

The Role of Electrolyte pH in Enhancing the Surface Morphology of TiO₂ Nanotube Arrays Grown on Ti Substrate

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Abstract - Among all transition metal oxides TiO₂ has become the most extensively studied and investigated compound in the field of materials science as it gives enormous opportunities to the researchers in the field of nanomaterials. The present work explains the formation of TiO₂ nanotube arrays fabricated by electrochemical anodization of titanium in fluoride-based ethylene glycol electrolyte, with an aim towards elucidating how the electrolyte pH influences the electrolyte properties and corresponding morphological features of TiO₂ nanotube array films. Commonly employed two electrode anodization setup was used for the purpose. The samples were anodized in different electrolyte compositions to study the effect of pH on the growth rate of TiO₂ nanotubes. Concentrated H₂SO₄ and NH₃OH at different molarities were used to vary the pH of the electrolyte solution. The synthesized samples were characterized with FESEM, EDX and XRD to study the morphology and crystal structure of the nanotubes.

Index Terms - Titanium dioxide, nanotubes, anodization, surface morphology, wall thickness, pore diameter, tube length, inter tubular spacing, electrolytes.

1 INTRODUCTION

THE The synthesis of TiO₂ nanotubes has become one of the most important research subjects in nanotechnology and its potential applications in various fields have been extensively studied, such as sensors [1], dye sensitized solar cells [2], [3], [4], [5], hydrogen generation by water photoelectrolysis [6], [7], [8], photocatalytic reduction of CO₂ [9] and super capacitors [10], [11]. The properties and possible applications of TiO₂ nanotubes are mainly dictated by the phase and shape of the nanotubes. It is well established that the properties of the TiO₂ nanotube arrays are dependent on their specific architecture, including nanotube array length, wall thickness, pore diameter and tube-to-tube spacing [5]. The geometrical features of the nanotube arrays are controlled by a variety of parameters that are not specific to one geometrical feature, including anodization potential [12], [13], temperature [14], [18], electrolyte composition and properties thereof (conductivity, viscosity) [15], [16] as well as anodization time [15]. Virtually identical tubes can be obtained in dissimilar electrolytes by the control of different anodization variables [17], [19], [20], [21]. Control of fabrication parameters has enabled variation of pore size, wall thicknesses and tube-to-tube spacing from adjacent to microns [22], [24], [25], [26], [27]. It was during the second synthesis generation of TiO₂ nanotubes that various studies were done on the effect of electrolyte pH on the formation of TiO₂ nanotubes. The electro-

lyte pH of the composite electrolyte solution was found to be an important parameter that has direct influence on the formation of TiO₂ nanotube structures [20], [23]. Literature review indicates that the influence of electrolyte pH in organic electrolytes on the nanotube formation has not been much investigated. In the present study, an attempt has been made to study the effect of pH on the nanotube morphology of TiO₂ synthesized in organic electrolyte (ethylene glycol) containing NH₄F. The study aims at bringing out the possibility of the synthesis of long nanotubes with desired pore diameter, wall thickness and inter-tubular spacing by adjusting the acid/base concentrations in the electrolyte solution.

2 EXPERIMENTAL SECTION

Two electrode anodization set up was used for the synthesis of TiO₂ nanotube arrays. Titanium foils (0.127mm thick, 99%, 1.5 × 1.5 cm², Sigma-Aldrich) were used as anode and platinum mesh (2 × 2 cm², Sigma-Aldrich) was used as cathode in a two electrode anodization set up. The interval between the working electrode and the counter electrode was about 3 cm. The Ti foils were degreased prior to anodization by sonicating in methanol, acetone and distilled water for 15 min each. The electrolyte composed of ethylene glycol (EG, 99.5%, Sigma-Aldrich), ammonium fluoride (0.35g) (NH₄F, 98%, Merck), and deionized water (DI). Different molarities of sulfuric acid (H₂SO₄) and ammonium hydroxide (NH₃OH) were used as sources to control the pH of the electrolyte solution. The anodizing voltage was kept as constant at 30 V during the entire process with a Keithley 2400 source meter. The anodization experiments were conducted at room temperature (~28 °C) with magnetic stirring of electrolyte to ensure uniform local current density and temperature over the surface of the Ti electrode.

