Effect of calcination temperature on the morphology and surface properties of TiO$_2$ nanotube arrays

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ABSTRACT

Well-ordered TiO$_2$ nanotube arrays were prepared by electrochemical anodization of titanium in aqueous electrolyte solution of H$_3$PO$_4$ + NH$_4$F at a constant voltage of 20 V for 3 h, followed by calcined at various temperatures. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS) and Photoluminescence (PL) were used to characterize the samples. The results showed that the as-prepared nanotube arrays before being calcined were amorphous and could transform to anatase phase at a heat treatment temperature higher than 400 °C. As the calcination temperatures increased, crystallization of anatase phase enhanced and rutile phase appeared at 600 °C. However, further increasing the calcination temperature would cause the collapse of nanotube arrays. PL intensity of the nanotube arrays annealed at 500 °C was the lowest, which was probably ascribed to better crystallization together with fewer surface defects of the nanotube arrays.

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1. Introduction

TiO$_2$ has been regarded as the most prominent photocatalyst by virtue of its biological and chemical inertness, strong oxidizing power and long-term stability against photocorrosion and chemical corrosion [1–3]. However, as photocatalyst, its efficiency is still low because of high recombination rate of photo-generated electrons and holes [4,5]. In recent years, a increasing attention has been given to fabricate highly ordered TiO$_2$ nanotube arrays, because it is expected that an remarkably enhanced photocatalytic activity can be achieved in comparison with other existence forms of TiO$_2$, which is closely related to the higher specific surface area and superior physical topology of nanotube arrays. Up to now, many paths have been developed to prepare TiO$_2$ nanotube arrays, such as sol–gel template method [6], liquid phase deposition template route [7] and electrochemical anodization approach [8–10]. Among these methods, direct electrochemical anodization method is considered to be the most ideal way due to the fact that the process is very simple and the thickness and morphology of such a nanotubular TiO$_2$ film can be easily controlled by tailoring

the anodization conditions [11,12]. Additionally, TiO$_2$ nanotube arrays with Ti substrate have good mechanical adhesion strength [13], which is beneficial to the electrochemical catalysis or photo-electrochemical catalysis owing to the excellent electronic conductivity of Ti. To date, most of the researches have been focused on the preparation and photocatalytic activity of TiO$_2$ nanotube arrays [14–16]. However, very little attention has been given to study on effect of post-thermal treatment temperatures on microstructure and surface properties of TiO$_2$ nanotube arrays, especially applying Photoluminescence (PL) measurement to forecast the photocatalytic performance of TiO$_2$ nanotube arrays. In this paper, therefore, TiO$_2$ nanotube arrays were prepared by anodization of Ti in aqueous electrolyte solution of NH$_4$F containing H$_3$PO$_4$, followed by calcined at various temperatures and characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS) and PL.

2. Experimental

2.1. Fabrication of TiO$_2$ nanotube arrays

The preparation procedure of TiO$_2$ nanotube arrays was similar to the reference reported by Allam and Grimes [17]. All reagents in the experiments were analytical and were used as received. All the solutions were prepared with distilled water. Titanium foils of high

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purity (99.6%, thickness 0.5 mm) with a size of 30 mm × 20 mm were used as starting materials. Prior to anodization, the foils were mechanically polished to a mirror image with No. 500 and 1200 silicon carbide abrasive paper successively, followed by rinsed with distilled water and dried in ambient air. After that, an electrically insulated copper wire was attached on the backside of Ti foil using carbon electric conductive adhesive, then thoroughly sealed with a mixture of rosin and paraffin except for a working area of 600 mm^2 exposed to the electrolyte solution. Finally, the electrode was chemically etched by soaking in a mixture of HF and HNO$_3$ (HF:HNO$_3$:H$_2$O = 1:4:5 in volume) for 20 s to eliminate the flaws resulting from polishing process. So far, a working electrode was obtained.

An anodization process was conducted in a conventional two-electrode configuration with magnetic stirring, in which the Ti foil was used as the anode and a Ni sheet with a size of 80 mm × 30 mm was served as the cathode. The distance between the two electrodes was 40 mm for all experiments. 0.2 M NH$_4$F containing 2.0 M H$_3$PO$_4$ was used as electrolyte solution. The anodization course was conducted at a constant voltage of 20 V for 3 h with a DC power supply under room temperature. After anodization, the samples were taken out from the electrolyte solution immediately and rinsed with a mass of distilled water, then dried at ambient atmosphere. Subsequently, the as-synthe-sized nanotube arrays were calcined at 300, 400, 500, 600, 700 °C for 2 h with a heating rate of 5 °C/min in air, respectively.

2.2. Characterization of as-formed and annealed TiO$_2$ nanotube arrays

The morphology of the samples was observed using an Inspect F FE-SEM (FEI Corporation). It was note that the cross-sectional images were obtained by observing mechanically fractured samples. The phase purity and crystal structure of the obtained products were examined by XRD using a Philip X' Pert PRO diffractometer equipped with Cu K_α radiation in the 2θ range 20–80°, employing a step size of 0.03°. The accelerating voltage was set at 40 kV with 40 mA flux. XPS were performed with a Kratos XSAM-800 spectrometer using Al K_α (1486.6 eV) X-ray source at 12 kV and 15 mA, and the analytical instrument was corrected by standard samples of Au and Ag. All the binding energies were referenced to the C 1 s peak at 284.8 eV of the surface adventitious carbon. PL measurements were conducted at room temperature on an F-7000 FL spectrophotometer using a 300 nm excitation light.

