

Robust Self-Organization of Oxide Nanotubes over a Wide pH Range

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Nanotubular materials have in the past decade attracted great interest because of their high surface-to-volume ratios, size-dependent properties, and remarkable potential applications, for example, in high-density recording media, biological nanopatterning, functional electrodes, and so forth. Since the first report of self-organized TiO₂ nanotube layers formed by electrochemical titanium anodization,¹ substantial effect has been devoted to the self-organization and growth.^{2–10} By optimizing the working parameters, various kinds of oxide nanotubes, for example, zirconium oxide,^{11–13} hafnium oxide,¹⁴ niobium oxide,^{15,16} tungsten oxide,¹⁷ tantalum oxide,¹⁸ and titanium oxide–niobium oxide,¹⁹ and so forth, have been realized on metals or metal alloys via this electrochemical self-organization approach.

The electrochemical conditions under which the nanotubes are self-organized, such as the anodization potential and time, as well as the composition and pH value of the electrolytes,

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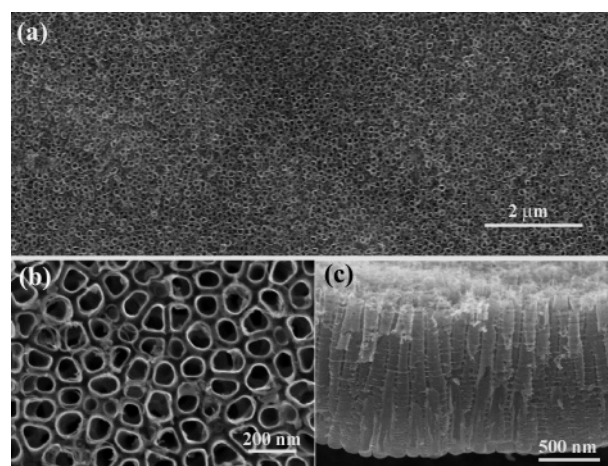


Figure 1. Parts a and b are field emission SEM top-view images of the as-anodized TiO₂ nanotube films at low and high magnifications, respectively. (c) Cross-sectional view of the aligned nanotube. These nanotubes are self-organized at 20 V for 1 h in a basic electrolyte at pH 8.4.

have great influence on the growth behavior of the nanotubes. Among these parameters, the electrolyte pH value is one of the most important factors.⁴ As known, the oxide nanotube growth is the result of a competition between electrochemical oxide formation at the tube bottom and chemical dissolution of oxide at the tip by fluoride ions. In strongly acidic solution, both the nanotube growth rate at the bottom and chemical dissolution rate at the tip are increased, and the length of the tube cannot be increased by prolonging the anodization time. On the other hand, increasing the pH value will decrease the chemical dissolution rate, while also decreasing the electrochemical oxide formation rate. This will affect the length to a certain extent if the electrochemical oxide formation rate is hampered more than the dissolution rate. So far relatively long nanotubes could be only prepared within a narrow acid pH range (around 4). For the future, robust industrial preparation and applications of oxide nanotubes is a demanding task and still a challenge to extend the aqueous electrolyte pH value to a wider range.

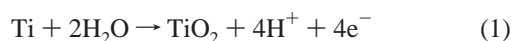
In this present work, we report a robust self-organization of TiO₂ nanotube layers within a wide pH range from acidic to basic conditions using a NH₄F/water/glycerol electrolyte. Importantly, we show that the basic environment (pH 8–9) is much more efficient for the self-organization of relatively longer nanotubes than the commonly used acidic condition (pH 3–5).^{1–10} Our method is simple and is based on operating close to spontaneous passivation conditions as described below. It can be applied to other metals or metal alloys for the preparation of anodic nanotubes. As a result of the achieved high growth efficiency, it is of high significance for future industrial production and applications.

Figure 1a,b shows typical scanning electron microscope (SEM) top-view images of the self-organized porous titanium oxide film anodized at pH 8.4 for 1 h at low and high magnifications, respectively, showing that a highly uniform and densely packed array of nanotubes was prepared over a large scale. The nanotubes have hollow structure with uniform diameter of approximately 100 nm and wall thick-

ness of about 6 nm. Figure 1c is a cross-sectional SEM view of the film, showing that the nanotubes grow perpendicularly onto the substrate and their lengths are about $1.39 \mu\text{m}$. These results indicate that large scale oxide nanotubes have been prepared in basic conditions.