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2.1 Surface characterization

The structural and morphological conditions of the TiO₂ nanotubes were characterized using a field emission scanning electron microscope (FESEM SUPRA 35VP ZEISS) operating at working distances down to 1 mm and extended accelerating voltage ranges from 30 kV down to 100 V. The instrument is also capable of energy dispersive X-ray spectroscopy (EDX). FESEM cross sectional observations were carried out on mechanically fractured samples. Powder X-ray diffraction (XRD) patterns of the TiO₂ nanotubes were recorded with a PHILIPS PW 3710 diffractometer using CuK_α radiation.

3 RESULTS AND DISCUSSIONS

3.1 Nanotube Array Formation

Among the various methods of preparation of TiO₂ nanotubes, the electrochemical anodization method seems to be effective in the formation of homogenous nanotubes. It allows systematic control of the geometry of TiO₂ nanotube arrays such as tubular length, pore diameter and surface roughness by optimizing the composition of the electrolyte and the anodizing parameters. The growth of TiO₂ nanotube array is driven by the competitive relation between oxidation reaction and chemical dissolution occurring in the anodization process [28]. The anodization technique creates a uniform film entirely over the surface of the foil by the formation of oxide growth at the metal surface due to the interaction of the metal with O²⁻ or OH ions. After the formation of an initial oxide layer, these anions migrate through the oxide layer reaching the metal/oxide interface where they react with the metal. In the next stage the metal (Ti⁴⁺) cations will be ejected from the metal/oxide interface under application of an electric field and that move toward the oxide/electrolyte interface. Due to the applied electric field the Ti-O bond undergoes polarization and is weakened promoting dissolution of the metal (Ti⁴⁺) cations. The Ti⁴⁺ cations dissolve into the electrolyte, and again the free O²⁻ anions migrate toward the metal/oxide interface to interact with the metal. The chemical dissolution of titania is determined by the F⁻ concentration and solution acidity (H⁺). This chemical dissolution, the key for the self-organized formation of the nanotube arrays, reduces the thickness of the oxide layer (barrier layer) keeping the electrochemical etching (field assisted oxidation and dissolution) process active. The electrochemical etch rate depends on anodization potential as well as concentration of electrolytes. The chemical dissolution rate is determined by the F⁻ concentration and solution pH. With increasing F⁻ and H⁺ concentrations chemical dissolution increases. So the presence of acid in the electrolyte increases the chemical dissolution at the same time reduces the viscosity of the electrolyte solution which leads to the fast formation of nanotubes.

Several parameters in electrochemical anodization, including the concentration of NH₄F (0.35 wt %), content of H₂O (2

vol %) and anodization potential (30 V) were taken in to consideration before choosing a particular electrolyte composition for the experiment. It was observed in our experiment that at low anodizing voltage, 10 and 20 V, only a compact oxide film formed on the surface of titanium. As the voltage increased to 30 V, the surface structures of the TiO₂ nanotubes become discrete, hollow, cylindrical and tubular. Well ordered nanotubes were also formed even at higher voltages in the same electrolyte composition but they were unstable after annealing at higher temperatures. It was observed during the synthesis of TiO₂ nanotubes in aqueous and formamide electrolytes, controlling the pH of the electrolyte solution was found to be a good method for the synthesis of nanotubes [20], [23]. Table 1 summarizes the electrolyte composition and the corresponding acid/ base concentrations for a potential difference of 30 V for 5 h of anodization duration in which the nanotubes were synthesized.

TABLE 1
VARIOUS ELECTROLYTE COMPOSITIONS USED IN THE
SYNTHESIS OF TiO₂ NANOTUBES

Exp. No.	Electrolyte composition	pH
1	EG, 0.35%NH ₄ F, 2% H ₂ O	7-8
2	EG, 0.35%NH ₄ F, 2% H ₂ O, 1M H ₂ SO ₄	1-2
3	EG, 0.35%NH ₄ F, 2% H ₂ O, 0.5 M H ₂ SO ₄	3-4
4	EG, 0.35%NH ₄ F, 2% H ₂ O, 0.25 M H ₂ SO ₄	5-6
5	EG, 0.35%NH ₄ F, 2% H ₂ O, 0.1 M NH ₃ OH	9-10
6	EG, 0.35%NH ₄ F, 2% H ₂ O, 0.3 M NH ₃ OH	11-12

The synthesized samples were taken out and washed immediately after 5 h of anodization and dried in air and annealed at 450 °C temperatures for 5 h in a furnace with air atmosphere to study the effect of annealing temperature on the morphology and crystal transformation of the TiO₂ nanotube arrays.

