

Preparation and Characterization of Nanostructured TiO₂ via Electrochemical Anodization in Aqueous Ammonium Fluoride

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Abstract: Electrochemical anodization of titanium (Ti) in acidic fluorinated electrolyte has emerged as a simple and straightforward method to synthesize TiO₂ coating on Ti substrates directly. In this study, attempt was made to perform the anodic oxidation of Ti foil in a standard two-electrode bath containing relatively mild electrolyte, NH₄F at various potentials for 1 hour. The resulting TiO₂ films were characterized with X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and linear sweep photovoltammetry. XRD analysis revealed the amorphous nature of the as-anodized samples which crystallize after calcination in open air atmosphere at 500 °C for 2 hours. TiO₂ films synthesized via anodization on polished Ti substrate demonstrated pure anatase phase only whereas anodization of etched Ti foil with HNO₃ showed a mixture of anatase and rutile phase. Different morphologies of TiO₂ could be obtained depending on the applied voltage used. Both as-anodized and calcined TiO₂ films showed photocurrent response when illuminated from 300 W halogen lamp with that synthesized via anodization of etched Ti foil exhibited relatively higher photocurrent than the other samples, demonstrating the important of surface treatment of Ti on the photoelectrochemical response of TiO₂ film.

Keywords: nanostructured, titanium dioxide, morphology, anodic oxidation

Introduction

One dimensional nanostructured TiO₂ such as nanowires, nanorods and nanotubes have attracted much interest due to their large surface area in a small geometrical area and fewer interfacial grain boundaries which can assist in promoting charge transport. As such, it has great potential applications in gas sensing, water splitting, photoelectrocatalysis, photovoltaic cell and other fields [1-4]. Recent developed methods for fabricating nanotubular TiO₂ arrays were the assisted template method, hydrothermal treatment and electrochemical anodization. Although hydrothermal method has emerged as powerful strategy for fabrication of TiO₂ nanomaterials, a very highly concentrated alkaline solution and long reaction time is needed during the synthesis process [5]. The template method, on the other hand, has been demonstrated to be effective in synthesizing nanostructured TiO₂ in which the TiO₂ nanoparticles were deposited within the preformed template such as anodic aluminium oxide by sol-gel or electrodeposition method [6]. However, these methods have some drawbacks such as complicated fabrication process and difficulty in removing the preformed template after the synthetic process. Therefore, a relatively simple, cheap and straightforward technique for fabricating highly ordered nanotubular TiO₂ arrays is vital for various applications. In this respect, electrochemical anodization method appeared to be very promising as nanotubular TiO₂ can be directly grown from Ti

metal at room temperature which strengthens the adhesion of nanotubular TiO₂ to the substrate. Most importantly, a required specific nanoarchitecture (structural and morphological features) of the attained TiO₂ can be controlled precisely by varying the electrochemical parameters such as applied voltage and bath temperature [7]. Even though potentiostatic anodization of Ti sheet has been successfully used to fabricate nanotubular TiO₂, most of the studies employed corrosive and toxic hydrofluoric acid as electrolyte in synthesizing process [8,9]. In view of this, development of environmental benign or 'green' electrolyte is crucial for industrial scale applications. Therefore, in this study, attempt was made to perform anodic oxidation in a relatively mild electrolyte such as NH₄F at various potentials. In addition, no published study on the effect of surface pretreatment on Ti foils prior to anodization has on the properties of TiO₂ been reported. Therefore, this article discusses the effect of surface pretreatment of Ti foils on the phase formation and photocurrent response of the resulting TiO₂ films.

Experimental section

Chemicals

Sheets of Ti foil (thickness 250 µm, 99.5% purity) were purchased from Alfa Aesar, USA. NH₄F (Fluka) and sulfuric acid, H₂SO₄ (Fisher Scientific, 96%) were obtained as analytical grade reagents and used without further purification. Deionized water

(Millipore Alpha Q system, 18.2 M Ω cm) was used throughout the experiments.

