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Fabrication of crack-free anodic nanoporous titania and its enhanced photoelectrochemical response

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ABSTRACT

Crack-free nanoporous titania was fabricated with an appropriate post-anodization treatment. Such a nanoporous structure shows enhanced photoelectrochemical response as compared to the conventional nanotubular titania of similar thickness. The enhanced photocatalytic activity is demonstrated through the photo-degradation of methyl orange and antibacterial-drop test, and is thought to result from the more efficient electron–hole separation in the porous structure. Further improvement in the photocatalytic efficiency can be achieved on thicker titania layers fabricated by extended anodization. This kind of nanostructured titania may find its potential applications in bactericidal process, photocatalytic decomposition of organic contamination, and wastewater purification.

1. Introduction

Photocatalytic degradation of organic compound is of great importance to the elimination of hazardous wastes [1]. Semiconducting TiO_2 as a durable photocatalyst has been widely studied for water and air purification [2]. For applications in pollution control, most research work was focused on nanoparticulate films or suspensions [3–6]. The photocatalytic activity of nanoparticulate film is limited by the small surface area, while for the particulate suspension, removal of the catalyst after use is technologically expensive and difficult. TiO_2 nanotube array made by electrochemical anodization was claimed to possess higher catalytic efficiency than the nanoparticulate film does [7,8]. However, there is an intrinsic limit on the photoelectrochemical response of the TiO_2 nanotube array due to its small wall thickness [9].

There have been extensive reports on the synthesis of anodic titania in aqueous or organic electrolytes [10–16] containing fluoride, chloride, or bromide [17–21]. In chloride or bromide solution, due to restricted electrochemical conditions, the anodized titania shows a much faster growth rate with less ordered morphology and less tunable dimensions than it does in fluoride solution. For anodization in aqueous electrolyte with fluoride, the length of nanotubes is determined by two competing factors, i.e., the formation of titania at TiO_2–Ti interface and the dissolution of titania at tube mouth. Due to the high dissolution speed of TiO_2 in acidic environment, the length of nanotubes is normally in the range of several hundred nanometers to a few micrometers. When organic electrolyte is used, the chemical dissolution of TiO_2 is negligible and much longer TiO_2 nanotubes could be obtained simply by the extension of anodization time [10]. However, the top surface of thus obtained TiO_2 was covered by a layer of TiO_2 nanowires, which might reduce the adsorption of organic dye and thus limit the applications in dye-sensitized solar cells or in waste water purification. The attempt to remove such surface debris by ultrasonic cleaning in deionized water is not successful as ultrasonication also results in shattered anodic TiO_2 layer [10]. By adopting a "self templating" method, highly order nanoporous anodic TiO_2 has been synthesized without the unwanted nanowire layer and has showed better photodegradation activity than nanotubular TiO_2 [22]. However, the detailed mechanism of such enhanced photoelectrochemical response was still not very clear. Another unsolved problem for this nanoporous anodic TiO_2 was that surface cracks can be easily produced when the sample is washed with deionized water directly after anodization, as shown in Fig. 1(a). In some occasions the nanostructured TiO_2 even peeled off, as shown in Fig. 1(b). Since a crack-free surface of anodic TiO_2 is crucial for many potential applications, in the present work, we will focus on the fabrication of crack-free anodic nanoporous TiO_2 films.

It has been reported that a small amount of F^- was always found in the as-anodized TiO_2 [23]. When it was washed with deionized

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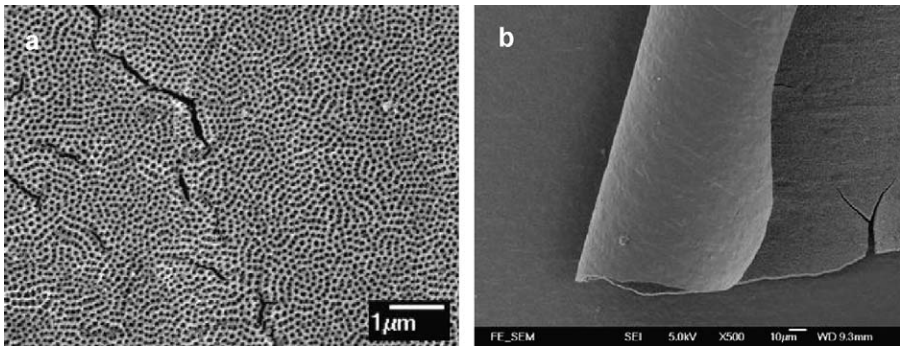

Fig. 1. FSEM images showing (a) cracks in nanoporous structure and (b) peeling off of TiO_2 film for anodic samples without appropriate post-anodization treatment.

