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EFFECT OF pH ON SYNTHESIS OF TiO_2 NANOTUBES BY ELECTROCHEMICAL ANODIZATION

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Abstract

Highly ordered TiO_2 nanotube arrays were fabricated via electrochemical anodization of high purity Ti foil using ethylene glycol as an electrolyte. The formation of ordered TiO_2 nanotube arrays was affected by acid concentration of an electrolyte solution and pH. FE-SEM images confirms the formation of nanotubular structure also nanotube length, wall thickness and pore diameter of all the samples were measured in nanometers. From XRD results, after high temperature annealing anatase and rutile phases of the titania were observed; both belong to tetragonal structure. Energy dispersive x-ray spectroscopy (EDAX) result shows the presence of only pure Ti nanoparticles in all samples and no other precipitates were present.

Key words: Titania, Nanotubes, Morphology and Electrolyte.

1. Introduction

Nanostructured TiO_2 materials show high biocompatibility, low toxicity and good retention of biological activity for protein binding. These properties of TiO_2 nanostructure materials were mainly ascribed to their quantum-confinement effects and large specific areas (Hoffmann *et al*., 1995). Since, Zwilling and co-workers reported porous structure formation in Ti *via* electrochemical anodization in fluorine containing electrolytes in 1999 (Zwilling *et al*., 1999), tremendous research efforts have been made to fabricate TiO_2 nanostructures by anodization. Compared with conventional TiO_2 nanoparticles, TiO_2 nanotubes (TNTs) offer some peculiar advantages, such as high specific surface area resulting from the hollow channel structure, high mechanical stability and unique nanoarchitecture with fewer interfacial grain boundaries, which promote charge transport and enhanced electron-hole separation (Yu *et al*., 2010).

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2. Experimental Methods

TiO_2 nanotubes were synthesized through electrochemical anodization technique. Before anodization the Ti foil was cut in to the size 1.5 cm × 1.5 cm. It was degreased by ultrasonication for 15 min in acetone, methanol and deionized (DI) water separately and dried in air. Ti foil was used as anode and platinum mesh of size 2.5 cm × 2.5 cm was used as counter electrode. Ethylene glycol was used as an electrolyte with 0.35wt % of ammonium fluoride (NH_4F) with an addition of 2% DI water. Sulphuric acid was used to vary the pH of an electrolyte. All chemicals and materials in the experiment were used as received without further purification. After five hours of uninterrupted reaction the foil was removed from the electrolyte and was sonicated in ethanol for 5 min to remove the debris from top of the nanotubes that were formed. The sonicated sample was then dried in air and was kept in a furnace for annealing at 450 ^oC for five hours.

Table – 1: The electrolytes used in this study and corresponding acid concentration ranges for which nanotube formation was observed.

Exp. No.	Electrolyte content	Acid concentration	Voltage (V)	pH
1.	Ethylene Glycol, 0.35%NH_4F, 2% H_2O	No	30	7-8
2.	Ethylene Glycol, 0.35%NH_4F, 2% H_2O	1 M	30	1-2
3.	Ethylene Glycol, 0.35%NH_4F, 2% H_2O	0.5 M	30	3-4
4.	Ethylene Glycol, 0.35%NH_4F, 2% H_2O	0.25M	30	5-6

3. Results and Discussion

Fig - 1 provides FE-SEM images confirming the nanotube morphology when anodized without acid concentration. The organic electrolyte without acid concentration results in a nanotube array that is more tightly packed and has a more uniform and consistent morphology compared with the electrolytes having different acid concentrations as shown in Fig - 2. On the other hand it can be observed from the images that those nanotubular structures formed in different acid concentrations have clear and distinct nanotubes.

The addition of H_2SO_4 increases the viscosity of ethylene glycol solution; therefore the anodization current was drastically suppressed, as the high viscosity limits the transport rate of oxygen and fluoride ions to the metal/oxide interface. In consequence, the nanotubes grown in acidic medium are shorter and their wall thickness was larger.