Preparation of TiO₂ films

A large piece of Ti foil was first cut into small rectangle of size 20 mm \times 15 mm. Two different surfaces pretreatment were applied to the Ti foil before anodization, namely etching and polishing treatment. For etching pretreatment, the Ti plates were degreased by ultrasonating in acetone, isopropanol and deionized (DI) water, for 15 minutes each followed by chemically etched in 6 M of HNO₃ for 10 minutes to form a fresh smooth surface. For polishing pretreatment, the Ti plates were polished with silicon carbide paper before sonicating in acetone and isopropanol. Then, the Ti foils were rinsed with excess DI water followed by drying in a stream of nitrogen. Electrochemical anodization of titanium was carried out in a dual-electrode chamber, in which the clean titanium foil with an area of 10 \times 15 mm² immersed in the electrolyte was used as the working electrode and high density graphite electrode as the counter electrode. The distance between the two electrodes was maintained at 2 cm. A DC power supply (Phillips Harris, England) was used to provide different electrical potentials between the two electrodes during anodic oxidation process. All experiments were conducted at room temperature in electrolyte contained 0.1 M NH₄F and 0.5 M H₂SO₄. After anodization, the resulting films were immediately rinsed with DI water and subsequently dried in nitrogen stream. The as-anodized films were amorphous initially. To induce crystallinity, the films were annealed at 500 °C in open air atmosphere in a Thermolyne 21100 furnace for 2 hours with a heating rate of 2 °C/minutes.

Characterization

The phase composition and crystalline structure of TiO₂ films were determined by X-ray diffraction (XRD, Philips PM 1730) using a diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) over the 2 θ range of 20-60°. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. Surface morphology of the as-anodized and calcined films was acquired by a field-emission electron microscope (Zeiss SUPRA 40VP, Germany). Photocurrent measurements were performed in 10 ppm methyl orange solution using a conventional three-electrode cell equipped with a flat quartz window. The synthesized TiO₂ film was employed as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The photocurrent was measured with a scanning potentiostat (μ -III AUTOLAB) under chopped irradiation from 120 V 300 W halogen lamp during a

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Results and discussion

Appearance of resulting TiO₂ film

The as-received Ti foil appeared to be dull due to the present of a thin native oxide layer. Nevertheless, the foil has a shining metallic appearance after polishing or etching in HNO₃ solution. During anodic oxidation, the surface of the electrode changed from shining to dark purple, blue and yellow colors with increasing anodization potentials. This is due to the changes in the thickness of the TiO₂ films which cause an interference phenomenon between the reflected beam from the oxide surface and that of the interface of the oxide and the titanium substrates [10]. It was noted that the colors of the as-anodized surfaces appeared to be vivid for samples prepared via etching pretreatment indicating smooth surface obtained under the anodization condition. In contrast, the colors of TiO₂ films synthesized via anodization on polished Ti foils were blurred. This result was expected as the surface of Ti foil becomes rough after polishing pretreatment. Fig. 1(a) and 1(b) depict the FESEM images of Ti foil which have been chemically etched or mechanically polished prior to anodization, indicating a distinct different of surface morphology resulted from different surface pretreatment of Ti foil.

Surface morphology of TiO₂ film

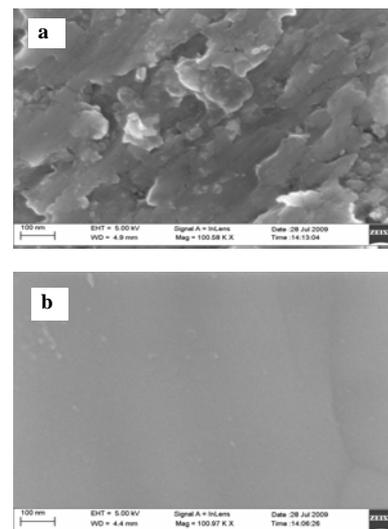


Fig. 1: FESEM images of bare Ti foil which has been a) mechanically polished b) chemically etched prior to anodization

FESEM images were also taken from a series of samples prepared using different anodization voltages as shown in Fig. 2. It can be seen that nanoporous structure is formed when potentials 10 to 20 V were applied (Fig. 2(a) to (c)). The average pores diameter for samples anodized at 10, 15 and 20 V was 19, 34 and 17 nm, respectively. It is believed that the fluoride ions induced pitting of the oxide layer on Ti substrate by forming soluble fluoro complexes and anodic bias permanently provides new oxide growth. After establishing a steady state between oxide formation and dissolution, an

equilibrium situation can be achieved leading to the formation of nanoporous layer [7].

