

## Research Article

# Self-Assembled TiO<sub>2</sub> Nanotube Arrays with U-Shaped Profile by Controlling Anodization Temperature

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TiO<sub>2</sub> nanotube arrays with uniform diameter from top to bottom were fabricated. The synthesizing approach is based on the investigation of the influence of electrolyte temperature on the tube diameter. We found that the inner diameter of the tubes increased with the electrolyte temperature. Accordingly, we improved the tube profile from the general V shape to U shape by raising the electrolyte temperature gradually. This is a simple and fast approach to fabricate uniform TiO<sub>2</sub> nanotubes in diameter. The improved TiO<sub>2</sub> nanotube arrays may show better properties and have broad potential applications.

## 1. Introduction

TiO<sub>2</sub> nanotubular/nanoporous structures stimulated significant research activity for these years due to their unique properties used in various functional applications including solar cells [1–5], electrochromic effects [6, 7], wettability [8, 9], gas sensitivity [10], and photocatalysis [11]. Electrochemical anodization technique is one of the simplest, cheapest, and most straight-forward approaches to fabricate ordered TiO<sub>2</sub> nanotube arrays. By controlling the electrochemical anodization parameters (applied potential, electrolyte species, electrolyte pH, temperature, content of F<sup>-</sup> and H<sub>2</sub>O in electrolyte, etc.), one can obtain TiO<sub>2</sub> nanotubes with various surface morphologies, tube lengths, tube architectures, and so on [12].

In general, diameter of TiO<sub>2</sub> nanotubes is reported to be linearly dependent on the applied anodic potential during anodization [13]. However, the diameter also can be changed under different electrolyte parameters, for example the F<sup>-</sup> content [14, 15], H<sub>2</sub>O content [16], and the electrolyte temperature [17]. Herein, we investigated how the electrolyte temperature influenced the tube diameter. Under the control of temperature, nanotubes with uniform diameter from top to bottom, so called U-shaped nanotubes, were obtained.

The general V-shaped profile of the nanotubes was successfully avoided.

## 2. Experimental

In this experiment, a common two-electrode electrochemical cell was used with the working electrode Ti foil (Strem Chemicals, 0.2 mm thickness, 99.6% purity) and the counter electrode Pt foil. Ti foils were degreased ultrasonically in acetone and ethanol for 10 min, respectively, followed by rinsing with deionized water. The two-step anodization was carried out in the electrolyte of ethylene glycol with 0.5 wt% NH<sub>4</sub>F and 3 vol% deionized water at a constant voltage of 60 V. The anodization current was measured by a sourcemeter (Keithley 2400). The first anodization time was 30 min. The as-anodized titanium foil was then ultrasonically cleaned in deionized water to strip off the TiO<sub>2</sub> surface layer and expose the underneath titanium substrate. Afterwards the titanium foil was subjected to the second anodization for 1 h to create nanotube arrays. To control the anodization temperature, the electrochemical cell was put in a water bath system, which can be set at a certain temperature. Field-emission scanning electron microscope (FE-SEM, FEI Sirion

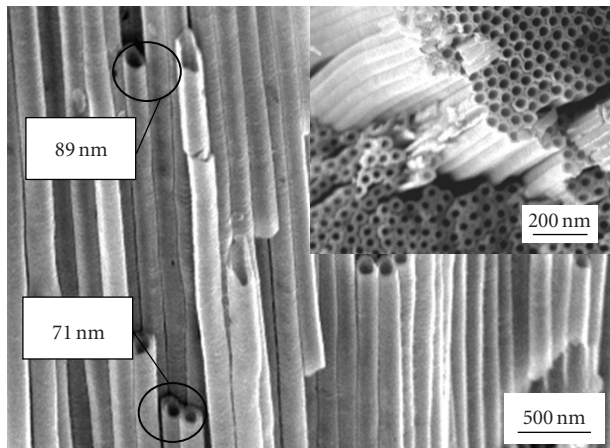


FIGURE 1: Cross-sectional image of tubes at 30°C, the inset shows top view.

200) was employed for the morphological and structural characterization of samples.

### 3. Results and Discussion

Through conventional anodization process with the electrolyte temperature fixed, TiO<sub>2</sub> nanotube arrays with a V-shaped wall profile can be obtained. Here, the V-shaped wall profile means that the wall thickness increases, namely the inner diameter of every nanotube decreases, along the tube from top to bottom. Figure 1 represents nanotubes anodized at 30°C for 1 h. As shown in Figure 1, the tube inner diameter decreases from 89 nm to 71 nm in about 2 μm distance. The cause of this V-shaped nanotubes is that the earlier formed parts of the walls are exposed longer to the etching fluoride environment [12]. Figure 2(a) schematically represents the growing process of V-shaped tubes. Based on our investigation of the dependence of tube diameter on electrolyte temperature, we found that the V-shaped structure can be avoided under control of the anodization temperature during the second-step anodization.