In order to explore the influence of electrolyte pH on the tube geometry, the nanotube length was measured for tubes grown at different pH values for 1 h. As shown in Figure 2a,b, when the samples were anodized at pH 4.5, the diameter of the nanotube did not change, while the length decreased from $1.39 \mu\text{m}$ to about $1.06 \mu\text{m}$. Figure 2c is the dependence of tube length on electrolyte pH value, indicating that the tube length increased significantly with the increase of the electrolyte pH value, and the increase of the nanotube length is much more rapid in basic conditions than in acidic conditions. The difference in the oxide growth behavior on the electrolyte pH value becomes even more evident when the anodization time is extended. Figure 2d is the dependence of tube length on anodization time. At pH 8.4, the tube length increased almost linearly from 1.39 to $3.11 \mu\text{m}$ when the anodization time increases from 1 to 4 h, while the length increased merely from 1.06 to $1.59 \mu\text{m}$ after 4 h of anodization at pH 4.5. These findings indicate that using the basic conditions of $\text{NH}_4\text{F}/\text{water}/\text{glycerol}$ electrolyte, a much more controlled self-organization of relatively longer oxide nanotube layers can be achieved.

To thoroughly understand the growth behavior of the oxide nanotube films at different pH values, the electrochemical and chemical reactions at the bottom and mouth of the nanotubes, which are two main factors governing the length of the nanotubes, are considered. At the bottom of the nanotube, the growth is governed by field-aided oxide growth, field-aided diffusion of ionic species, and solvation at the oxide/electrolyte interface.⁸ This situation can also be expressed as competition between electrochemical oxidation (reaction 1) and chemical dissolution (reaction 2):⁴



Metallic Ti is first oxidized to TiO_2 and then selectively dissolved by F^- ion. This makes the pore deeper and deeper. For this, a sufficiently acidic environment at the tube bottom is needed. Figure 3a shows that at an elevated pH of 8.4 a viscosity induced threshold between an active tube growth and passivation conditions at the tube bottom exists. In other words, in a water glycerol electrolyte of a low viscosity (4:1), only minor tube growth can be observed. The process is essentially slowed down after a brief initiation period (see Supporting Information). While in the high viscosity electrolyte, water/glycerol (1:1), a steady tube growth is maintained. The reason for this drastic active/passive behavior can be ascribed to the fact that OH^- in the bulk solution and H^+ produced via reaction process (reaction 1) show a lower diffusion rate in the more viscous electrolyte. The pH value at the tube bottom is mainly controlled by the self-acidification process (reaction 1) and much less influenced by the bulk electrolyte pH value. As a result of the suitable viscosity, an acidic environment can be better confined at

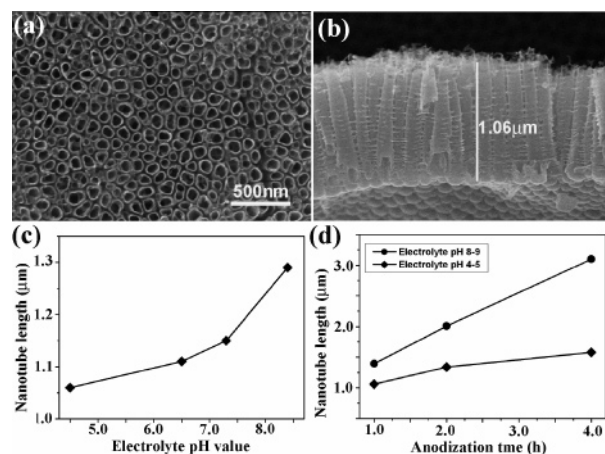


Figure 2. Parts a and b are respectively field emission SEM top and side views of TiO_2 nanotube layers that were formed by self-organization at 20 V for 1 h in an acidic electrolyte at pH 4.5. (c) Dependence of nanotube length on electrolyte pH values. (d) Dependence of nanotube length on anodization time in basic and acidic electrolytes.

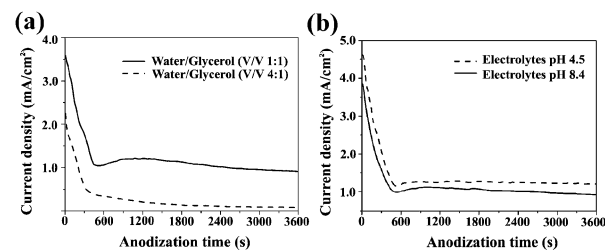


Figure 3. (a) Current density transient curves for the anodization of titanium at 20 V for 1 h in basic electrolytes (pH 8.4) with different water/glycerol volume ratios. (b) Current density transient curves for the anodization of titanium at 20 V for 1 h in acidic (pH 4.5) and basic (pH 8.4) electrolytes.

the pore tip, and this effect prevents passivation at the pore bottom even in basic solution.