3.2 Current behavior

Fig.1 shows the I-t curve of titanium foils anodized in electrolyte with different acid/base concentrations recorded during holding the foils at 30 V for 5h, in electrolyte containing EG, 0.35 wt% NH₄F, 2 vol % H₂O both in neutral condition as well as with different concentrations of H₂SO₄ and NH₃OH. In H₂SO₄-EG electrolyte, the current rapidly decreases with formation of the barrier layer, which then slightly increases with formation of the porous structure, and then stays relatively constant with time. In contrast, for NH₃OH containing EG electrolyte, the current decrease relatively slowly to minimum, and then slowly increase reaching a plateau at approximately 20 minutes. The current-time behaviors during fixed potential anodization of Ti samples in EG electrolytes with different concentrations of acid/ base are broadly similar. All exhibit

initially stable or near-stable anodization current followed by a rapidly decreasing current until the current reaches a well defined plateau and current starts rising again and keep steadily. The current-time curve showed clearly three different stages of nanotube formation. Such curves are typical for the formation process of the TiO₂ nanotube arrays in organic electrolytes [19].

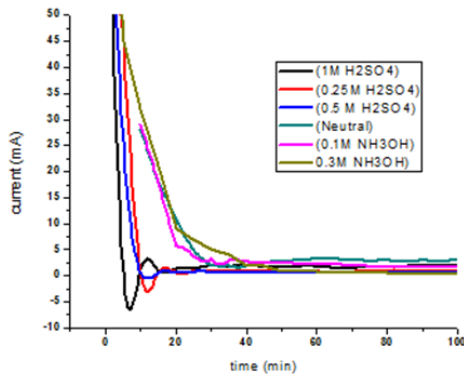


Fig. 1 I-t curve recorded during the anodization of Ti foils

In electrolytes containing acid, the anodization current drops sharply from a high initial value to a lower value in the first few seconds of anodization. This is due to the initial formation of an insulating oxide layer. In the case of electrolyte solution containing 1 M H₂SO₄, the current dropped from the initial value to 1 mA within 5 min time. A similar phenomenon was observed in electrolyte containing H₂SO₄. In the first stage with the onset of anodization, a thin barrier layer of titania forms and that leads to the current decay. It was observed that as the acid concentration increases the current decay becomes faster. In the second stage, due to the solubility of the titania in F-containing acidic solution, the current starts to increase. The increase in current is caused by the formation of pits and enlargement of the pits on the oxide layer. Beyond this point, current is almost steady, indicating the growth of the nanotube arrays.

3.3 Morphological study

Electrolyte pH affects both the behavior of the electrochemical etch and chemical dissolution owing to the hydrolysis of titanium ions. Fig. 2 provides FESEM images contrasting the nanotube morphology when anodized in different pH concentrations of the electrolyte. The nanotubes synthesized in neutral electrolyte medium (Fig 2.a) results in the formation of nanotube arrays that are more tightly packed and have a more uniform and consistent morphology, compared with the nanotube arrays synthesized in electrolytes having different pH. It is observed from the images that those tubular structures formed in different pH concentrations show clear and distinct variations in pore diameter, wall thickness and tube length (Table. 2).

With increasing pH the hydrolysis content increases, which slows the rate of chemical dissolution. As shown in Fig.

2 and Table 2, (for 30 V) longer nanotubes are be formed in neutral electrolyte, with pH increasing from strong acidity (pH ~1) to weak acidity (pH ~6), nanotube length increased from 3.5 μm to 5.2 μm; for the same voltage. Alkaline solutions with lower pH range (pH: 8-10) are also found to be favorable for the formation of nanotubes. At pH ~10 the tube length was found to be 5.6 μm (30 V, 5 h). But higher alkaline solutions (pH >12) are not favorable for the formation of self-organized and longer nanotubes. The length of the nanotubes formed at pH ~12 was found to be 1.8 μm.

