectures similar to those obtained using Pt. The maximum pore size with Pt was 116 nm for the sample anodized at 60 V, whereas, charcoal produced the largest pore size of 143 nm for the same voltage. Nanotube arrays produced using Pt was shorter than those produced by charcoal. At 60 V the tube length produced by Pt was 25.4 µm and at the same voltage, 116.5 µm nanotubes were produced by charcoal at 3 h of anodization. Table 1 illustrates the differences in detail. It indicates that there is a superior growth rate in tube length and pore size with charcoal as cathode material. Similarly FESEM cross-sectional images show that charcoal fabricated nanotube arrays are more highly aligned than those fabricated using Pt. The results confirm that the nature of the cathode material plays a significant role on the morphology of TiO_2 nanotube arrays.

Fig. 1 XRD pattern of TiO_2 nanotubes prepared with a) Pt and b) Charcoal as cathode materials showing similar peaks of predominantly anatase phase.

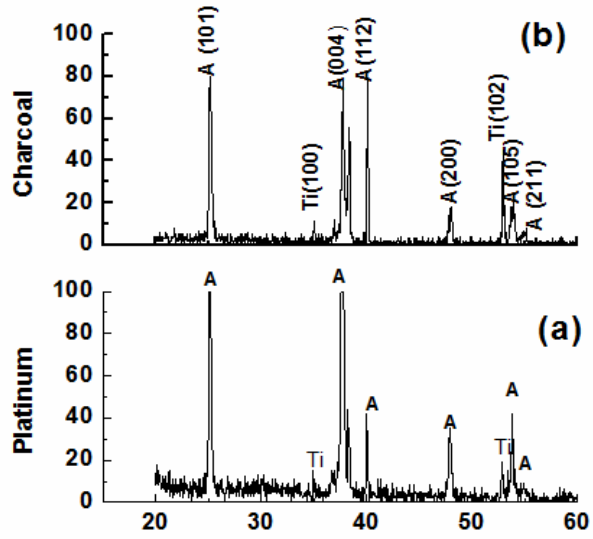
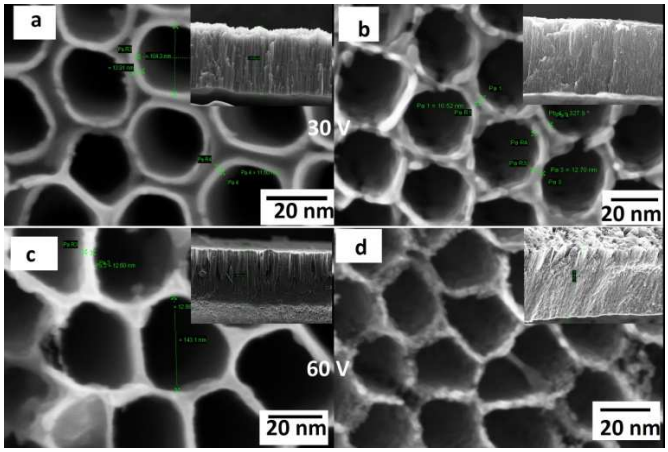


Table 1 The cathode materials tested with the average diameters and lengths of the nanotube arrays fabricated in EG/NH_4F electrolytes for 3 h anodisation duration.

Cathode material	Voltage	Pore diameter (nm)	Tube length (µm)
Platinum	30	80	6.4
	60	116	25.4
Charcoal	30	104	10.5
	60	143	116.5

Fig. 2 FESEM images of the TiO_2 nanotube arrays synthesized with Charcoal (a & c) and with Pt (b & d) as cathode materials at 30 V and 60 V. The images at the insets shows the vertical images of the nanotube arrays



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