

# Fabrication of a patterned TiO<sub>2</sub> nanotube arrays in anodic oxidation

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**Abstract** In general, the fabrication of self-ordered TiO<sub>2</sub> nanotube arrays, under conventional constant-voltage anodization, results in only straight nanotube arrays. In the present work, we report on variation of nanotube morphology by modifying the anodization conditions. This approach offers substantial advantages over conventional anodization processes in terms of the fabrication of flexible dimensional architectures. We could see small variation of the nanotube diameter in the experiments using rocking voltage applied anodization in the ethylene glycol based electrolyte. Applying of abruptly increased voltage induced to separate into two nanotube segments having different diameters. We suggest that these new types of nanotube array architecture will be useful for new base materials for the development of nano-scale devices.

**Keywords** Self-organization · Titanium oxide · Anodic oxidation · Nanoporous

## 1 Introduction

One-dimensional porous array architectures on the nanometer scale have attracted great interest for various

applications, such as electronic, magnetic and optical devices [1, 2]. Self-organized porous structures with high aspect ratios fabricated by the anodization method have shown a large potential in view of designing of the shape of the hole in nanometer dimensions. Anodic alumina oxide films with a hexagonal arrangement of monodisperse nanopores have become a popular template for the synthesis of various functional nanostructures [3]. Porous alumina templates with hexagonal, square, triangular openings, [4] periodically modulated [5] and Y-branched nanochannels [6] by controlling anodization conditions were reported. Recently by following comparable strategies of synthesis, the anodization of titanium foils to directly obtain thin films of vertically aligned TiO<sub>2</sub> nanotube arrays have also acquired the great attention [7, 8]. As compared with alumina template, to date, there are few reports about designing the shape of TiO<sub>2</sub> nanotube array except of tapered conical shape TiO<sub>2</sub> nanotube and multilayer nanotube [9–11].

It is reported that TiO<sub>2</sub> nanotube arrays of various pore sizes, lengths and wall thicknesses can be made by controlling electrochemical conditions [12]. However, the reported results are about arrays composed of straight, pipe-like nanotube. In this work, we introduce a process modification providing means for the fabrication of flexible dimensional architectures and report results for variation of morphology. By controlling the anodization conditions, we tried to induce the variation of nanotube morphology. We expect that altering the shape of the nanotubes can be used to modify their physical and chemical properties.

## 2 Experimental

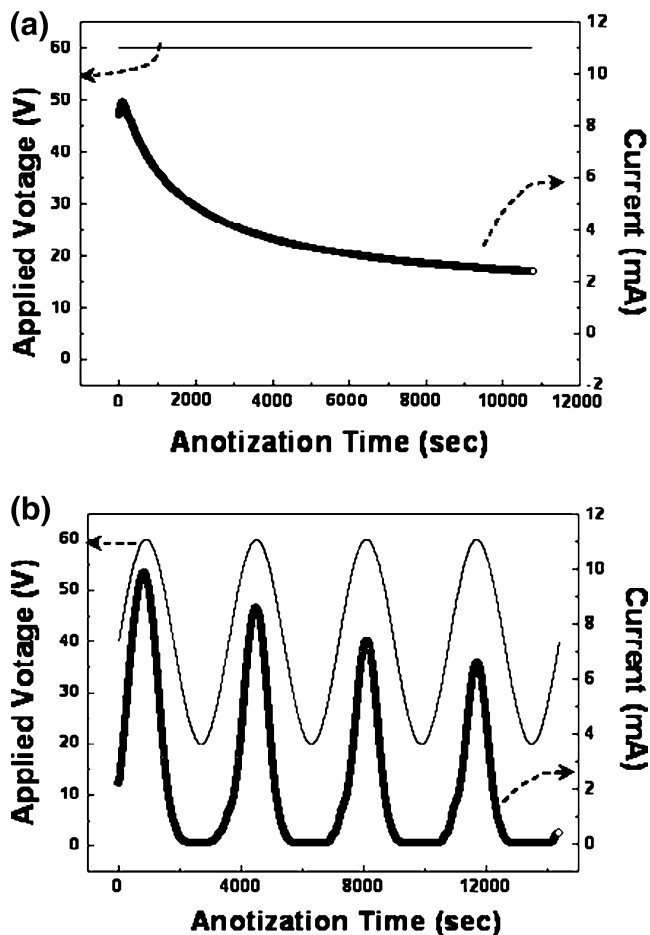
High-purity titanium foil (99.99%, Alfa Aesar, thickness of 0.127 mm) and titanium thin film sputtered on transparent