Variation in Wall Thickness and tube length

Electrolyte pH affects both the behaviour of the electrochemical etch and the chemical dissolution due to the hydrolysis of titanium ions. With increasing pH the hydrolysis content increases and it, in turn, slows the rate of chemical dissolution. As shown in Fig - 2 longer nanotubes are formed in higher pH solution. With a potential of 30 V and with pH increasing from strong acidity to weak acidity, nanotube length increased from 4 µm to 6 µm. Also, at a specific pH, the pore size and wall thickness of the nanotubes increases.

The EDX analysis confirmed that the nanotubes were pure titanium dioxide with some TiO_2 precipitate, as shown in Fig - 3. We believe the precipitates hindered the continuous and uniformly distributed flux of ions. As a result, the nanotubes produced were non- uniform and not well organised.

Effect of sulphuric acid Concentrations

The concentration of the sulphuric acid added to the electrolyte was varied from 1 M to 0.25 M to observe the changes in pore diameter, wall thickness and length of titania nanotubes. Fig - 4 shows the images of the foil anodized in H_2SO_4 for 5 hours. The wall thickness of the nanotubes increased as the H_2SO_4 concentration increased from 0 M to 1 M. However, for 0.25 M H_2SO_4, the pore diameter was relatively small and a very loose coverage of titania nanotubes formed on the substrate, as shown in Fig - 4e. As we know, the formation of titania nanotubes depends on the oxide growth rate and the dissolution rate we believe that in the absence of H_2SO_4, the dissolution rate was very slow and thus resulted in small pore size. With increasing acid content the dissolution rate increased and resulted in big pores.

X-ray diffraction

The synthesized samples were subjected to X-ray diffraction after high temperature annealing at 450 °C. As shown in Fig - 5, the diffraction peaks at 2θ of 25.3º, 37.1º, 37.9º, 48.1º, 54.0º and 55.2º can be indexed to the characteristic peaks of anatase phase (JCPDS No 89-4921).

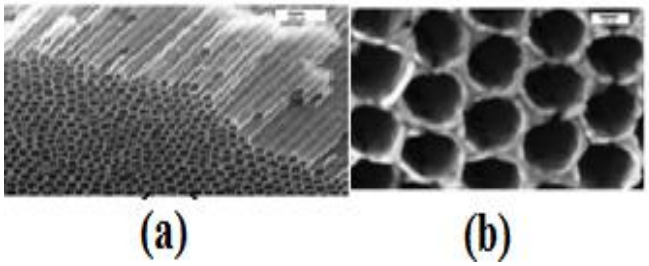

Fig – 1: FE-SEM images
(a) TiO_2 of nanotubes synthesized without acid concentration inEG electrolyte
(b) Top view of TiO_2 of nanotubes

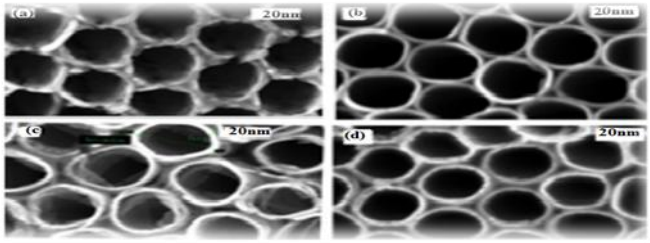

Fig – 2: The effect of H_2SO_4 concentration on the surface of anodized titanium (30V, 0.35Wt % NH_4F, 2% H_20, EG)
(a) Without H_2SO_4, (b) 1M H_2SO_4, (c) 0.5M H_2SO_4(d) 0.25M H_2SO_4

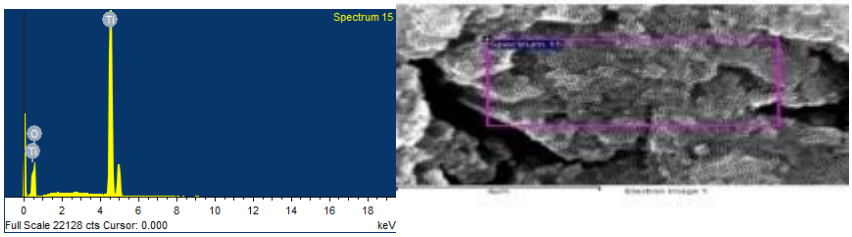

Fig – 3: EDX spectraof oxideresidual found onthe surface.

