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Letter

Electrode distance regulates the anodic growth of titanium dioxide (TiO_2) nanotubes

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Abstract

Electrochemical anodization of titanium has been used widely to produce self-organized TiO_2 nanotube arrays. Many experimental parameters, such as anodizing voltage and electrolyte composition, have been investigated extensively in the anodic growth of TiO_2 nanotubes. The effect of electrode distance on the anodic growth of TiO_2 nanotube arrays, however, remains elusive. This could be an important problem when *in situ* growth of TiO_2 nanotubes is required in microdevices. Here, we show that decreasing the electrode distance at a constant anodizing voltage enhances the anodic growth of TiO_2 nanotubes and the change of nanotube structures becomes more sensitive to the electrode distance at high voltages. We further demonstrate the correlation between electrode distance and current density during the anodic growth of TiO_2 nanotubes and suggest that the change of current density regulated by electrode distance controls the growth of TiO_2 nanotubes. The present study offers an effective approach to enhance the production of TiO_2 nanotube arrays without changing the anodizing voltage and electrolyte composition and thus provides useful insights to the anodic growth of TiO_2 nanotubes at reduced electrode distances.

Supplementary material for this article is available online

Keywords: electrochemical anodization, TiO_2 nanotubes, electrode distance

(Some figures may appear in colour only in the online journal)

1. Introduction

TiO_2 nanotubes are equipped with unique physical and chemical properties and have attracted great interest in the fields of solar cell, biosensor, and photocatalysis [1–4]. Although many approaches such as sol–gel [5], electrochemical lithography [6], and hydrothermal synthesis [7] have been developed to produce TiO_2 nanotubes, anodic growth of TiO_2 nanotubes is one of the most common methods to produce highly ordered nanotube arrays [8–10]. During anodization, titanium metal is first oxidized to a TiO_2 layer on the top of the metal surface, which is subsequently dissolved via a field-assisted electrochemical process to produce TiO_2 nanotubes. The continuous competition of field-assisted oxidation and dissolution is believed to be responsible for the growth of TiO_2 nanotube arrays [10–14].

Although the definitive mechanisms of anodic growth of TiO_2 nanotubes remain elusive [9, 15], a wide range of experimental parameters including pH [16, 17] and composition [18, 19] of the electrolyte, applied electrical voltage [20–23], anodization time [24–26], and temperature [27, 28] has shown to be able to control the growth of TiO_2. Increasing the concentration of F^- ions in the electrolyte solution, for example, accelerates the electrochemical dissolution process and results in an increased length of nanotubes [16, 18, 29]. Extending the anodization time or increasing the applied voltage will also lead to an increased length. Elevated voltage can further cause an increased outer diameter of the nanotubes