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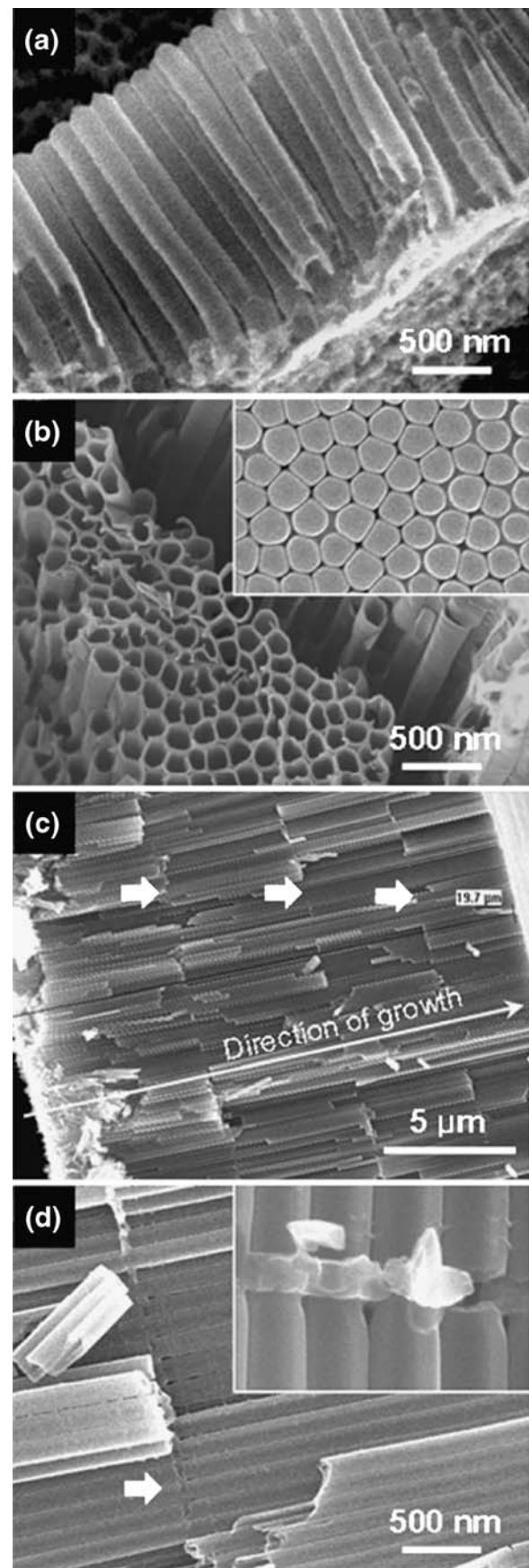
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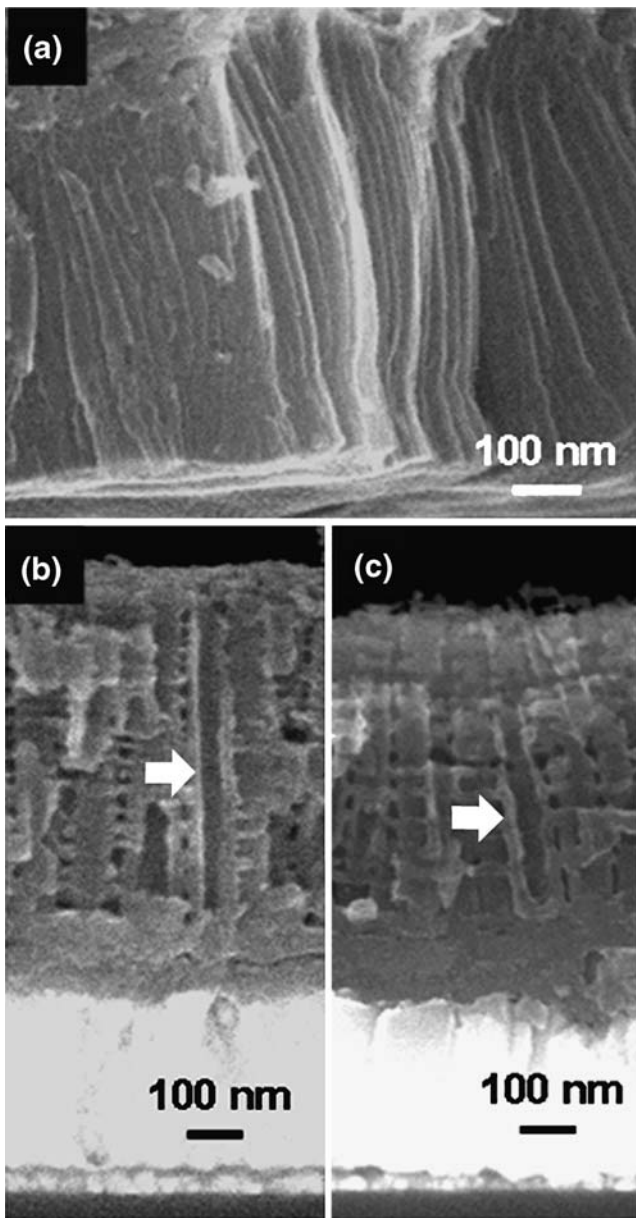