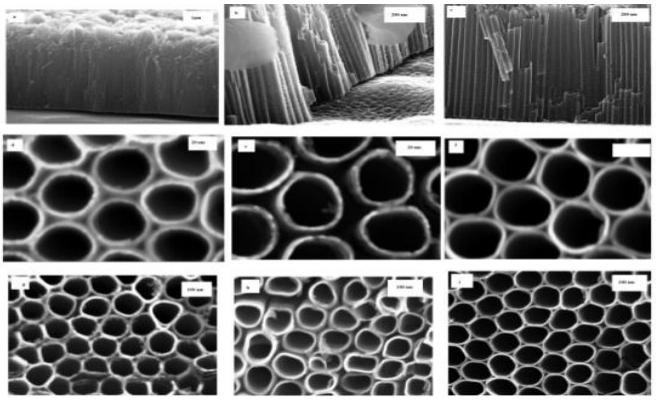

Fig – 4: FE-SEM images of TiO_2 nanotubes prepared in (a,d,g) 0.25 M H_2SO_4, (b,e,h) 0.5 M H_2SO_4 and (c,f,i) 1 M H_2SO_4

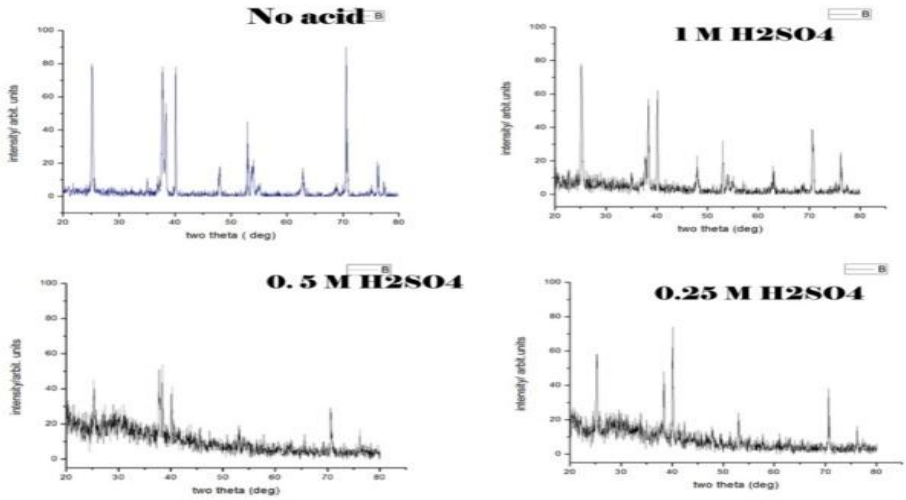

Fig – 5: X-ray diffraction patterns of the titania nanotube array films prepared in EG at different acid concentartions

The other peaks are the characteristic peaks of the original Ti foil. The results indicate that the crystallization of titania nanotube arrays is improved after annealing. Anatase and rutile are two ordinary phases of the titania; both belong to tetragonal structure.

4. Conclusion

Instead of hydrofluoric acid, ammonium fluoride with Sulphuric acid along with ethylene glycol proven in this study to be a competent source to assist in the formation of titanium dioxide nanotubes using the anodization method. Unlike those short and rough nanotubes prepared in aqueous electrolyte as stringent chemical dissolution of Ti occurs, the use of ammonium fluoride with sulphuric acid in the organic electrolyte provided excellent control over the length and other surface morphologies of the nanotube. The geometry of nanotubes, such as length, pore diameter, wall thickness, space between tubes and surface roughness, can be controlled by varying the electrolyte acid concentration.

5. Reference

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