In fact, during the growth process the chemical dissolution reaction (reaction 2) is also going on at the mouth of the tubes. The pH value at the mouth is mainly controlled by the bulk solution. In acidic electrolyte, the low pH value induces a high chemical dissolution rate, and the as-anodized nanotube tip is dissolved away gradually. As time goes on, the electrochemical oxide formation rate at the bottom decreases slowly, while the chemical dissolution rate keeps constant at the mouth. As a result, the final growth rate of the nanotube decreased (as shown in Figure 2d). On the contrast, in basic conditions, the chemical dissolution reaction (reaction 2) at the mouth is extremely slow. As a result, the as-formed nanotubes can survive for significantly longer times. Therefore, oxide nanotubes grow almost linearly with time in basic condition.

Figure 3b shows the difference of current density in basic and acidic electrolytes during the anodization process. For both electrolytes, with pH values of 4.5 and 8.4, respectively, the current density decreases gradually during the self-organization process. Once ordered oxide structures are created, the steady current density obtained at pH 4.5 is higher than that obtained at pH 8.4, indicating that the electrochemical etching rate at the tube bottom is faster in an acidic environment than that in basic conditions. However, the final tube length obtained in basic electrolyte is longer (Figure 2d). This indicates that current efficiency, the

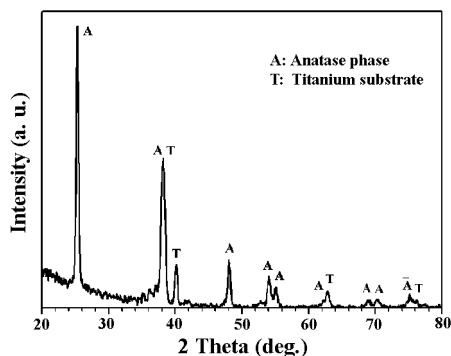


Figure 4. XRD patterns of the nanotubes after annealing at 450 °C for 1 h in air. The nanotubes are prepared in basic electrolyte at pH 8.4 and 20 V for 4 h.

effective observed tube length of the nanotube per electric charge applied during the anodization process, is higher in basic conditions. According to our calculation, after 1 and 4 h of anodization, the current efficiencies obtained in alkaline solution (pH 8.4) are about 60% and 84%, respectively, which are higher than 38% and 33% obtained in the acidic one (pH 4.5). This shows that an efficient growth of relatively long nanotubes can be achieved using an alkaline electrolyte with adjusted viscosity.

Many applications of TiO₂ nanotubes require a crystalline structure.^{20,21} Therefore, the TiO₂ nanotubes prepared in basic electrolyte (pH 8.4) for 4 h was crystallized through annealing. Figure 4 shows the X-ray diffraction pattern for the tubes after annealing at 450 °C for 1 h in air. In the pattern of the as-formed nanotubes, only reflections assigned to the Ti substrate occur (not shown here), confirming the amorphous nature of the nanotubes. After annealing at 450 °C, strong reflections assigned to anatase-type TiO₂ appeared. These self-organized porous crystalline TiO₂ nanotube layers

have many potential applications. For example, ordered TiO₂ nanotubes may give higher solar energy conversion efficiency as losses owing to grain boundaries can be avoided.²² Additionally, TiO₂ shows a controllable wettability^{23–25} and a high degree of biocompatibility in biomedical applications,²⁶ for example, as dental or hip implants.

In summary, TiO₂ oxide nanotubes were successfully prepared in a wide pH range via the electrochemical self-organization approach. Our experimental results show that oxide nanotubes can be prepared not only in acidic conditions but also in basic conditions and further demonstrate that basic conditions are much more efficient for the self-organization of relatively long oxide nanotubes using an adjusted basic electrolyte. This strategy is simple and can be applied to other metals and metal alloys for the preparation of oxide nanotubes (see Supporting Information, Figure S2). The achieved high growth efficiency is of high significance for future industrial production and applications.

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Supporting Information Available: Detailed experimental section and characterization; SEM image of the sample prepared in electrolyte at pH 8.4 with a water/glycerol ratio of 4; and SEM images of nanotubes prepared on metal Zr and alloy Ti–Zr using an electrolyte with pH of 8.4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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