**Fig. 1** Current transient curves during anodization of titanium foil samples in the 0.25 wt%  $\text{NH}_4\text{F}$ +ethylene glycol electrolyte: (a) conventional constant-voltage anodization (60 V), (b) rocking-voltage anodization (sine wave, 20~60 V)

conductive oxide (TCO) coated glass substrate were prepared for anodic oxidation. Bulk titanium foil was cleaned with acetone, isopropanol (2-Propanol), methanol and de-ionized water with ultra sonication for degreasing the surface prior to experiment. Tantalum foil of 0.25 mm thick and  $50 \times 50$  mm size (99.9% purity, Aldrich Chemical Company Inc., Milwaukee, USA) was used as a counterpart electrode. Metal electric wires were attached to two electrodes and sealed by polyester from acid electrolyte. The anodization voltage was applied by a DC power supply (Model XKW600-1.7, Xantrex). The time variable current was monitored using a digital multimeter (Model 34401A, Agilent Technologies, Inc.) interfaced with a computer. Power supply and multimeter were computer-controlled

**Fig. 2** FESEM images of samples anodized in Fig. 1: (a) side-view **b** top-view images of  $\text{TiO}_2$  nanotube fabricated by constant-voltage anodization; the inset of (b) is the image of the nanotube bottom, (c) side-view and (d) enlargement images of nanotube fabricated by rocking-voltage anodization; the *arrows* indicate border sections and magnified image is shown in the inset of (d)

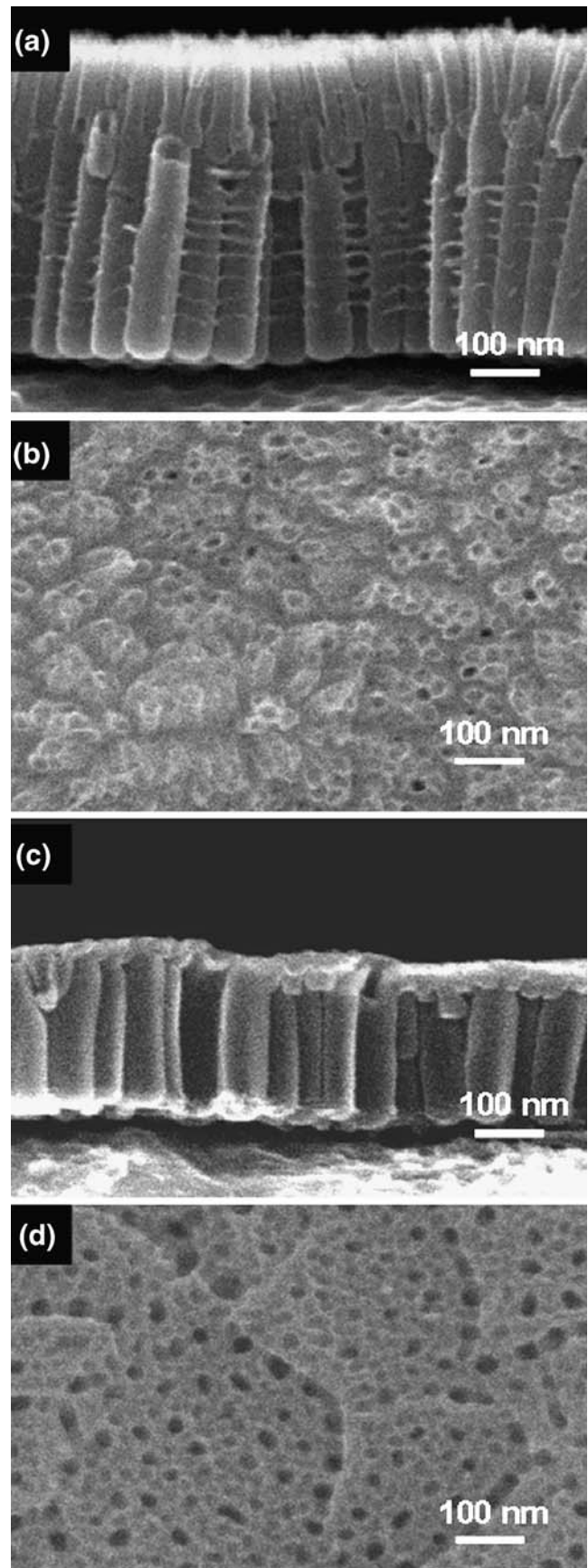




**Fig. 3** Side-view FESEM images of samples anodized in 0.5 wt%  $\text{NH}_4\text{F}$ +glycerol electrolyte: (a) titanium foil sample, thin film titanium sample sputtered on TCO/glass substrate anodized by (b) constant-voltage and (c) triangular-voltage anodization; the *arrows* indicate single nanotube exposing inner wall of the tube

with GPIB interface and LabVIEW program (National Instrument). The temperature of electrolyte was maintained at 30°C in a large water bath. Solution of 0.5 wt%  $\text{NH}_4\text{F}$  in glycerol and 0.25 wt%  $\text{NH}_4\text{F}$  in ethylene glycol were used as an electrolyte [13–16]. For the morphological characterization, Philips field emission scanning electron microscopy

