

Annealing effects on the compact titania nanotube arrays: Evolution of microstructure and enhanced photoelectric response



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ABSTRACT

Well-aligned titania nanotube arrays (TNAs) fabricated by electrochemical anodization at high voltage of 120 V have shown superior photoelectric properties than those with similar morphology prepared by traditional anodic conditions at low voltage of 60 V. Firmly-structured TNAs with initial oxide layer can be obtained under 120 V for a growth time as short as 40 s. Effects of annealing on the TNAs structure, optical property, and photoelectric property are systematically investigated at different temperatures. It is found that the microstructures, such as crystallinity, grain size, and phase composition, can be optimized by calcination at moderate temperature around 600 °C, under which the desired optical absorption and the optima photoelectric quantum yield are also observed respectively from diffusion reflection spectroscopy and transient photoelectric response analysis. The extreme fast and economic route for synthesizing firmly-structured TNAs at high voltage is promising for exploring 3D electrodes with an optimized structure and enhanced photo-electrochemical performance.

1. Introduction

Highly-ordered TiO₂ nanotube arrays (TNAs) thin film prepared by a simple electrochemical anodization of a titanium substrate has attracted more and more attention due to its one-dimensional carrier pathways for electrons and holes, possessing unique advantages in many applications [1–11]. Structural parameters, such as pore diameter, tube length, wall thickness, and space between neighboring tubes, are solely dependent on the anodic conditions. The tube morphology and structure play an important role in different applications [12,13]. It has been reported that the optimized morphologies of TNAs can be obtained via modifying anodization voltage [14–20], ion concentrations in the electrolyte [3,21–24], and anodization duration [25], etc. Traditionally, longer anodic duration leads to a longer tube length [26–28]. But the long time exposure of TNAs in the electrolyte also led to the enlarged space between the tubes and the thinner tube walls due to the prolonged chemical etching, which increases the risk of tube damage during post-growth processing [28]. In this work, TNAs with narrow separation between adjacent tubes were prepared under a high anodic voltage of 120 V in a short time of tens of seconds. Compared with those obtained under traditional anodic conditions with a lower anodic voltage of 60 V and a longer anodization duration of several

hours, the TNAs obtained at the high voltage display a significant improvement in mechanical strength and photoelectric properties.

Thermal treatment is an important post-growth processing to enhance the photo-electrochemical properties of TNAs because it provides a facile route to control grain size, particle morphology, and microstructures [27,29–36]. Meanwhile, the improved crystalline phase of the TiO₂ nanotubes is also critical for photoelectric performance. Among the anatase, brookite, and rutile phases, the most stable crystalline structures of TNAs are anatase and rutile [28,37]. The rutile phase is widely used in paints and ultraviolet absorbents due to the highest refraction and ultraviolet absorptivity, while the anatase is applied in dye-sensitized solar cells and catalysts due to its chemical and optical activities [38]. It has been reported that the appropriate phase ratio of anatase to rutile in TNAs obtained under appropriate annealing temperature promote their photoelectric performance [28]. However, to our best knowledge, there are few reports on the heat treatment of the TNAs with different structures. Moreover, many reports showed that the normal annealing temperature was 450 °C and the tubular structure would be destroyed as the temperature was further increased [7,14,39]. In this work, the evolution of the morphologies and microstructure of TNAs under heat treatment were studied in detail. The photoelectric properties of the annealed TNAs and their

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relationship with the microstructure were also investigated. The facile and economic synthesis route of firmly-structured TNAs at a high voltage is promising for large-scale production. The appropriate post-growth processing also offers a new opportunity for exploring 3D electrodes with an enhanced photo-electric performance.

2. Experimental sections

2.1. TNAs preparation

Titanium foils (0.1 mm in thickness, 99.6% purity) were degreased prior to anodization by sonicating in acetone, rinsing with alcohol and deionized (DI) water subsequently and drying in nitrogen gas. The cleaned Ti foils were then chemically polished in the solution containing HF, HNO₃, and DI water (1:1:5 volume ratio) for 20 s, and then rinsed and dried successively. The electrochemical setup consists of Interlock potentiostat-galvanostat (IPD-12003SLU) and a classical two-electrode cell with 1.5 cm separation between counter and working electrodes. An area of 1 cm² Ti surface was exposed to an electrolyte which contains 0.4 M NH₄F dissolved in a solution of ethylene glycol and DI water (30:1 volume ratio). The anodization of Ti foil was performed at an applied voltage of 120 V without magnetic stir. Consider that high voltage leads to the high speed of field-assistant oxidation of Ti metal at the interface of barrier layer/Ti substrate, resulting in the quick increasing of electrolyte temperature, which may lead to the uncontrollable growth and ununiform morphology of TNAs. Thus, the temperature of electrolyte was controlled at 10 °C by water bath and the anodized durations were 40, 60, and 80 s, respectively. The as-prepared samples were rinsed with DI water and then dried by high purity nitrogen gas. The samples were referred to as TNA120 series. In order to compare the structural stability and photoelectric response of TNA120 series with those samples prepared by traditional conditions, an TNAs sample was prepared at 60 V for 3 h in the electrolyte which contains 0.27 M NH₄F dissolved in a solution of ethylene glycol and DI water (30:1 volume ratio). This control sample was referred to as TNA60 (3 h). The resulted samples were post annealed in atmosphere at different temperatures for 2 h with a heating rate of 5 °C min⁻¹.

