

The Effects of Variable Water Content during Growth of Anodic TiO₂ Nanotube Arrays

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Abstract—In this study, anodic TiO₂ nanotube (TNT) arrays were grown by electrochemical method. Anodization processes were performed under voltage of 30 V for 3 hours in an electrolyte. The water content of electrolyte was changed from 1 wt% to 5 wt% during anodization. The crystal structure, morphology and elemental composition of TNT arrays were characterized by using X-Ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX) methods. The results show that water content changing is significant phenomena for the parameters of TNT arrays.

Keywords —Anodic oxidation, TiO₂ nanotubes, water content.

I. INTRODUCTION

Titania is very important material for applications in industry, medicine and scientific research [1–3]. One-dimensional TiO₂ nanotube arrays grown by electrochemical methods are extensively used in dye-sensitized solar cells[4], photodegradation of pollutants[5], humidity sensors[6] and hydrogen generation[7]. One dimensional TNTs are like a highway for electrons because of long electron pathways and rapid electron transportation[4]. Zhu et al. reported that the charge recombination in TNT based photoanodes was much slower than TiO₂ nanoparticle based photoanodes [8]. Also, surface morphology is very important for TNT based applications. Nanotube diameter, wall thickness and length can be changed by changing of anodization parameters. These morphologic parameters are directly related with surface area of TNT arrays. The wall thickness and length of TNT are very sensitive to water content of electrolyte [9].

In this study, anodic TiO₂ nanotube arrays were grown by electrochemical method. During anodization, the water content of electrolyte was changed from 1 wt% to 5 wt% to investigate the effect of variable water content. Also, another TNT array was grown with an electrolyte containing constant 5 wt% water for comparative purpose. The crystal structure, morphology and elemental composition of TNT arrays were characterized by using X-Ray diffraction (XRD), field emission

scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX) methods.

II. EXPERIMENTAL

TiO₂ nanotube arrays were grown by electrochemical method on Ti foils (0.25 mm, 99.7% purity from Sigma Aldrich) as Fig. 1. Pieces of 1.3 x 2.5cm Ti foils were cleaned by ultrasonic bath in acetone, 2-propanol and deionized water for 30 min, respectively, then dried with nitrogen gas. Ti foil and Pt mesh electrodes were placed to Teflon beaker as working and counter electrode. At the beginning, Teflon beaker was filled with an electrolyte solution containing ethylene glycol, 0.4 %wt NH₄F and 1 %wt deionized water. The water content was changed from 1 wt% to 5 wt% by adding deionized water in constant time intervals during anodization. Additionally, for comparative purpose, another TNT array was grown with an electrolyte containing constant 5 wt% water. Anodization processes was performed at room temperature with magnetic stirring. After anodization, ultrasonic cleaning was applied to TNT arrays in methanol for 1 min to remove residuals, then dried with nitrogen gas. Finally, TNT arrays were annealed at 450 °C for 1 h (ramp:15 °C/min) in air ambient for anatase phase transition.

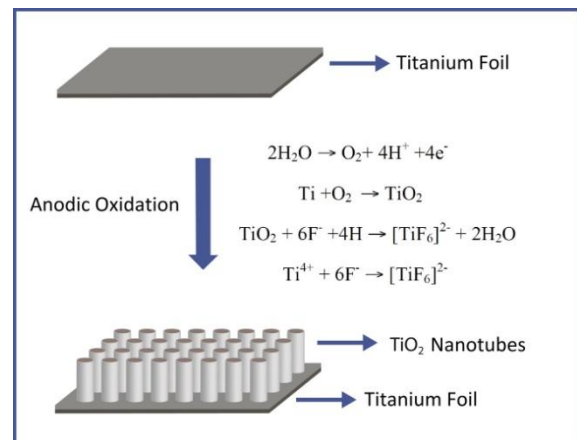


Fig. 1. Schematic illustration of TiO₂ nanotube synthesis.

The crystal structure of TNT arrays was investigated by using a X-ray diffractometer

(PANanalytical, Empyrean), using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$, 45 mV and 40 mA). The morphology and elemental composition of TNT arrays were characterized by using a field emission scanning electron microscope (FESEM, FEI Quanta 450) integrated energy-dispersive X-ray spectroscopy (EDX) detector.

III. RESULTS AND DISCUSSION

Fig. 1 shows the synthesis steps of TiO₂ nanotube arrays. Also detailed formation mechanism of TNT arrays was given in our previous study [4]. In this synthesis route, water content is crucial parameter for formation of TNT.

Fig. 2 shows XRD patterns of as-prepared and annealed TNT arrays. As seen from Fig. 2, as-prepared TNT arrays are transformed from amorph to anatase phase. The diffraction patterns for annealed TNT at $2\theta = 25.3^\circ, 37.1^\circ, 38.0^\circ, 48.2^\circ, 54.3^\circ$ and 55.1° are assigned to (101), (103), (004), (200), (105) and (211) anatase diffractions of TiO₂ (JCPDS No. 21-1272). The other peaks are originated from Ti foil.

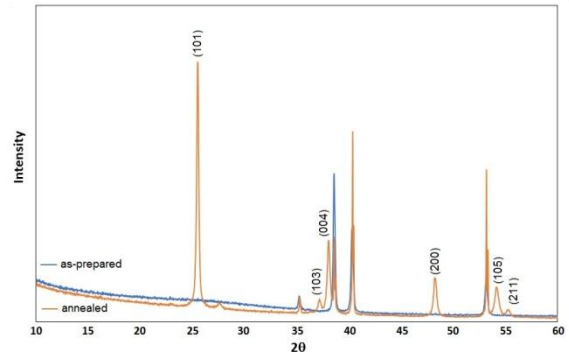


Fig. 2. XRD patterns of as-prepared and annealed anatase TNT arrays.

