

Synthesis of high-aspect-ratio, top-open and ultraflat-surface TiO₂ nanotubes through double-layered configuration

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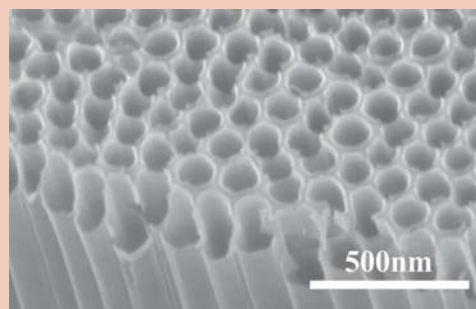
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In this Letter, a novel modified anodization was utilized to synthesize high-aspect-ratio, top-open and ultraflat-surface TiO₂ nanotubes. The interruption of voltage during anodization leads to the formation of a double-layered structure. Due to the weak mechanical connection between the upper and the underlying layer, the two parts can be easily detached. Compared with the conventional ultrasonication method to remove the clusters of nanotubes where rough surfaces resulted, this efficient and reliable strategy may facilitate further applications of TiO₂ nanotubes in diverse conditions.



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1 Introduction Titanium dioxide (TiO₂) nanotubes fabricated through electrochemical anodization with tailored geometries and multidimensional structures have been intensively explored recently. The comparatively large specific surface area and excellent electron mobility are capable for numerous important applications, including photocatalysis, photovoltaics, sensors, batteries and photonics [1–5]. During an anodization process, chemical dissolution plays an important role in the formation of TiO₂ nanotubes, leading to complex surface morphologies. Dissolution of the tops and sides of nanotubes during anodization results in tapered tubes with enlarged openings on the top of the anodized layer [6, 7]. If the tube wall is very thin, during the drying process, capillary force will bend the tubes and lead to bundles of tubes on the surface [8]. For over-anodized samples, nanowires with different lengths may be present on the top. These irregular surfaces were particularly observed during the fabrication of high-aspect-ratio tubes, which requires concentrated fluoride, a high applied voltage or sufficiently long duration of anodization

[9, 10]. Surface morphology of nanotubes strongly affects their performances in various applications. In TiO₂ nanotube based dye-sensitized solar cells (DSSCs), higher power conversion efficiencies can be obtained after the removal of irregular tops on the anodic nanotubes [11, 12]. Moreover, to facilitate electrolyte infiltration, tube filling or surface functionalization, well-defined openings are required. Generally, the as-anodized samples have to be ultrasonically treated with moderate ultrasound energy for several minutes to reach top-open morphology [13–16]. However, the surface after the treatment becomes rather rough and cracked. With the aid of protective layers, the undesired morphology introduced by chemical dissolution can be suppressed, such as annealed TiO₂ layers [17], polished layers [11], or pre-coatings [12, 18]. However, top remnant may still exist after these procedures. The fabrication of controlled morphology with regular top surface and applicable tube length is still a challenge.

Previously, the formation of layered, branched or periodic TiO₂ nanotube structures has attracted vast attention.

In the present work, a versatile technique to eliminate the surface disorder was developed. By combining a voltage-interruption-induced layer separation and subsequent ultrasonication, high-aspect-ratio nanotubes with well-defined openings and ultraflat surfaces can be obtained.

2 Experimental Titanium foils (99.7% in purity) were anodized with a two-electrode arrangement. Prior to anodization, the titanium foils were sonicated in acetone, methanol, and deionized (DI) water successively. Anodic TiO₂ nanotubes were grown in ethylene glycol (EG)-based electrolyte, with the addition of 0.5 wt% ammonium fluoride (NH₄F) and 3 vol% DI water under a constant applied voltage of 60 V and at a temperature of ~30 °C. A conventional anodization process and a modified one were adopted for comparison. The conventional anodization was conducted with duration of 0.5–1.5 h. In a modified anodization, an intermediate pause was performed during the process to obtain highly ordered nanotubes with smooth surfaces and high aspect ratios. This modified anodization can be divided into three stages, with stage I anodization of 8 or 15 min, stage II a pause of 10–15 min, and stage III continued anodization of 1 or 2 h. After the anodization process, the samples were kept in the electrolyte for 1 h, and then ultrasonicated in water/ethanol (1:1 v/v) for 10–20 min at 80 W to remove the first layer, leaving behind the underlying regular tubes. Structure and morphology of the TiO₂ nanotubes were analyzed using FEI Sirion 200 scanning electron microscopy (SEM).