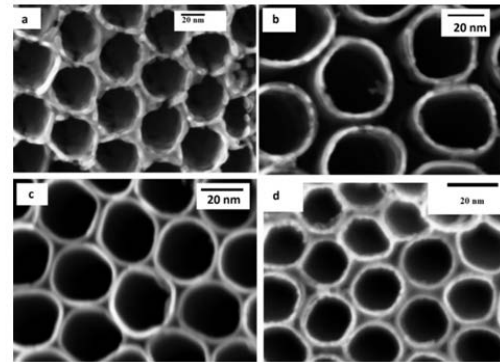


Fig. 2 FESEM images of TiO₂ nanotubes synthesized in electrolyte containing EG, 0.35 wt % NH₄F, 2 vol % H₂O at pH ≤ 7 (a. neutral medium, b. 0.25 M H₂SO₄, c. 0.5 M H₂SO₄, and d. 1 M H₂SO₄)

TABLE 2
WALL THICKNESS, PORE DIAMETER AND TUBE LENGTH OF TiO₂ NANOTUBES AT DIFFERENT pH LEVELS

pH(conc. of acid/base)	Wall thickness (nm)	Pore diameter (nm)	Tube length (μm)
1-2 (1M H ₂ SO ₄)	9.3	81.5	3.8
3-4 (0.5M H ₂ SO ₄)	8.15	81.9	4.7
5-6 (0.25M H ₂ SO ₄)	7	89.2	5.2
7-8 (Neutral)	6.3	80.34	6.5
8-9 (0.1 M NH ₃ OH)	14.7	83.4	5.6
11-12(0.3 M NH ₃ OH)	11.6	35.4	1.8

In strongly acidic solutions (pH<2) increasing the anodization time does not increase the nanotube length [28]. In nanotubes obtained at pH ~2, further increasing the anodization time doesn't result in change in the nanotube length but resulted in a more uniform nanotubular structure, both in shape and size (Fig. 4). It is because; increasing pH decreases the chemical dissolution rate, and apparently prolongs the time needed to reach equilibrium between the rate of nanotube growth and the dissolution rate. As the pH increases the nanotube length appears to be time dependent (in neutral electrolyte medium longer nanotubes are formed by increasing the anodization time).

Careful analysis of the wall thickness shows there is a variation in wall thickness based on the pH of the electrolyte (Fig. 5b, Table. 2). There is an appropriate increase in the wall thickness as the pH of the electrolyte increases up to 10, above that there is a gradual decrease in the wall thickness and pore diameter. With increasing pH, the wall thickness increases from 6.3 nm to 14.69 nm. But as the alkaline nature

of the electrolyte increases there is a structural disorder noticed on the surface morphology of the nanotubes (Fig. 3). At pH 12 the pore diameter (~35 nm) and wall thickness (~11.4 nm) drastically decreases and appears to be of nanoporous nature (Fig. 3b). It is also observed that the voids in both the inter-pore areas and tubes become interconnected.

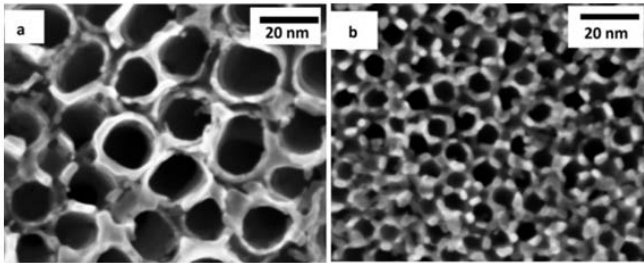


Fig. 3 FESEM top view images of TiO₂ nanotubes synthesized in EG electrolyte at (a) pH~9 and b. pH~12)

The self-aligned tubular structure exhibited in the FESEM image shown in Fig. 2a, has an average inner pore diameter of 80 nm and a nearly uniform wall thickness above 6.3 nm. Meanwhile, for the sample anodized in a mixture of NH₄F 0.35 wt.% and H₂SO₄ (1 M) acidic electrolytes at EG, shown in Fig. 2d, the resulting inner pore diameter is approximately about 81.5 nm and the wall thickness of the pores about 9.3 nm, a clear increase of 3 nm is evident.

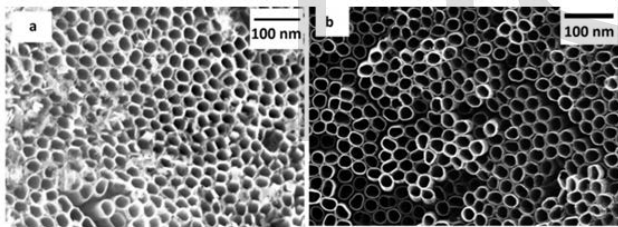


Fig. 4 FESEM top view images of TiO₂ nanotubes synthesized in EG containing 1 M H₂SO₄ at 30 V for a) 5 h and b) 10 h of duration

