

TiO₂ NANOTUBE ARRAYS: EFFECT OF SUBSTRATE THICKNESS AND CLEANING AGENT

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Nanotube arrays with length over 22 μm was obtained upon anodizing 0.03 mm thick Ti foil compared to 0.1 mm and 0.05 mm thick Ti foil. These finding show that thin foil are preferable for the formation of TiO₂ nanotubes with a fast rate. Acetone and DI water were used as a cleaning agent. The nanotubular structure of TiO₂ was revealed by washing in sonicated acetone and no precipitate structure was found to remain on the surface. The as-anodized TiO₂ nanotubes were annealed at 400 °C and the photocatalytic activity of the nanotubes produced was evaluated by the degradation of methyl orange. The detail observation was discussed thoroughly in this paper.

Keywords: TiO₂ Nanotubes, Anodization, Photocatalytic

INTRODUCTION

Vertically oriented, highly ordered TiO₂ nanotube arrays made by anodization of Ti thin or thick films are of increasing importance due to their impressive properties in a variety of applications including dye-sensitized solar cells, [1-3] hydrogen generation by water photoelectrolysis, [4-8] photocatalysis, [9-12] and gas sensors; [13-14]. Understanding the formation of nanotubes arrays is important in order to have controlled dimensions for specific applications. Recently, a large number of literatures on the formation of thick TiO₂ nanotubes in organics electrolytes have been reported.

Achieving longer nanotube arrays from thicker Ti films requires increasing concentrations of NH₄F and H₂O. Herein we describe the complete anodization of a various thickness of Ti foil film sample. In this work, we also examine the morphological effects induced by cleaning method performed on oriented TiO₂ arrays formed from anodized titanium. Capillary forces that arise during evaporative drying of wetted nanotubes films from the cleaning step are found to cause clustering of nanotubes and film cracking, the extent of which depended on the film thickness and surface tension of the cleaning solvent. Eliminating capillary stress during the drying process is shown to result in bundle-free films.

MATERIALS AND METHOD

Titanium foils (Strem Chemicals, 0.03, 0.05 and 0.1 mm thick, 99.97% purity) were electrochemically anodized at 60V in 5 wt% NH₄F +

1% H₂O in Ethylene Glycol (EG). After electrochemical anodization, the as-deposited nanotubes were cleaned by one of cleaning approach. For the first approach (A1), the sample were sonicate in deionized water (DI), and air dried, the second approach (A2), the sample were sonicate in acetone and air dried while the third approach (A3), the sample were sonicate and Nitrogen dried. After cleaning the nanotubes were annealed at 400 °C in argon atmosphere to induce anatase phase. The film morphology of the nanotubes was characterized using field emission scanning electron microscope (FESEM) and crystal structure was studied using X-ray diffraction (XRD). The photocatalytic activity of TiO₂ nanotubes were evaluated by the degradation of methyl orange under UV irradiation. The concentration of methyl orange solution after degradation process was analyzed using UV-Spectrometry.

RESULTS AND DISCUSSION

Fig. 1. shows the FESEM images of TiO₂ nanotubes obtained in the anodization of 0.03, 0.05 and 0.1 mm thick Ti foils in electrolytes containing 5 wt% NH₄F and 1 % H₂O in EG at 60V. The diameter of the nanotubes, as shown in Figure 1a -1c is approximately 100 nm. From 0.03 – 0.1 mm thick Ti foil, 0.03 mm foil sample could be completely anodized resulting in 22 μm nanotubes arrays separated by thin barrier layer. Nanotubes of 20 μm length were obtained from a 0.05 mm Ti foil while anodizing 0.1 mm foil, the maximum individual nanotube array length obtained was 18 μm .

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The formation of the nanotube arrays is the result of three simultaneously occurring process; (1) field-assisted oxidation of Ti metal to form TiO_2 , (2) field-assisted dissolution of Ti metal ions in the electrolyte and (3) chemical dissolution of Ti and TiO_2 in the presence of hydrogen and fluoride ions [15]. When a voltage is applied, due to the high electric field [16], positive ions, Ti^{4+} move outward from the anode while negative ions (O^{2-} , OH^- , F^-) are driven inward into the thin oxide layer to reach anode. The field-assisted rate at which the Ti – TiO_2 interface moves to thin Ti foil is retarded which allows the formation of thinner barrier layer, hence accelerate the mobility of negative ions and improved the dissolution in the vertical direction into the bulk Ti, thus allowing the formation of long nanotubes. Using thick Ti foil, the nanotube layers were limited by the availability of the negative ions. This finding strongly suggest that to achieve long nanotube layers using thick Ti foil requires increasing concentration of NH_4F and H_2O .