3 Results and discussion If the dissolution of TiO₂ is not severe, the top surface reveals a porous morphology. However, after substantial etching, the porous layer connected to the underneath nanotubes was etched away. Tube bundles appeared on the surface after anodization of 1 h. The nanowires, which are actually the severely etched individual tubes, started to form after prolonged anodization of 1.5 h. That is to say, there exists a maximum length of tubes without bundling on the surface.

In the case of normal over-etched surface after prolonged chemical etching, after ultrasonication, thin and broken tube walls were observed over the surface. The surface was not very uniform, with a disparity of tube length over a large scale. The continuous transition between surface irregular parts and the underlying tubes led to a rough top surface. Also, cracks formed and spread into the underlying network of tubes during bundling, and after sonication this feature remained.

In the present work, the anodization process was modified by introducing a short pause intermediately. Thus, the whole process can be divided into three stages, with stages I and III for anodization, and stage II just a pause. After the surface was ultrasonically cleaned, a relatively flat top surface can be obtained (see Fig. 1). The interposed pause during the anodization was thus confirmed to play a key role in the improvement of surface morphology, as will be illustrated in detail below. The colour of the surface

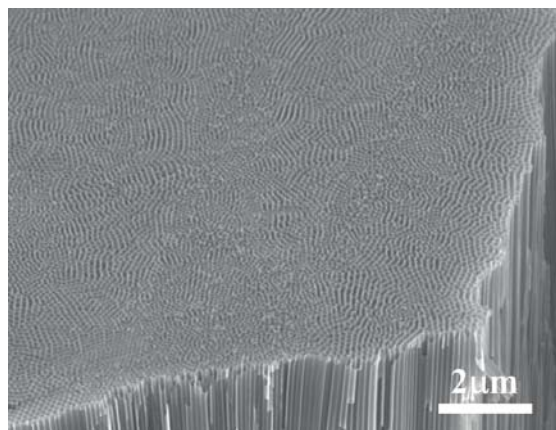


Figure 1 Tilted top view of highly ordered and top-open tubes with an ultraflat surface.

changed from slightly gray to light yellow after removing the clutches of tubes on the top surface.

The interruption of voltage during anodization leads to layered nanotubes. The upper and lower layers connected together with a distinct interface, determined by the pause of anodization. As depicted in Fig. 2(a), the anodization current of stage III is an extension of that of stage I, with current density lying in the same decreasing tendency with

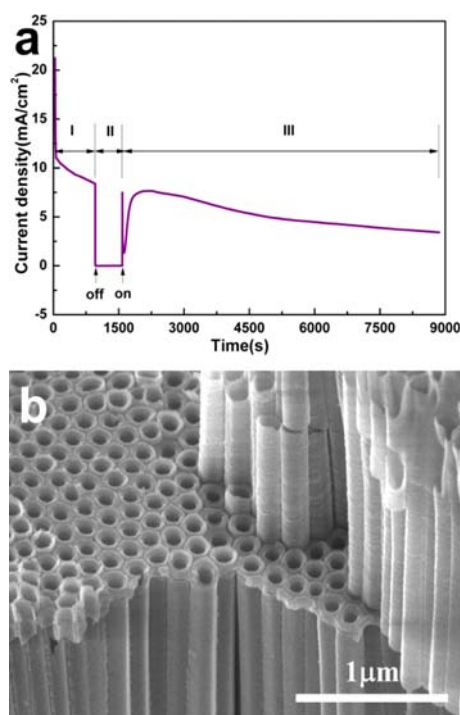


Figure 2 (online colour at: www.pss-rapid.com) (a) Transient current density during modified anodization with a pause of 10 min. The entire process is divided into three stages (I, II, and III). (b) Tilted view of a double-layered structure before completely detaching the two layers by ultrasonication. The interface is distinct, and the surface of underlying layer is smooth.