water right after anodization, the residual F^- ions might hydrolyze to generate HF and lead to the dissolution of TiO_2. Such etching process would result in surface cracks and even peeling off of the film. The dissolution of TiO_2 in F^- containing electrolyte is highly dependent on the pH value of the solution, with acidic environment as the requisite [13]. There is no chemical etching for TiO_2 in F^- containing non-aqueous solution. Therefore, a very straightforward method to produce crack-free anodic TiO_2 is the post-anodization treatment in certain organic solvent which has high solubility of F^- ions to remove the residual F^- ions. In this paper, we will describe how crack-free nanoporous TiO_2 is obtained through a simple process. The photoelectrochemical response of the obtained nanoporous TiO_2 will be examined and compared with the conventional tubular TiO_2. An improved photocatalytic activity in nanoporous TiO_2 is demonstrated through the decomposition of methyl orange (MO) and antibacterial study. The detailed mechanism behind this enhancement is investigated. This kind of nanostructured TiO_2 may find its important applications not only in bactericidal process, wastewater purification and photocatalytic decomposition of organic contamination, but also in photocleavage of water and dye-sensitized solar cells.

2. Experimental

The detailed methodology of fabricating highly ordered anodic nanoporous titania has been published elsewhere [22]. Hence only the key points of the anodization process are summarized here. Titanium foils (0.25 mm thickness, 99.6% purity, Strem Chemicals, USA) were degreased ultrasonically in acetone and ethanol for 10 min, respectively, followed by rinsing with deionized water and drying in hot air. The anodization voltage was set at 50 V and the electrolyte was ethylene glycol with the addition of 0.25 wt.% NH_4F. No water was added in order to suppress the chemical dissolution of TiO_2 in the electrolyte. The lack of chemical dissolution is crucial in obtaining the porous structure. In our previous work, a three-step anodization was carried out to achieve the perfectly ordered structure [22]. In this study, the aim is to produce crack-free films. To save time, a two-step anodization process was adopted to produce nanoporous TiO_2. For the first step, the potential was ramped at a rate of 0.5 V/s to 50 V. For the second step, a voltage of 50 V was applied instantaneously at the beginning of anodization. The anodization time was 4 h in the first step. The as-anodized sample was then ultrasonically cleaned in deionized water for 5 min to remove the anodic TiO_2 layer from the titanium substrate. Afterwards, the exposed titanium substrate was subjected to the second anodization for different duration (5 and 100 min, respectively) to create nanoporous TiO_2 layer with different thickness. To achieve crack-free nanoporous structure, the as-grown TiO_2 layer was placed into a methanol bath with the anodized surface facing upward. After 3 days' soaking, the sample was taken out and washed thoroughly with deionized water. For the comparison of the photocatalytic activity, nanotubular TiO_2 was electrochemically anodized in 0.2 wt.% HF aqueous solution. The anodization time and voltage were 30 min and 20 V, respectively.

The morphology of the anodic TiO_2 was examined by field emission scanning electron microscope (FESEM, JEOL JSM-6335F). Both tubular and porous as-anodized TiO_2 were amorphous. They were crystallized to anatase phase after being annealed at 450 °C for 3 h, with a heating rate of 4 °C/min. X-ray diffraction (XRD, Philips PW3020) analysis was carried out to investigate the crystal structure. The electrochemical measurements were performed in a standard three-electrode configuration, with platinum the counter electrode and saturated calomel electrode (SCE) the reference. The photocurrent was measured using an electrochemical workstation (CHI 660B) with a UV lamp (central wavelength: 369 nm, irradiation intensity: 6 W/m^2) as the light resource and 0.1 M H_2SO_4 as the electrolyte. The sweep rate of the potential was 0.05 V/s. The photo-decomposition of MO solution (12 mg L^{-1}) was carried out under the illumination of the same UV lamp as used in the photocurrent measurement. The nanostructured TiO_2 was under normal incidence with a distance of 4 cm to the UV source. Titanium foil without anodization was used as a blank. The change of MO concentration with the radiation time was monitored by measuring the absorbance of MO solution at a wavelength of 464 nm using a UV–vis spectrophotometer (Shimadzu, UV-2550). The bactericidal activity against *Staphylococcus aureus* (SA) was studied using the antibacterial-drop test [24]. SA was cultivated in Luria-Bertani (LB) medium at 37 °C for 24 h and diluted to the concentration around 10^7 colony forming units per milliliter (CFU ml^{-1}). Then 100 μl bacteria containing solution was added dropwise onto the surface of anodic TiO_2 with an area of 6 cm^2. The test was carried out at room temperature for 0.5, 1 and 2 h. After each time period the bacteria containing drops were washed away from the samples using 20 ml double distilled water. Then 40 μl of each bacteria suspension was dispersed on the agar plate. The number of surviving bacteria was counted after incubation for 24 h at 37 °C.

3. Results and discussion

3.1. Morphology and microstructure characterization

Fig. 2 shows the SEM images of anodic TiO_2 after the post-anodization treatment (3 days' soaking in methanol and thorough washing with deionized water). The diameter of pores is around 60 nm and the interpore distance ranges from 130 to 150 nm. Nanoporous structure can be clearly seen and is different from the conventional tubular morphology [10–15,17]. Such regular nanostructure is very similar to that of the anodic aluminium or titanium aluminide [25–27], and is the result of preferred pore nucleation in self-templated titanium substrate [22]. The cross-section image