At a particular pH, the pore size of the nanotubes was found to be increasing with electrolyte pH as shown in Fig 2. However, the pore size was independent of the pH when it approaches neutral electrolyte (pH 6 and 7), whereas at higher pH values (Fig. 3) the wall thickness reaches the maximum value of 14.7 nm at pH ~9 and further increase of pH reduces the wall thickness (11.5 nm at pH ~12). A same phenomenon is observed in the case of pore diameter, as the alkaline nature of the electrolyte increases. There is an increase of pore diameter up to 83.4 nm at pH ~9 and a drastic drop to 35.4 nm when the pH level reaches at 12. The variation in pore size depending on different pH levels of the electrolyte solution are depicted in the FESEM images shown in Fig. 5.

As shown in Table. 2 and graphically represented by Fig. 6 reveals that with a potential of 30 V and with pH increasing from strong acidity to weak acidity, nanotube length increased from 3 μm to 6 μm. Higher pH values produced shorter and thickly packed nanotubes and lower pH values produce longer and clean tubes.

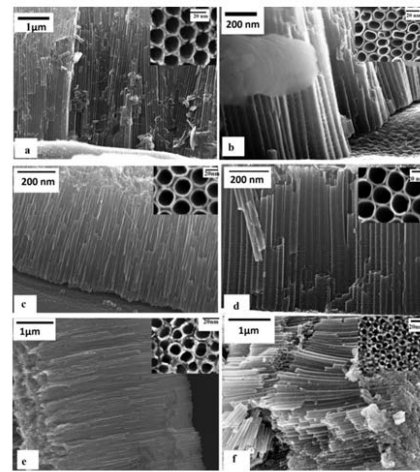


Fig. 5 Lateral view of the nanotubes formed in different pH solutions (pH>1). Variation of pore size with different electrolyte pH is shown in the inset

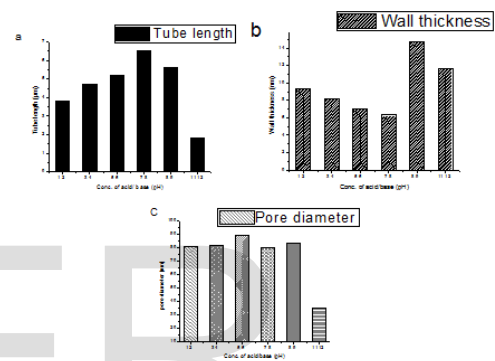


Fig 6 A graphical representation of variation in (a) Tube length, (b) Wall thickness and (c) Pore diameter of TiO₂ nanotubes at different pH levels

As the physical and chemical properties of TiO₂ nanotube arrays are strongly dependent on their geometrical aspects such as tube diameter, length, wall thickness and tube-to-tube spacing, this will affect the devices performance based on TiO₂ nanotubes [29]. Since these are factors that purely depend on anodization voltage, anodization time and electrolyte composition [17], [18], [20], [21], developing nanotubes with particular desired geometry has become a big challenge today. Yuan et al. reported the formation of ultrathin tube wall (nearly 10 nm) at higher anodic voltage (90-270 V) and longer anodic time [30]. The formation of nanotubes at different voltages 25 and 40 V were reported by Yoriya et al. and it was found that the wall thickness ranges from 8-17 nm for 24 h anodization [31]. In both the cases either high anodization voltage or longer anodization time were taken to achieve the desired thinner tube walls. Whereas in our present study, we were able to develop nanotubes with thinner walls (5-9 nm) by varying the electrolyte composition at a particular interval of time and the tubes observed were also of micrometers in length (~6 μm).

In terms of the structure of nanotubes, for a given length, the thinner the wall thickness, the larger the surface area per unit volume [32]. Larger surface areas can increase the liquid contacting area of TiO₂ and subsequently improve its performance in photocatalytic applications. In addition, a larger nanotube surface area in dye-sensitized solar cells can

increase the contact area between the nanotube and the dye and it can improve the efficiency of dye-sensitized solar cells. Haring et al. reported that dyes or polymers can be adsorbed to the outside of the nanotubes if they are spaced apart, fully utilizing the available surface area [33]. The usage of highly ordered TiO₂ nanotube arrays of variable wall thickness to photocleave water under ultraviolet irradiation was reported by Mor et al. and it was found that the nanotube wall thickness is a key parameter influencing the magnitude of the photoanodic response and the overall efficiency of the water-splitting reaction [34].