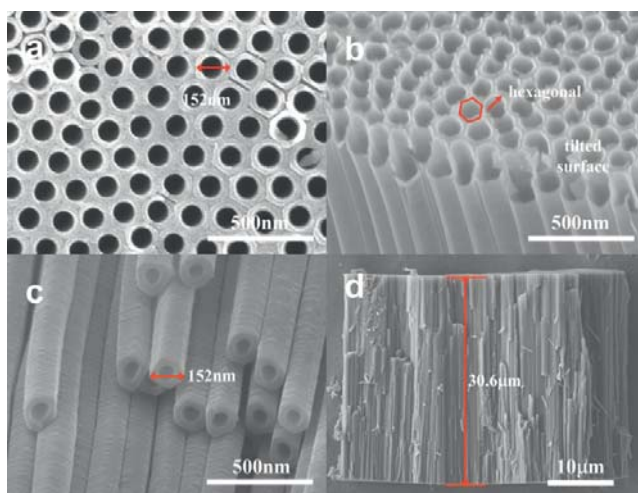


Figure 3 (online colour at: www.pss-rapid.com) Highly ordered, top-open and high-aspect-ratio nanotubes with an ultraflat and tubular surface morphology: (a), (b) top surface, (c) side view of hexagonally packed tubes, and (d) aligned tubes with a length of $\sim 30 \mu\text{m}$ after anodization for 1 h.

time. After the pause, when the voltage is re-applied, a recovery of current was observed in a short time. The interface was etched off by fluoride and gradually the two layers ruptured at the interface. Figure 2(b) shows the film surface with the irregular top layer partially removed by ultrasonication. Due to the relatively weak mechanical connection at the interface, the top layer preferentially peeled off along this surface. It is noteworthy that a proper duration of the first stage is required (e.g., stage I of 8 or 15 min corresponding to stage III of 1 or 2 h). If the first layer is very thick, the two layers may not be fully separated. Conversely, a thin top layer can be completely dissolved during stage III, thus fails to protect the surface of the second layer.

After removing the etched layer by ultrasonication with a proper period of time, highly ordered top-open tube arrays can be obtained, with a tubular surface morphology. In our case, for films with a thickness up to $60 \mu\text{m}$ (anodized for 2 h), the adhesion to the Ti substrate is still quite firm. The top-view images in Fig. 3(a) and (b) reveal that after the removal of the top irregular layer, the surface of the underlying tube structure is leveled, due to the distinct transition between the two layers. In spite of the randomly initiated pores with poor ordering in the top layer, the inherent self-ordering during volume expansion leads to highly ordered tubes in the second layer [19], where the tubes were separated, intact and hexagonally packed (Fig. 3(a–c)). The outer diameters of the tubes were 152 nm at both top and bottom positions. By eliminating surface etching, high-aspect-ratio tubes were synthesized via this easy processing procedure without clumping (Fig. 3(d)). By optimizing the thickness of the first layer, the required tube length of the underlying layer can be obtained, with $30\text{--}60 \mu\text{m}$ in length obtained in 1–2 h. These

results indicate that this modified anodization with an intermediate pause is a useful route to improved morphological features.

4 Conclusions In this work, successful improvement of surface morphology has been achieved by a simple modified anodization process. Due to the weak connection and distinct transition between the top irregular layer and the underlying one, a well arranged and top-open surface configuration could be conceivably obtained through the double-layered structure. The results inspire a facile and reliable approach to solve the commonly existing problem of tube bundling and to fabricate highly ordered TiO₂ nanotubes with ultraflat surfaces and large aspect ratios in a short time.

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