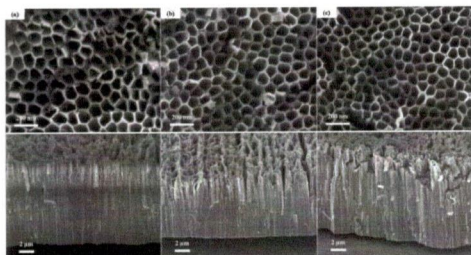


Fig. 1. FESEM images of (a) 0.03 mm, (b) 0.05 mm and (c) 0.1 mm Ti foil anodized in 5 wt% NH_4F + 1 % H_2O in EG at 60 V.

The corresponding XRD patterns of the 0.03, 0.05 and 0.1 mm thick Ti foil annealed at 400 °C in argon atmosphere are shown in Fig. 2. The intensity of the anatase peak is increasing with thicker Ti foil, indicating that the TiO_2 nanotubes formed on 0.1 mm substrate is highly crystallized. Higher degree of crystallinity will improved the photocatalytic property of TiO_2 nanotubes.

Cleaning the Ti foil after anodization is necessary in revealing the TiO_2 nanotubes structure formed on the Ti surface. The purpose of cleaning process is to remove the residual electrolyte on the Ti foil surface and to reveal the microstructure of TiO_2 nanotubes. Generally, broken nanotubes and other debris were formed on the surface of nanotube arrays and could be removed by proper washing technique [17]. The FESEM images of TiO_2 nanotubes formed

on 0.1 mm foil with different cleaning method are shown in Fig. 3.

From the figure it can be seen that the morphological disorder in the film are similar for sample A1 and A2. However there are reduced presence of bundle nanotubes and the associated cracks for sample A2 compared to A1. Zhu et al, 2007 [18] suggesting that the observed deformation is caused by the NT lateral deflection resulting from the action of capillary forces between adjacent nanotubes during evaporative drying of the wetted films. There is no evident of bundles in the FESEM image of sample A3. It is suggested that in the absence of surface tension, clean and nice surface of nanotubes could be obtained.

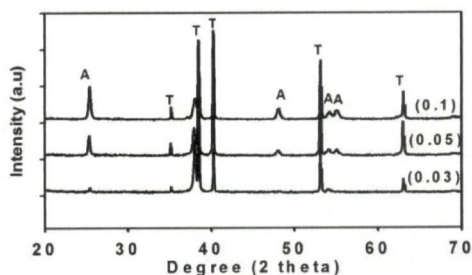


Fig. 2. XRD pattern of Ti anodized in 5 wt% NH_4F + 1 % H_2O in EG at 60 V and annealed at 400 °C in argon atmosphere.

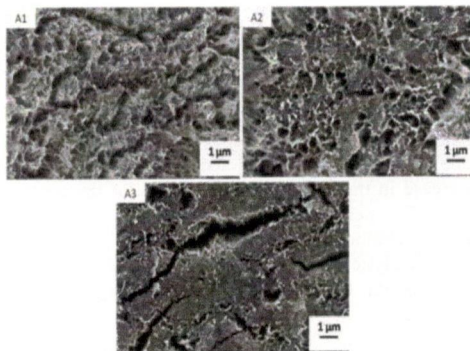


Fig. 3. FESEM images of as-anodized TiO_2 nanotubes cleaned in different cleaning agent, (a) A1, (b) A2 and (c) A3

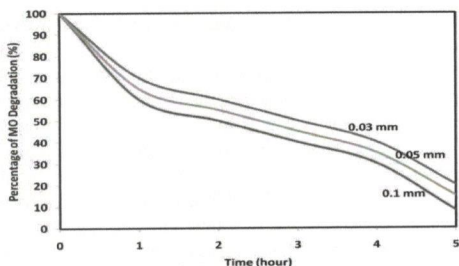


Fig. 4. Percentage of MO degradation using TiO₂ nanotubes formed on different thickness of Ti substrate

The photocatalytic activity of the TiO₂ nanotubes was evaluated by photodegradation of methyl orange aqueous solution after 5 hours UV irradiation. The effect of foil thickness on the degradation of methyl orange was carried out and the result is shown in Fig. 4. It can be clearly observed that nanotubes formed on 0.1 mm Ti foil showed excellent degradation as compared to other samples. It may understand that cleaned surface and high degree of crystallinity favor increasing photocatalytic activity because more reactant is absorbed inside the nanotubes.

CONCLUSION

The effect of substrate thickness and cleaning agents on the morphology of TiO₂ nanotubes formed in EG was successfully investigated. The optimum individual nanotube arrays length (22 μ m) was obtained by anodization of 0.03 mm Ti foil. The sample cleaned in acetone sonication and N₂ dried is the best way to achieved clean surface with no evidence of bundles nanotubes. The photodegradation efficiency increases with the increase in the degree of crystallinity of the anatase phase. The percentage of MO concentration remained after photodegradation was ~10 %. The photocatalytic efficiency of TiO₂ nanotubes strongly depends on the surface area and the degree of crystallinity.

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