**Fig. 4** FESEM images of samples anodized by applying of abruptly increased voltage: (a) side-view (b) top-view images for abruptly increased voltage method, (c) side-view (d) top-view images for abruptly decreased voltage method



(FESEM) XL 30SFEG was employed. The side-view images were taken from mechanically cracked samples.

### 3 Results and discussion

Figure 1 shows the representative current transient recorded during anodization of titanium foil samples in the ethylene glycol based electrolyte. Before recording the current transient, the voltage was slowly increased to target voltage with the speed 0.1 V/s. In the early stage of the anodization process, thin oxide layer is formed and small pits are created due to the localized dissolution of the oxide. Then current decreases while competing between oxidation and dissolution of titanium. And pores grow into the inside of titanium remaining porous oxide layer. It is well known that the diameter and length of the nanotube made by anodization method are proportional to the anodization voltage and anodization time [17, 18]. In this work, we tried to modulate pore diameters of the nanotube by applying the not-constant voltage in a single anodization process. Figure 1(a) and (b) show the current transient of the conventional constant-voltage anodization (60 V) and that of rocking-voltage anodization (sine wave, 20~60 V), respectively. As the applied voltage changes, the measured current was oscillated with the similar trace.

Figure 2 shows FESEM images of samples anodized in Fig. 1. Conventional constant-voltage anodization resulted in straight and cylindrical nanotube array as shown in Fig. 2(a). They had an open top and closed bottom as shown in Fig. 2(b). An average outer diameter of the nanotube was 150 nm. In the case of rocking-voltage anodization, we found that nanotube array divided into four segments as shown in Fig. 2(c). The length of each segment of nanotube array was shortened along the direction of growth. This can be understood that the pore growth rate in the anodization process decreases as increasing anodization time [19]. An existence of four segments over length is related to four peaks of the current transient curve in Fig. 1(b). In spite of rocking applied voltage (20~60 V), an average outer diameter of the nanotube was mostly similar to that of constant-voltage anodization (60 V). Only at the borders between segments, we could see small variation of the diameter. Figure 2(d) shows magnified cross-section of the border section. The length of each segment of nanotube array can freely be controlled by varying the period of the applied rocking voltage.

To investigate an effect of electrolyte in nanotube growth process, the anodization of titanium foil in glycerol based electrolyte was performed. Figure 3 shows the side-view FESEM images of thin film titanium anodized in the glycerol based electrolyte. The voltage was applied as a type of a triangular wave (linearly increases and decreases

between 5~15 V). As compared to ethylene glycol based electrolyte, we could find gradual diameter variation of the nanotube. Moreover, in the case of thin film titanium sample sputtered on TCO/glass substrate, the variation of inner diameter in nanotube array was observed. Figure 3(b) and (c) show that straight and zigzag-like inner surfaces were formed by constant-voltage and the voltage of several cyclic triangular waves, respectively. It is considered that the rings (ripples) on outer wall are caused by unwilling water contents in the electrolyte [13].

Abrupt change of the applied voltage induced very interesting results. Using the thin film titanium sample in glycerol based electrolyte, we applied constant voltage of 5 V for 2 h, following this, abruptly increased to 15 V and maintained at 15 V for 2 h. The resultant nanotube array was clearly separated into two segments having different diameters, as shown in Fig. 4 (a). However, in the reversal case of abruptly decreasing from 15 to 5 V, we could not find any differences in appearance with constant-voltage (15 V) anodization, as shown in Fig. 4(a). Because the nanotube diameter is proportional to the anodization voltage, abruptly increasing or decreasing the voltage results in different diameter nanotube appearing in order to maintain the original total area of the interface. However, it is difficult to understand that these appearances happen only in the case of abrupt voltage increasing.

### 4 Conclusions

We tried to induce the variation of nanotube morphology by varying the anodization conditions compared with conventional anodization process. We could see small variation of the nanotube diameter in the experiments using rocking voltage applied anodization in the ethylene glycol based electrolyte. As compared to ethylene glycol based electrolyte, gradual diameter variation of the nanotube was shown when glycerol based electrolyte was used. Applying of abruptly increased voltage induced to separate into two nanotube segments having different diameters. These new types of nanotube array architecture will be useful for new base materials for the development of nano-scale devices.

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