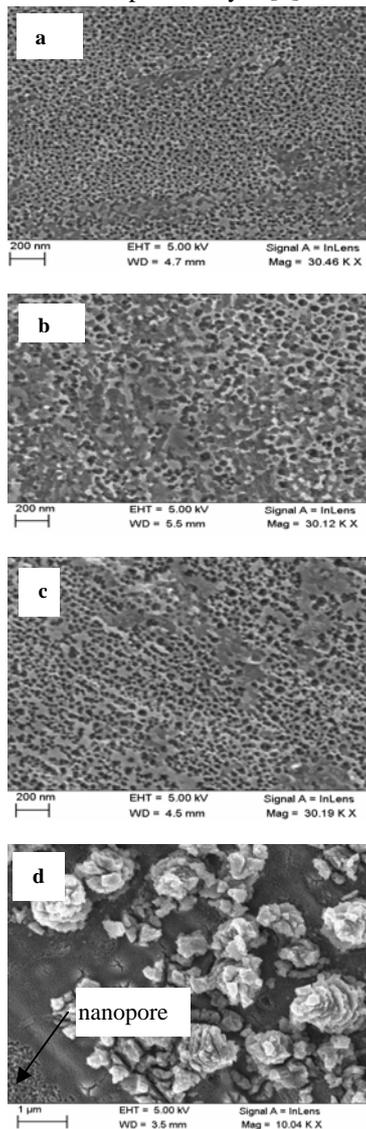


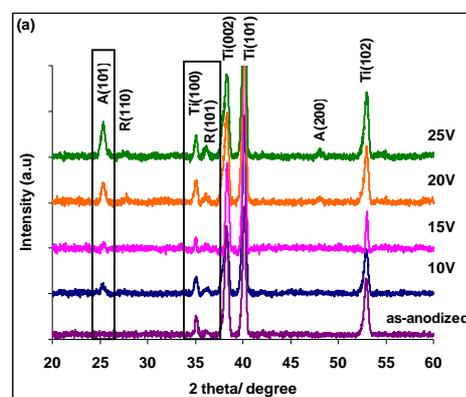
Fig. 2: FESEM images of TiO₂ thin films produced with anodization potentials of (a) 10 V, (b) 15 V (c) 20 V and (d) 25 V

Surface pretreatment (polishing or etching) on Ti prior to anodization has no influence on the TiO₂ nanopore morphology. However, an entire different morphology observed when electrochemical oxidation was performed at much higher voltage of 25 V. At this voltage, there are many irregular rose-like clusters grown from the surface of TiO₂, which consist of submicron TiO₂ particles. Careful inspection of the FESEM micrograph reveals the formation of nanopore besides the rose-like clusters. The effect of anodizing voltage on morphology has been studied by many groups of researchers [9,11,12]. For instance, a study conducted by Gong et al. using aqueous HF solution showed that the morphology of TiO₂ films change from porous to particulate, then to hollow, cylindrical tube-like features, when

anodization voltage increased from 3 to 20 V [12]. However, such morphologies changes are not being observed in our study. Even though similar irregular rose-like nodules structure has been reported previously by Si et al. using aqueous HF/chromic acid solution, however, they only observed such morphology at much higher anodization voltage of 40V [10]. To date, the exact formation mechanism for this irregular rose-like morphology is still unclear. It may be attributed to a combination of oxide expansion and etching speed variation at different position during anodic oxidation process. Furthermore, different growth rate at different position might generate mechanic stress within the oxide layer. This phenomenon in return results in inhomogeneous etching by fluoride ions present in the electrolyte and thus induces formation of non-flat oxide layer [10]. No signal of fluorine was observed after heat treatment at 500 °C for 2 hours, suggesting that the fluorine impurities could be easily removed by calcination. This observation is in good agreement with the literature [13].