3. Results and discussion

Fig. 1 shows the XRD patterns of the nanotube arrays without and with calcination at 300, 400, 500, 600, 700 °C for 2 h, respectively. Only peaks of Ti were observed for the samples of freshly prepared and calcined at 300 °C, demonstrating the nanotube arrays were amorphous at a heat treatment temperature lower than 300 °C. However, at 400 °C, some distinct peaks occurred except for the peaks of Ti, which were well indexed to the standard anatase phase (JCPDS No. 21-1272), suggesting the phase transformation temperature from amorphous to anatase was ca. 400 °C. At 500 °C, the peak intensity of anatase phase became stronger and the width of the peaks became narrower. As the temperature increased to 600 °C, a minor but discernible peak at 27.45° appeared, which was assigned to rutile phase (JCPDS No. 21-1276). Further increasing the temperature up to 700 °C, rutile and anatase phases co-existed, in which the rutile phase was predominant. The phase content could be calculated from the integrated intensities of anatase (101), rutile (110) and brookite phases according to the methods previously reported by Zhang and Banfield. [18]. The contents of rutile phase in the samples calcined
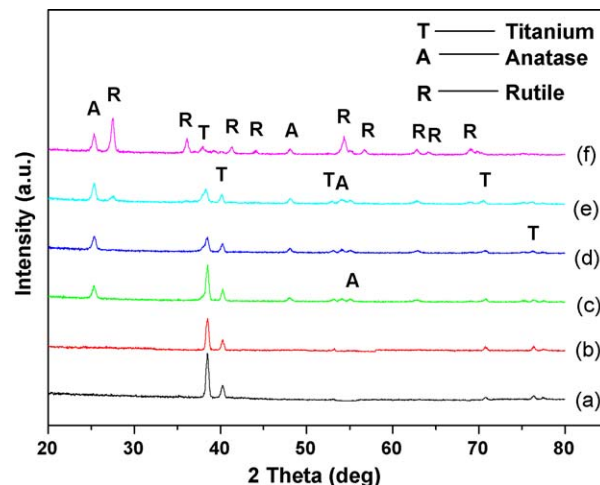

Fig. 1. XRD patterns of the freshly prepared and annealed nanotube arrays: (a) freshly prepared, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f)700 °C.

at 600 and 700 °C were 19.5 and 68.5%, respectively. In comparison with samples calcined at other temperatures, it was note that the peak intensity of Ti substrate was negligible at 700 °C, implying that there probably occurred a phase transformation directly originated from Ti to rutile.

The FE-SEM images of the nanotube arrays without and with calcination at various temperatures are shown in Fig. 2. For the freshly prepared sample, it was apparent that the whole surface was covered by uniform and discrete pores from Fig. 2(a1). As can be seen from the cross-sectional view (Fig. 2(a2)), the pores exhibited tubular characteristic in the direction vertical to Ti substrate, suggesting formation of ordered nanotube arrays. The average pore size was ca. 50 nm, and thickness of tube wall and length of the nanotube arrays were about 55 and 530 nm, respectively. As for the samples calcined at 400, 500 and 600 °C, no obvious changes were discerned from Fig. 2(b)–(d), in which all maintained well-ordered tubular structure. This indicated that the nanotube arrays had an excellent thermal stability. It was remarkable that nanotube arrays after being calcined seemingly had a better ordered structure than that of without calcination, which was probably attributed to the removal of residual such as F$^-$ or other volatile impurities on the surface or in the channels of the nanotube arrays during heat treatment process. Furthermore, pore size of the nanotube arrays after calcination was 95 nm, being much larger than that of before calcination, which was not reported elsewhere previously [19,20]. It might be ascribed to the shrinkage of the tube wall during the thermal process, resulting in tube thickness decreased from about 55 to 30 nm. As the annealing temperature increased up to 700 °C, there still existed some pores on the surface (Fig. 2(e)). However, large parts of the surface was covered by solitary island-like aggregates with size range from 60 nm to sub-micro grade, demonstrating that the well-ordered nanotube arrays were destroyed to great extent. This might be responsible for the phase transformation originating from the anatase to rutile and directly from Ti to rutile. Xiao et al. [21] studied the thermal stability of TiO$_2$ nanotube arrays obtained by anodization Ti in NH$_4$F–H$_2$SO$_4$ electrolyte system. They proposed that nanotube arrays stabilized only at a temperature lower than 600 °C. However, the stability of the nanotube arrays in our experiment could be stable at a temperature as high as 600 °C. This stability difference likely resulted from the different preparation conditions. In our experiment, phosphoric acid of high concentration was used, thus, it was no surprised that some amount of PO$_4^{3-}$ could be incorporated into as-prepared nanotube arrays. It was well known that some kinds of anions, such as SO$_4^{2-}$ [22], PO$_4^{3-}$ [23], could retard the phase