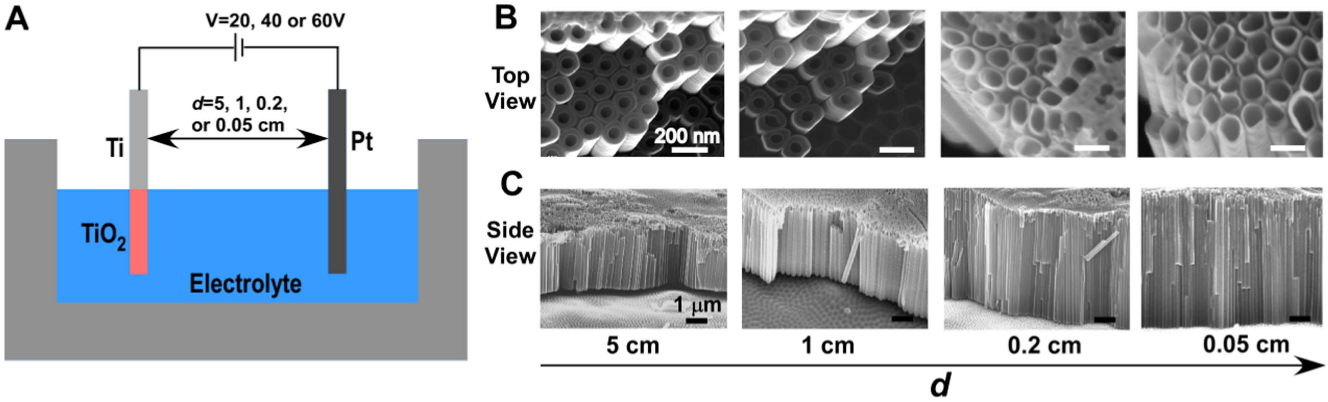

Figure 1. Electrode distance regulates the anodic growth of a TiO_2 nanotube. (A) Schematics of the anodic growth of TiO_2 nanotubes. The anodizing voltage (V) is kept at 20, 40 or 60 V. The distance between the cathode (Pt) and anode (Ti) (d) varies at 5, 1, 0.2, or 0.05 cm for each anodizing voltage. SEM images of (B) top view and (C) side view of TiO_2 nanotubes fabricated at 60 V when the electrode distance is controlled at 5, 1, 0.2, or 0.05 cm.

due to enhanced electrochemical dissolution. To date, however, it remains unclear whether the distance of electrodes during anodization influences the growth of nanotubes. A lack of such knowledge could be an important problem for *in situ* growth of TiO_2 nanotubes in miniature devices [30, 31] or microelectronics [32].

Here, we investigate the effect of electrode distance on the anodic growth of TiO_2 nanotubes and show that the length and diameter of nanotubes increase with a decrease of electrode distance. At elevated anodizing voltages, the change of the length and diameter of nanotubes becomes more sensitive to the change of electrode distance. The present study reveals a previously unidentified effect of electrode distance on the growth of TiO_2 nanotubes and provides a new approach to enhance the growth of TiO_2 nanotubes without increasing the applied voltage or changing the electrolyte composition. The developed approach may find applications in the development of TiO_2 nanotube-based micro-devices for sensing, photocatalysis, and biomedical engineering.

2. Experimental

2.1. Materials

0.5 mm thick titanium (Ti) film (99.2% pure) and 0.001″ thick platinum (Pt) film (99.9% pure) were purchased from Alfa Aesar (Ward Mill, MA). The electrolyte solution for anodization was prepared by mixing 15 wt% NH_4F (Sigma Aldrich) and 3 ml DI water with 145 ml Ethylene Glycol (VWR). HCl (37%) was purchased from Sigma Aldrich.

2.2. Instruments

An electric power supply (TKD-Lambda) was used to conduct the electrochemical anodization. The current density during anodization was recorded by BenchVue software. High resolution images of TiO_2 nanotubes were obtained by using a scanning electron microscope (FIB-SEM, Zeiss Cross Beam).

2.3. Electrochemical anodization

Ti and Pt films were submerged in the electrolyte solution in a 150 ml beaker. Titanium film was connected to the power supply as the anode, whereas the Pt film was connected to the cathode. Distances between the Ti and Pt films were controlled at 5, 1, 0.2, or 0.05 cm during anodization. A caliper or spacer with a thickness of 0.05 cm was used to control the distance between the electrodes. The applied voltage between the anode and cathode was controlled at 20, 40 or 60 V for each electrode distance. Anodization was conducted for 30 min at room temperature (25 °C) for all experiments.

2.4. Imaging and statistical analysis

The TiO_2 samples were etched with HCl for 2–5 min and then cleaned with acetone before SEM imaging. Image J software was used to measure the length and diameter of TiO_2 nanotubes based on SEM images. To determine significant differences of data between experimental parameters, a Student's *t*-test was performed, where $P < 0.05$ was considered as significant. Each set of experiments was conducted more than three times. The data was expressed as mean +/− standard deviation.