XRD analysis of TiO₂ films

The crystalline form of TiO₂ films prepared by electrochemical anodization at different anodization potential was investigated by XRD. Fig. 3 shows the XRD patterns of the as-anodized and calcined samples at various potentials. Regardless of the anodization voltage, all the as-anodized samples demonstrated only diffraction peaks of Ti at 35.09° (100), 38.42° (002), 40.17° (101) and 53.01° (102) which were well indexed to JCPDS No. 44-1294, indicating the nanoporous TiO₂ maintained an amorphous structure. This means that low voltage anodization (25 V in this study) did not lead to TiO₂ crystallization. Si et al. only observed anatase phase in as-prepared TiO₂ film using anodization voltage of 60 V in very acidic and oxidizing HF/chromic acid solution [10]. However, in this study, the amorphous regions of the as-anodized TiO₂ on etched Ti foils were gradually crystallized to form a mixture of anatase (JCPDS No. 21-1272) and rutile phases (JCPDS No. 21-1276) after calcination at 500 °C as shown in Fig. 3 (a).



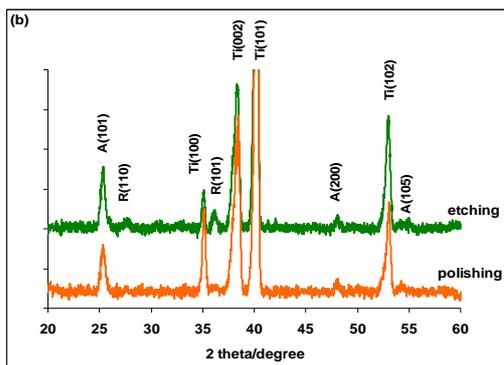


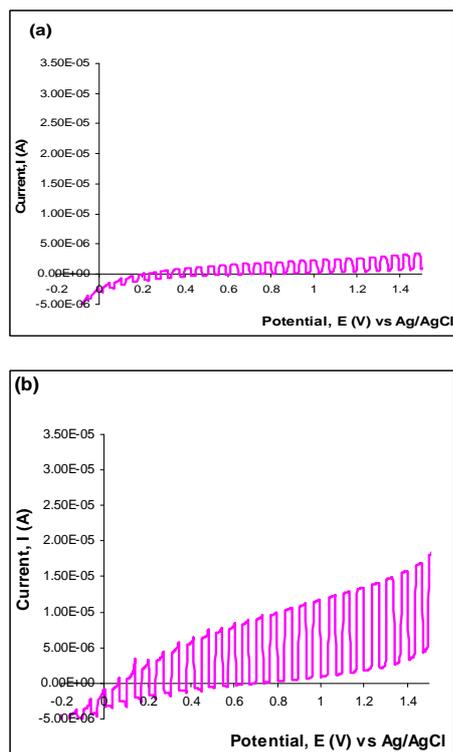
Fig. 3: (a) XRD patterns of TiO₂ film synthesized via anodization on chemically etched Ti foils at various potentials and (b) comparison of XRD patterns of TiO₂ prepared on Ti foil with different surface pretreatment prior anodization

The TiO₂ films possessed characteristic peaks at 25.4° (101), 27.6° (110), 36.2° (101), and 48.2° (200) respectively. In accord to the previous findings, thermal treatment at this temperature did not alter or disrupt the TiO₂ nanopore morphology [4]. The peak intensity of anatase phase became stronger as the anodization voltage increased from 10 to 25 V. No peak shift is observed as a function of anodization voltage. It is worth mentioning here that different surface pretreatment applied to Ti foil prior to anodization results in different phase obtained as shown in Fig. 3(b). From our observation, a mix phase of anatase and rutile exist for sample prepared via etching pretreatment whereas only pure anatase (101) and (200) phase was observed when the Ti foil was mechanically polished prior to anodization. This observation, however, has not been reported previously. It is therefore believed that the surface roughness play a vital role in phase formation of TiO₂.

Photoelectrochemical response of TiO₂ films

The photoelectrochemical response of TiO₂ thin films were recorded by intermittently irradiating the electrodes from halogen lamp using linear sweep photovoltammetry. This technique consists of slow potential ramp coupled with interrupted irradiation of the film surface periodically. In this respect, both the 'dark' and the light induced photocurrent response of TiO₂ films can be evaluated in a single experiment and under identical experimental conditions. As shown in Fig. 4, all as-anodized and calcined samples showed photocurrent response to the illumination condition in which crystallized TiO₂ exhibited enhancement of photocurrent in comparison to the as-anodized samples. This result is expected as the amorphous structure of as-anodized sample implies the presence of a high number of defects (localized states) which act as traps and recombination centers for the photogenerated electrons and holes. Apart from this, it can be observed that the photocurrent increased with increasing anodization voltage, where the