Fig. 3 shows FESEM images of TNT arrays in different magnifications. As seen from top view (Fig. 3(a-b)), TiO₂ nanotubes are high-ordered and uniform. The average inner tube diameter and wall thickness of TNT were measured as 57 nm and 17 nm, respectively. It has also been observed that nanotubes have slightly sharp ended as magnified in Fig. 3(b) due to variable water content during anodization. The side walls of TNT are like bamboo shape and has approximately 3 μm length.

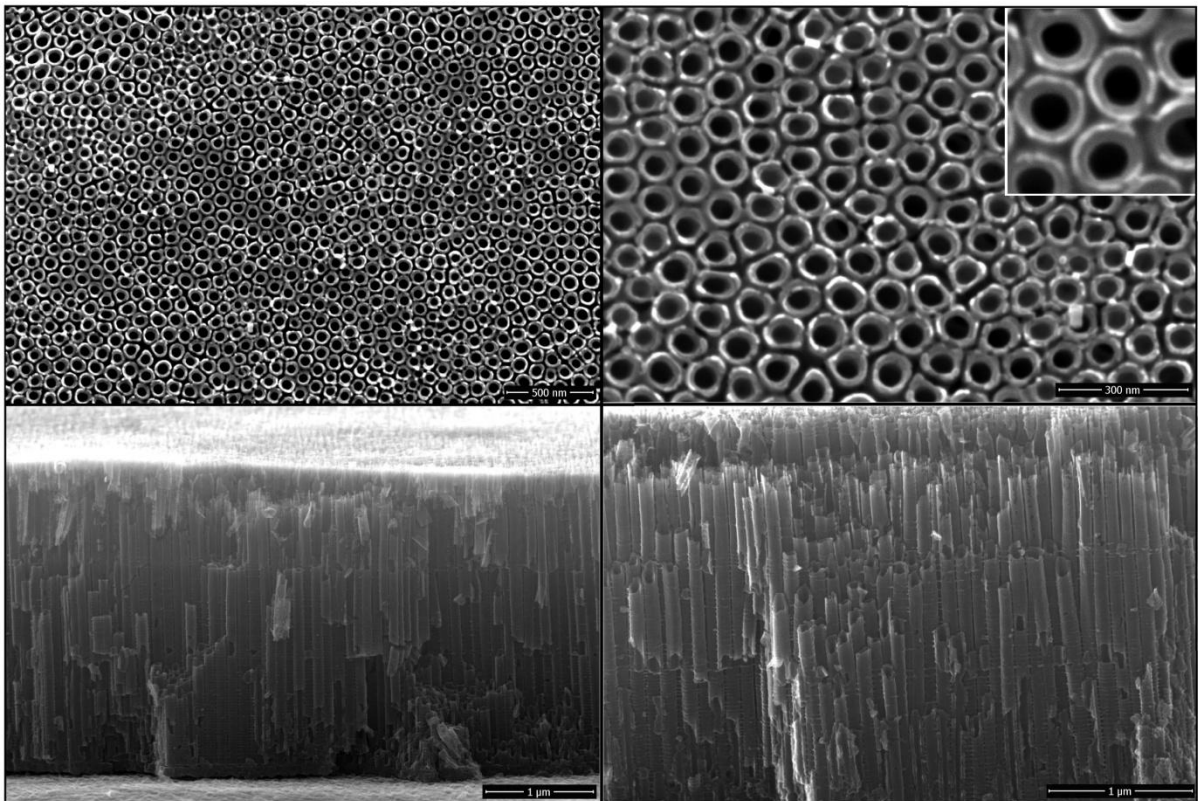


Fig. 3. FESEM images of TNT arrays (a-b) top views, (c-d) side views.

An energy-dispersive X-ray spectroscopy (EDX) detector which is integrated to FESEM was used to determine elemental composition of TNT arrays. Fig. 4 shows EDX spectra of TNT arrays. EDX spectra

indicates the existing of only Ti and O elements on TNT surface.

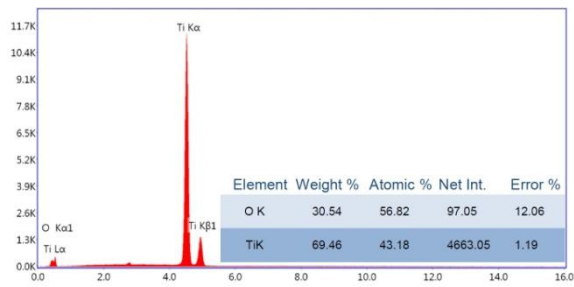


Fig. 3.EDX spectra of TNT arrays.

IV. CONCLUSIONS

The high-ordered TiO₂ nanotube arrays were grown on Ti foil by electrochemical method. The crystal structure, morphology and elemental composition of TNT arrays were characterized by using X-Ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX) methods. During anodization, the water content of electrolyte was changed from 1 wt% to 5 wt% to investigate the effect of variable water content. The XRD results showed that amorph TiO₂ nanotubes were transformed to anatase phase after annealing process. FESEM images showed that nanotube diameter, wall thickness and length of TNT are approximately 57 nm, 17 nm and 3 μm, respectively. Also, sharp-ended TiO₂ nanotubes was observed due to variable water content during anodization.

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