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Effect of agitation mechanism on the anodization process of titanium dioxide nanotube arrays

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ABSTRACT – Titanium dioxide, TiO_2 nanotubes were fabricated by anodization process of pure titanium substrate in ethylene glycol containing fluoride. The anodization process has been conducted with 2 different agitation mechanisms which are magnetic stirring, and air bubble. The morphology and the structure of the as-anodized TiO_2 was determined using field emission scanning electron microscope and Raman spectroscopy.

1. INTRODUCTION

Nanostructured titanium dioxide, TiO_2 material has been one of the widely investigated metal oxide due to its enormous potential for photocatalysis, photovoltaic, sensing, and electrochromic application. In the form of nanotubes, TiO_2 exhibit semiconductor nature with high surface area and aspect ratio [1]. Several process have been studied to produce highly ordered nanotube arrays such as sol gel, hydrothermal, and anodic oxidation [2]. Apparently amongst other methods, anodization has attracted much attention for their exceptional advantages in fabricating TiO_2 nanotubes. The morphologies of the TiO_2 nanotubes structure can be controlled by adjusting the anodization parameter such as type of electrolyte, applied voltage, time and temperature [3]. Yasuda and Schmuki [4] reported that the nanotube growth is controlled by the ionic species diffusion in the electrolyte. Thus, an agitation mechanism such as magnetic stirring [5] and air bubble [6] is necessary in the anodization process as to increase the rate of ion diffusion. This paper presents the effect of agitation mechanisms which are magnetic stirring and air bubble on the formation of TiO_2 nanotubes.

2. METHODOLOGY

Prior to anodization, titanium foils were degreased by successive ultrasonication in ethanol and distilled water for 5 minutes each and dried using air gun. For all experiments, ethylene glycol solution were used which contains 0.55% NH_4F and 1% H_2O. Anodization was performed in a two-electrode configuration connected to a DC power supply with a titanium foil as the working electrode and graphite rod as the counter electrode. The agitation mechanism was varied using magnetic stirrer and air bubble during anodization process. All the anodization experiments were carried out under a constant 40 V anodic potential for 30 minutes at room temperature. The as formed nanostructures were rinsed using distilled water and dried using air gun.

Subsequently, Raman spectroscopy and FESEM were used to determine the TiO_2 nanotube structure and morphology.

3. RESULTS AND DISCUSSION

Figure 1 shows the current profile of anodization process in different agitation mechanisms which are magnetic stirring and air bubble. It is evident that the current profile present typical curve for highly organized oxide of pore arrangement or formation of nanotubes in both sample [7]. The current density of air bubbling mechanism is higher at the beginning which is 12 mA/cm^2 compared to the current density of magnetic stirring which is 10 mA/cm^2. Both sample reached the stabilization at 6 mA/cm^2. However, the time required for the stabilization of current density with magnetic stirring is faster than air bubbling which is about 6 minutes and 25 minutes respectively.

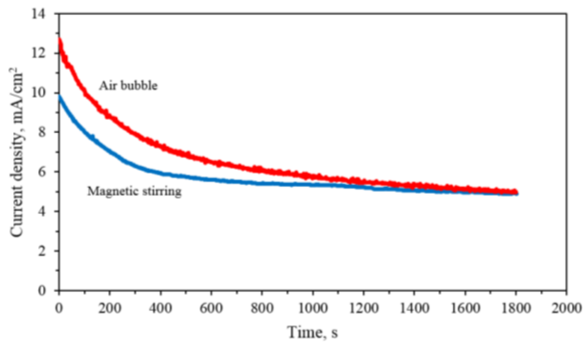

Figure 1 Current profile for nanostructures obtained in EG based electrolytes.

The morphology of the as-anodized TiO_2 grown with air bubble and magnetic stirring is shown in Figure 2 (a) and (b) respectively. Both images indicate the formation of open pores with the diameter of 60 nm for air bubbles and 90 nm for magnetic stirring. Smaller diameter is seen in Figure 2(a) compares with Figure 2(b) which indicates that the dissolution in magnetic stirrer is faster than air bubbles. The tube wall of the nanotubes in magnetic stirrer is vigorously dissolved and hence provide larger diameter. This is also proven by the rapid stabilization of current density for magnetic stirring agitation. As seen from the figures, the top surfaces of the as anodized TiO_2 seem to be covered by some precipitation emanating from the dissolution of barrier layer.

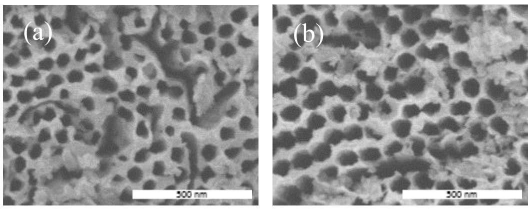

Figure 2: FESEM top images of as-anodized TiO_2 grown with (a) air bubble and (b) magnetic stirring.

Raman spectra of as-anodized TiO_2 nanotubes with different agitation mechanism are shown in Figure 2. The Raman analysis was done over range of 200 to 700 cm^{-1} which is the optimal range for discriminating between crystal phases of TiO_2 [8]. Since titanium has metallic nature, it has free electrons that preventing the lattice vibrations. The Raman spectrum of Ti foil as shown in Figure 2(a). Both Raman spectrum for as-anodized TiO_2 with magnetic stirring and air bubble exhibit broad peaks near 612, 420, 284 cm^{-1} due to amorphous titania, similar results reported in previous study [9].

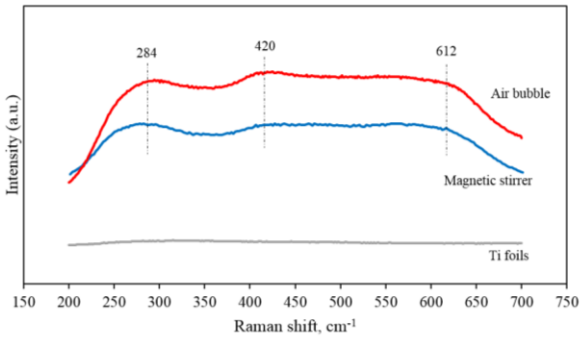

Figure 2 Raman spectra of Ti foils, anodized with magnetic stirring, and air bubble.

4. CONCLUSIONS

The TiO_2 nanotubes were successfully fabricated by anodization process where the formation mechanism of nanotubes can be seen by the current profile. Besides, the investigation of agitation mechanism on the structure of as-anodized TiO_2 nanotubes has been done using Raman spectroscopy. The Raman spectra indicate that the as-anodized TiO_2 nanotubes for both sample of magnetic stirring and air bubble is amorphous since the peak is broad.

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