photoresponse from 25 V sample is much higher than that of 10, 15 and 20 V samples. This might be attributed to different surface morphology obtained at different anodization potentials. According to Tacconi et al., the correlation between surface morphology and photoelectrochemical response behavior is "complex" [14]. They have demonstrated that anodization conditions yielding other morphologies apart than nanopore and self-organized nanotubes do result in respectable photoresponse quality. Herein, we have shown here that different morphologies obtained under various anodization potentials do exhibit distinctive photoresponse and hence this could provide simple approach to tailor the photoactivity of porous TiO₂ films. Interestingly, it is observed that TiO₂ films synthesized via anodization on etched Ti foils (Fig. 4(e)) demonstrated relatively higher photocurrent response than that prepared via polishing treatment (Fig. 4(f)). This might attribute to different phases (mixture of anatase and rutile) exist in this sample as revealed by XRD analysis, suggesting the influence of surface pre-treatment on phase formation of TiO₂ by electrochemical method.



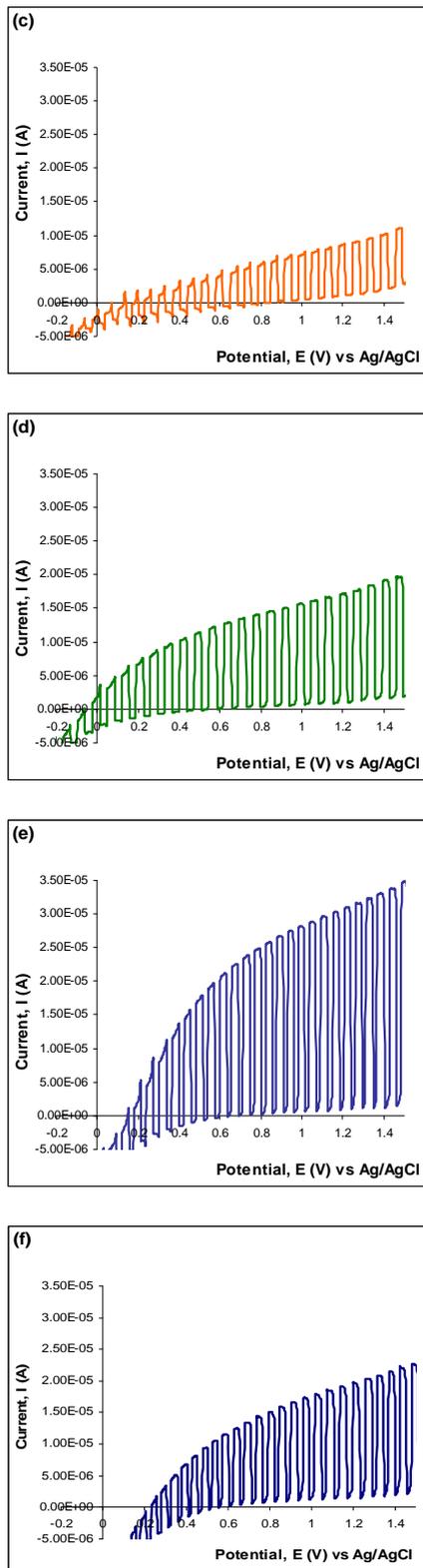


Fig. 4: Photocurrent response of samples prepared via etching pretreatment: (a) as-anodized sample (b) to (e) calcined sample with anodization potentials of 10 V, 15 V, 20 V and 25 V respectively (f) calcined sample prepared via polishing pretreatment and anodized potential of 25 V

Conclusion

Nanoporous TiO₂ films have been successfully fabricated by electrochemical method with aqueous NH₄F as the electrolyte. Surface pretreatment on Ti foil prior to anodization resulted in formation of different phase of TiO₂ which has contributed substantial different in the photocurrent response when illuminated from halogen lamp. The surface morphology was controlled by the anodization potential with irregular rose-like nodules were obtained at 25 V. This method can be used to produce nanostructured TiO₂ films with desired surface morphology for application in various fields such as photocatalysis, hydrogen gas generation, self-cleaning coating and solar energy conversion.

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