3. Results and discussion

The anodic growth of TiO_2 nanotubes was conducted in a static bath with an electrolyte that contained ethylene glycol and NH_4F (figure 1(A)). Platinum foil was used as the cathode and titanium foil served as the anode. We kept the composition of the electrolyte and anodization time (30 min) the same for all experiments and decreased the distance between the anode and cathode at constant anodizing voltages. Figures 1(B) and (C) showed typical SEM images of, respectively, the top and side views of TiO_2 nanotubes produced at 60 V with varied anode-to-cathode distances. Nanotubes produced at 20 V and 40 V are shown in figure S1 available at stacks.iop.org/NANO/28/25LT01/mmedia.

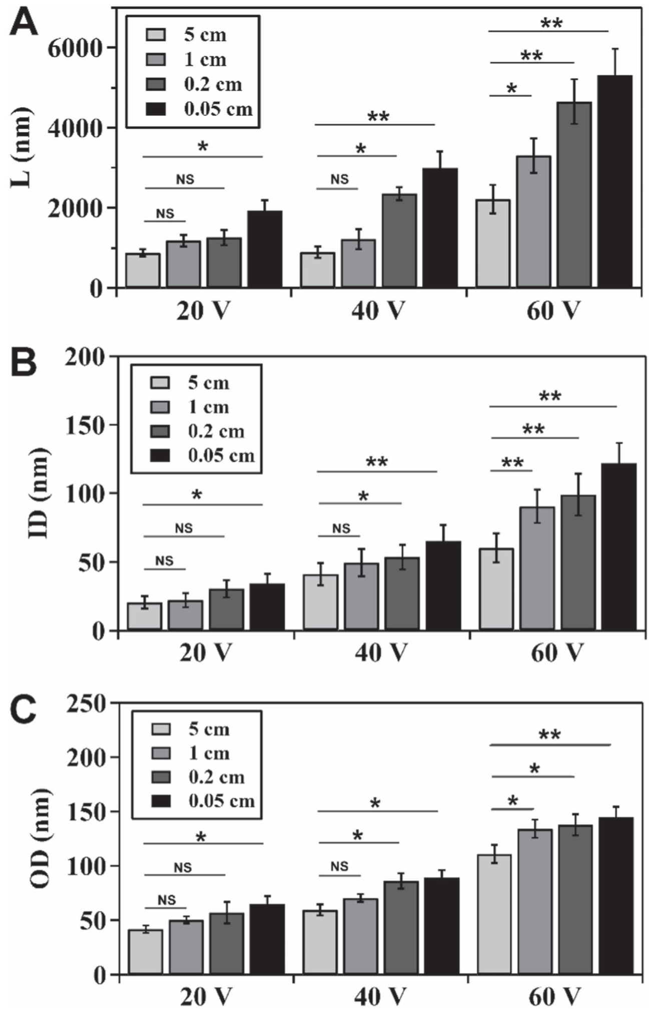

Figure 2. Effect of electrode distance (d) on the growth of TiO_2 nanotubes at different anodizing voltages. The dependence of (A) length (L), (B) inner diameter (ID) and (C) outer diameter (OD) of TiO_2 nanotubes on d at an anodizing voltage of 20, 40 or 60 V. $^{**}P < 0.01$, $^{*}P < 0.05$, and non-significant (NS) were calculated based on paired student's t-test analysis.