3.4 XRD analysis

Fig. 7 shows the XRD pattern of the TiO₂ nanotube samples prepared in EG electrolyte. The synthesized TiO₂ nanotubes before annealing show the amorphous phase of the crystalline structure [35]. The sample after annealing showed anatase peaks and Ti-peaks. Ti-peaks were again present because the information from the substrate was revealed.

Fig. 8 illustrates the X-ray diffraction pattern of the TiO₂ nanotubes array films prepared in EG electrolyte at different pH levels. Similar characteristic peaks corresponding to the sample prepared in neutral electrolyte were observed in all the other samples prepared at different pH levels. The samples were annealed in air ambient at a high temperature of 450 °C for 4 h using the optimized ramping rate of 1 °C /min. Fig.7 reveals that the as-anodized TiO₂ films were transformed to the crystallized phases including predominant anatase (101) and some trace of titanium (100) at the peak positions of $2\theta = 25.3^\circ$ and 35.2° , respectively.

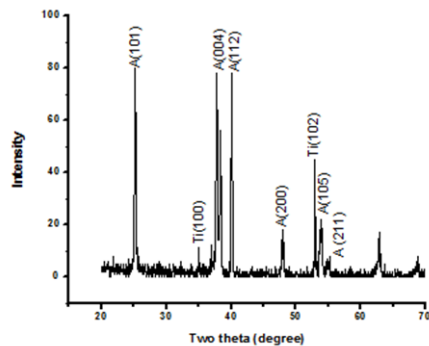


Fig. 7 XRD pattern of TiO₂ nanotubes prepared in EG electrolyte

The high temperature annealing condition employed in this work, however, showed no effect on the formation structure of array film; the tubular structure still remains during the phase transformation from amorphous to anatase crystalline phase. As shown, the diffraction peaks at 2θ of 25.3° (100), 37.1° (004), 37.9° (112), 48.1° (200), 54.0° (105) and 55.2° (211) can be indexed to the characteristic peaks of anatase phase (JCPDS No 89-4921).

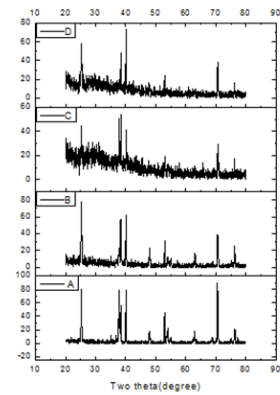


Fig. 8 XRD patterns of TiO₂ samples prepared at different pH levels
A & B in acid electrolytes C & D in alkaline electrolytes

The other peaks are the characteristic peaks of the original Ti foil. All of these anatase phase peaks are enhanced by the increased length of the TiO₂ nanotube arrays. The results indicate that the crystallization of TiO₂ nanotubes arrays transformed as the annealed temperature rised. The EDX analysis confirmed that the nanotube arrays consisted of pure titanium dioxide (Fig. 9).

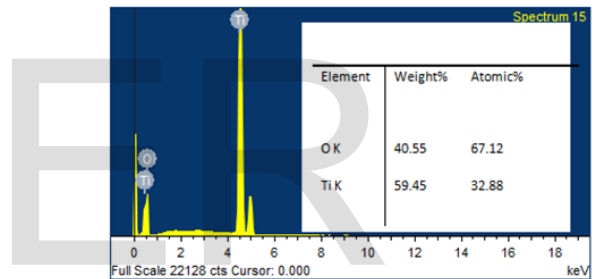


Fig. 9 EDX spectrum of TiO₂ nanotubes

4 CONCLUSION

In the present work, by varying the acid concentrations in the organic electrolytes, we were able to grow nanotubes on Ti substrate. The surface morphology of a nanotube array sample anodized at 30 V for 5 h showed a uniform, clean and regular structure. We were able to achieve well-ordered TiO₂ nanotubes with clear and distinct tubular morphology by utilizing the electrolyte with different pH levels. The as prepared TiO₂ nanotubes arrays was amorphous, crystallized to anatase at an annealing temperature of 450 °C. The study has demonstrated that nanotubes, using organic electrolytes can be prepared not only in neutral conditions but also in strong acidic and alkaline conditions. By controlling the pH of the electrolyte we can control the surface morphology of the nanotube arrays by way of increasing the tube length, the wall thickness and the inter-tubular spacing of the nanotube arrays. 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.

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