We first investigated how the nanotube inner diameter varied with the electrolyte temperature. Figure 3 reveals the dependence of tube inner diameter on temperature from 10°C to 35°C. The diameter increases with electrolyte temperature, which accords with the research of Macak and Schmuki [17]. In the anodization process, oxide growth is controlled by field-aided ion transport, and chemical dissolution of the formed TiO<sub>2</sub> by F<sup>-</sup>. According to Stokes-Einstein relation ( $D = k_B T / C \pi \eta \sigma$ , here  $k_B$  is Boltzmann constant,  $T$  is absolute temperature,  $C$  is a numerical constant determined by the hydrodynamic boundary condition, and  $\sigma$  is the diameter of the hard sphere particle), the diffusion coefficient  $D$ , is proportional to  $1/\eta$ , where  $\eta$  is the solution viscosity [18, 19]. With the increase of the temperature, the viscosity of the electrolyte (ethylene glycol) decreased. Consequently, the diffusion coefficient  $D$  increases with the temperature. The increasing  $D$  leads to faster F<sup>-</sup> drift velocity, hence the oxide dissolution gets faster [16].

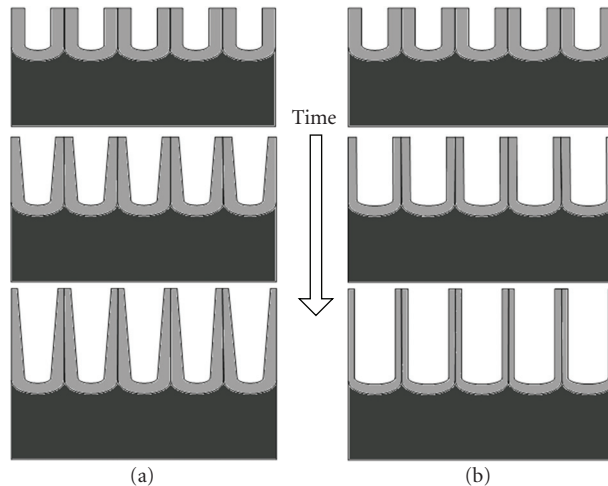


FIGURE 2: Schematic representation of nanotube arrays formation: (a) V-shaped tubes at fixed electrolyte temperature; (b) U-shaped tubes when electrolyte temperature was gradually elevated.

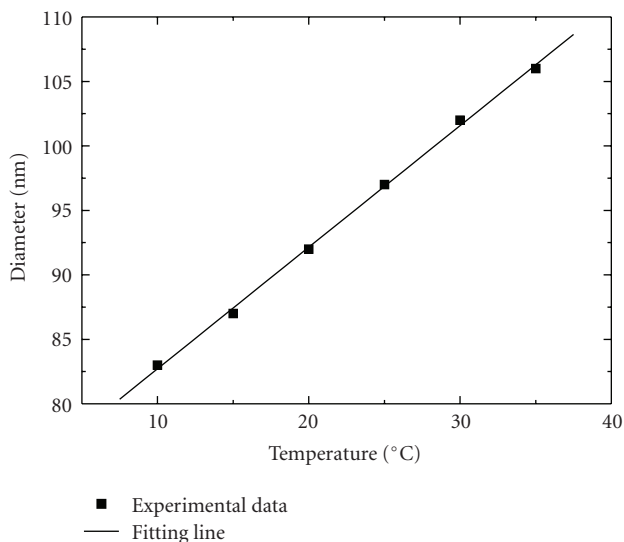


FIGURE 3: Variation of tube diameter with electrolyte temperature.

With the increase of the dissolution rate, the diameter of the tip of the tube bottom becomes larger. Figure 4 shows the time-dependent anodizing current densities at electrolyte temperature from 10°C to 35°C. Increased current densities are observed with a rise in electrolyte temperature, which accords with the increase of the diffusion coefficient.