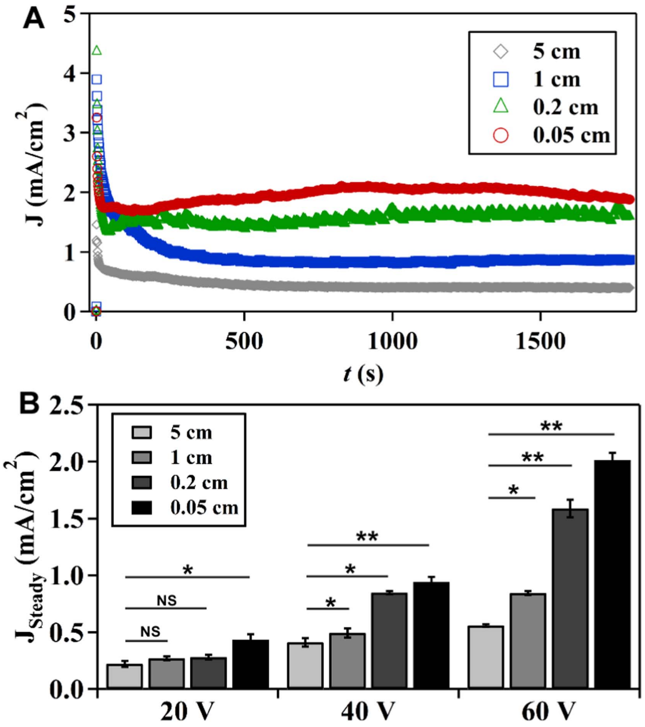

Figure 3. Electrode distance (d) regulates current density (J) during the anodic growth of TiO_2 nanotubes. (A) The typical change of current density with electrode distance when anodizing voltage is 60 V. (B) The dependence of steady-state current density on d at different anodizing voltages. $^{**}P < 0.01$, $^{*}P < 0.05$, and non-significant (NS) were calculated based on paired student's t-test analysis.

Evidently, both the diameter and the length of nanotubes increased with a decrease of electrode distance. In addition, the effect of electrode distance on the length of the nanotubes became more significant when the magnitude of the anodizing voltage increased. For example, the electrode distance did not significantly affect the growth of nanotubes when the anodizing voltage was 20 V (except when the electrode distance decreased to 0.05 cm ($P < 0.05$)) (figure 2(A)). However, the length of the nanotubes increased significantly with decreasing electrode distance when the anodizing voltage was 40 V and 60 V. The effect of electrode distance on the inner and outer diameter of the nanotubes shows a similar trend (figures 2(B) and (C)), suggesting a regulatory role of electrode distance in the growth of TiO_2 nanotubes. We note that the pore diameter of TiO_2 nanotubes close to the substrate also increased with a decrease of electrode distance (figure S2).

To explore why the electrode distance affects the growth of nanotubes, we examined the anodizing current density at different electrode distances. Figure 3(A) showed the current-time characteristics of anodization at 60 V at different electrode distances. Current-time curves showed typical patterns of growing nanotubes [9] and the magnitude of the steady state current density increased with the decrease of electrode distance (figures 3(A) and (B)). Such an increase of current density at a constant voltage could be attributed to the increased electric field, E, as the electrode distance decreased, where $E = V/d$, V is voltage, and d is the electrode distance. In addition, because the magnitude of the steady state current density correlates positively with the length of nanotubes [10, 18], the increased current density at a short electrode distance contributes to the observed effect of electrode distance on the length of the nanotubes (figure 2(A)). Increased current density could also cause a rapid electrochemical dissolution and lead to the widening of the pore structures and thus produces nanotubes with enlarged diameters. Thus, it is likely that the decreasing electrode distance results in a significant increase of electric field and consequently an increased current density, which in turn promotes the electrochemical dissolution process and helps nanotubes to penetrate into the oxide layer in a more effective manner. Note that the temperature change before and after anodization was not significant (~2 °C during 30 min anodization at 60 V) and thus would not affect the results significantly [10, 33].

Moreover, because elevated voltages will increase the current density at a constant electrode distance, decreasing