2.2. Characterization

A scanning electron microscope (SEM) Hitachi FE-SEM S4800 was employed for characterizing the morphology of the samples. The crystalline structures of the TNAs were checked by means of X-ray diffraction (XRD, MAC M18XHF) using Cu k_{α} radiation at room temperature. The diffuse reflection absorption spectra (DRS) were measured by a UV-Vis spectrophotometer (ShimadzuUV-265). The photoelectric response of the samples was recorded with an electrochemical workstation (CHI660E). A white light source was utilized as an excitation source (intensity: 100 mW cm⁻²).

3. Results and discussion

3.1. Morphologies of as-synthesized TNAs

Fig. 1 shows the SEM images of the TNAs anodized at 120 V for different times. Due to the remained initial oxide layer, TNA120 (40 s) as shown in Fig. 1(a) displays the smallest pore diameter and no separation can be found on the top surface. One typical inner diameter was marked by red lines and determined to be about 70 nm. Though the pore diameters are not uniform, the cross-sectional image shown in the inset of Fig. 1(a) indicates that the well-aligned nanotubes with a length of several micrometers have been formed in an anodic duration as short as 40 s. In the central area of the top view in Fig. 1(b), one can see that part of the initial oxide layer was chemically etched away from the top of the TNA120 sample after anodization for 60 s. Meanwhile, some of the top tubes started to be separated from each other. The typical inner diameter of the separated nanotubes and the top wall thickness were determined as 80 and 10 nm, respectively, indicating a slight increase of the inner diameter after the diminish of the initial oxide layer. As the anodization time was increased to 80 s, uniformly distributed top tubes become independent from each other [Fig. 1(c)] while no obvious change can be found in the inner diameter and the top wall thickness. Fig. 1(d) shows the surface and cross-sectional images of the sample TNA60 (3 h). It can be obtained that the average inner diameter is about 100 nm and the top wall thickness is about 15 nm indicating that

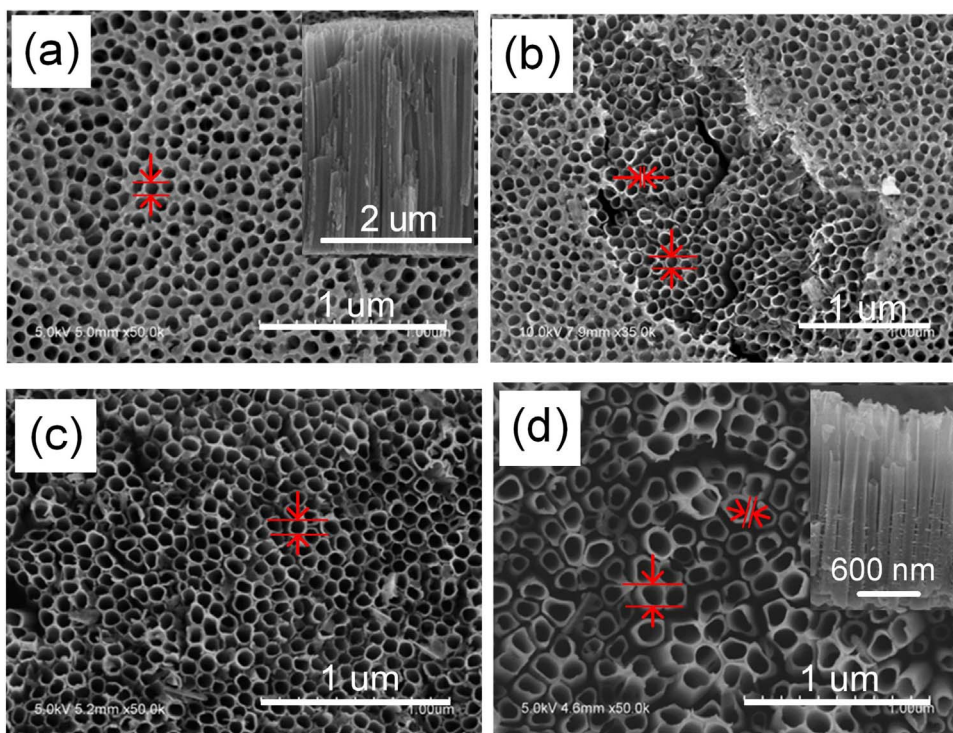


Fig. 1. SEM images of the TNAs anodized at 120 V for 40 s (a), 60 s (b), and 80 s (c), and under 60 V for 3 h (d).

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