Based on our investigation above, we planned to elevate the electrolyte temperature gradually to fabricate U-shaped nanotube arrays. This shaped nanotube arrays have the same inner diameter along the tubes from top to bottom. The growing process is schematically represented in Figure 2(b). Assume that the pores start to form at time  $t_0$ . After an ultrashort time  $\Delta t_1$ , nanotubes of small length are formed. Then the temperature was elevated slightly to ensure that

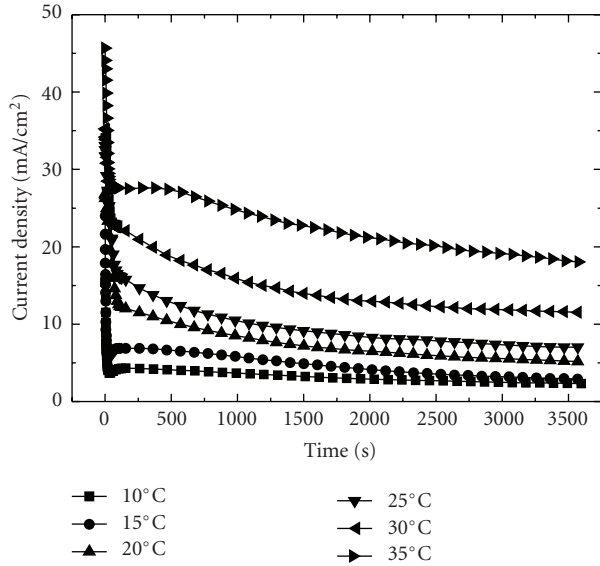


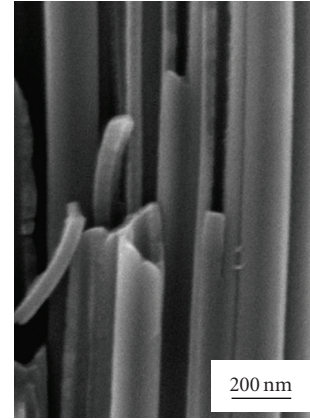
FIGURE 4: Time-dependent anodic current density curves at different temperature.

the following formed nanotubes, in a time  $\Delta t_2$ , have the same inner diameter as the early formed part after  $\Delta t_2$  duration dissolution. This process revolves, and a  $\text{TiO}_2$  layer with uniform of inner diameter nanotube arrays is finally obtained.

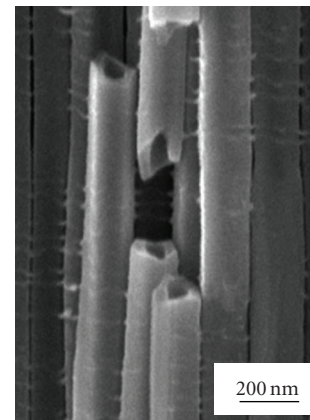
In our experiment, the initial temperature was set at  $15^\circ\text{C}$ . The pores started to form at about 100 s, according to the anodizing current density curve at  $15^\circ\text{C}$  [12]. The current density then was about  $5.5 \text{ m} \cdot \text{cm}^{-2}$ , and it was kept at this value by means of gradually elevating the electrolyte temperature. During the 2-hour anodization, the temperature increased from 15 to  $27^\circ\text{C}$ . Figures 5(a), 5(b), and 5(c) represent the cross-sectional view of the portion about  $3 \mu\text{m}$  from the top, the middle, and about  $3 \mu\text{m}$  from the bottom of the tube arrays, respectively. The total tube length is about  $22.5 \mu\text{m}$ . The average value of the diameter is about 60 nm near the top, 58 nm in the middle and 56 nm near the bottom, respectively.

#### 4. Conclusions

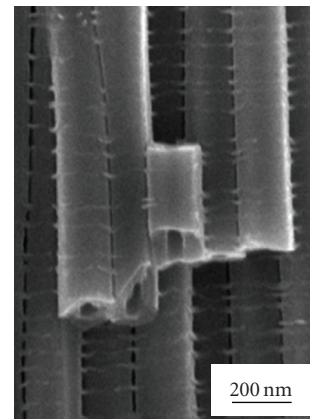
We have successfully synthesized self-organized  $\text{TiO}_2$  nanotube arrays with U-shaped tube profile. These  $\text{TiO}_2$  nanotube arrays have uniform diameter from top to bottom. The synthesizing approach is based on the investigation of the influence of electrolyte temperature on the tube diameter, that is, the inner diameter of the tubes increases with the electrolyte temperature. Based on this, we improved the tube profile from the general V shape to U shape by gradually raising the temperature. This approach is simple and fast, and the improved  $\text{TiO}_2$  nanotube arrays may show better properties for applications.



(a)



(b)



(c)

FIGURE 5: Tubes formed under rising temperature. (a) About  $3 \mu\text{m}$  from the top. (b) In the middle. (c) About  $3 \mu\text{m}$  from the bottom of the tube layer.

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