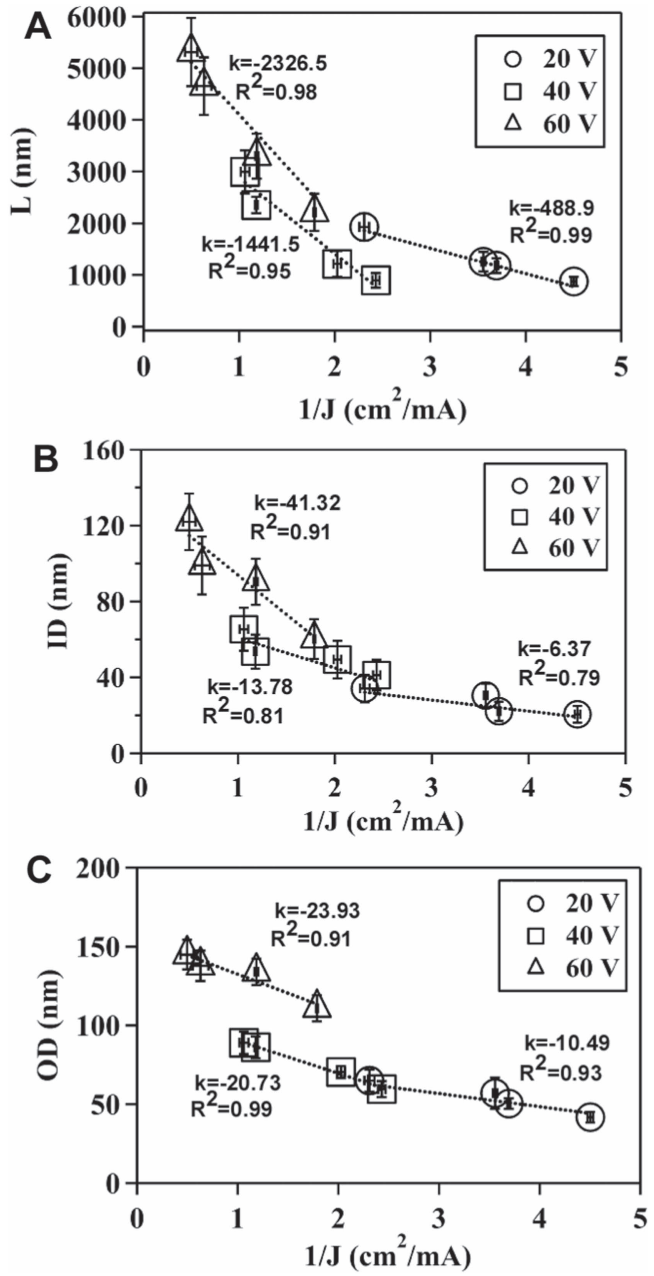

Figure 4. Inverse of the current density (J) correlates linearly with the dimension of TiO_2 nanotubes. The dependence of (A) length (L), (B) inner diameter (ID) and (C) outer diameter (OD) of TiO_2 nanotubes on $1/J$ at an anodizing voltage of 20, 40, or 60 V. R^2 is the correlation of determination and k is the slope of the linear regression fitting curve.

electrode distance at high voltages shall further increase the current density and impact the nanotube structure more effectively. Indeed, when we correlated the nanotube diameter and length with the steady current density at different electrode distances and voltages (figure 4), the length of the nanotubes changed linearly with the inverse of current density and the slopes of these linear regression curves increased with the increase of voltage (e.g., 489, 1442, and 2327 nA dm^{-1} for 20 V, 40 V and 60 V, respectively), demonstrating that the growth of nanotubes is more sensitive to the change of electrode distance at high voltages. A similar trend was found for the inner (figure 4(B)) and outer diameter (figure 4(C)). These results demonstrate that the anodic growth of TiO_2 nanotubes is enhanced at decreased electrode distances and the growth of TiO_2 nanotubes is sensitive to electrode distances at high voltages.

4. Conclusions

In summary, we demonstrated a previously unidentified regulatory role of electrode distance in the anodic growth of TiO_2 nanotubes. By decreasing the electrode distance, both the diameter and length of TiO_2 nanotubes can be improved due to the enhanced steady-state current density. The growth of TiO_2 was also found to be more sensitive to the change of electrode distance at high anodizing voltages. Because the enhanced growth of TiO_2 nanotube can be achieved without increasing the anodic voltages, the present study provides a promising approach to fabricate TiO_2 nanotubes in a more energy-efficient manner. In addition, the understanding of the roles of electrode distance in the regulation of TiO_2 nanotube growth will provide useful insights to the development of TiO_2 nanotube-based microdevices for biomedical research, solar cells and micro-sensors.

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