Fabrication of uniform size titanium oxide nanotubes: Impact of current density and solution conditions

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The synthesis of TiO_2 nanotube arrays on titanium foil was investigated under various electrochemical conditions. The following two conditions were shown to affect the nanotube diameter and number density. First, as the anodic current density for the foil increased from 10 to 30 mA cm^{-2}, the mean inner diameter of TiO_2 nanotubes increased from 30 to 145 nm. Second, as the ratio of methanol to water increased, the TiO_2 nanotube number density decreased and resulted in larger spaces between the nanotubes. © 2006 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Titanium dioxide (TiO_2) is one of the most actively studied versatile materials. For example, it has been used in a variety of applications, e.g. photocatalyst, photovoltaic material, structural ceramic, electrical circuit varistor, gas sensor, optical coating, biocompatible material for bone implants and spacer material for magnetic spin valve systems [1–3]. Consequently, the ability to control the architecture of titania on a nanoscale level can be expected to positively impact a variety of economically important technologies. A number of fabrication methods have been used to form nanometer-sized TiO_2 tubules, wires, dots and pillars: anodic oxidation [4], electrochemical lithography [5], photoelectrochemical etching [6], sol–gel processing [7], hydrothermal synthesis [8] and template synthesis [9,10]. Among these processes for preparing TiO_2 nanostructures, the electrochemical anodization of titanium in fluorinated electrolytes is a relatively simple method to synthesize porous or tubular structures. TiO_2 nanotubes fabricated by this method are highly ordered, have high-aspect ratios and are oriented perpendicular to the substrate, e.g. Ti foil. The nanotube arrays have a well-defined pore size, wall thickness and tube length. Thus far, various electrolytes, such as HF electrolytes [4], HF/H_2SO_4 mixtures [11], KF/NaF electrolytes [12], SO_4^{2-} electrolytes containing small amounts of fluoride ions and citric acid [12], chromic acid/HF mixtures [13], NF/Na_2SO_4 solutions [14],

$NH_4F/(NH_4)_2SO_4$ electrolytes [15], $(NH_4)H_2PO_4/NH_4F$ solutions [16], H_3PO_4/HF mixtures [16] and HF/acetic acid mixtures [17] have been used to form the TiO_2 nanotube arrays. These methods have used constant-voltage conditions (i.e. under potentiostatic conditions). In this research, constant-current conditions were used to produce the nanotubes.

Various organic solvents have been used in the anodic fabrication of macroporous silicon and aluminum oxide. However, very little information on electrochemical etching of titanium in organic solvents has been reported. Recently, Ruan et al. [18] have presented the electrochemical anodization of titanium under potentiostatic conditions in fluorinated dimethyl sulfoxide (DSMO) and ethanol mixture electrolytes. However, long anodization times (70 h) and high HF concentration were needed to produce TiO_2 nanotubes.

In this work, TiO_2 nanotubes on titanium substrates (i.e. Ti foil) were fabricated using galvanostatically anodic oxidation in methanol and water mixture electrolytes in the presence of 1 wt.% HF under constant-current conditions. In this process, different tube diameters could be produced by controlling the current density during the electrolysis. Furthermore, as the concentration of methanol in the electrolyte increased, the number density of TiO_2 nanotubes decreased (the TiO_2 nanotube number density is defined as the number of tubes per one square centimeter counts cm^{-2}).

The high-purity titanium foils that were used in this study were purchased from Alfa Aesar, USA (250 μm thick, 99.5% purity). Hydrofluoric acid (48%)

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and methanol (99.9%) were purchased from Aldrich Corp. (Milwaukee, WI). A fluorinated (1 wt.% HF) methanol and water mixture electrolyte was prepared using ultrapure water. The ultrapure water was obtained by treating distilled water with the Nanopure Diamond Ultrapure Water Treatment System (Barnstead Thermolyne Corporation, Dubuque, IA).

The electrochemical anodization of titanium was galvanostatically performed using a DC power supply (BK PRECISION, CAT.II MODEL 1715A, 0–60 V, 0–2 A, 210 W). A constant-current was maintained by adjusting the voltage.

Prior to the electrochemical treatment, titanium foils were polished mechanically to a mirror image. They were then chemically degreased and etched by immersing them in methanol and 6 mol l^{-1} nitric acid solution for 5 and 10 min, respectively. Next, they were rinsed with ultrapure water and dried in air at room temperature.

All anodization experiments were carried out at room temperature using two electrodes that were separated by 20 mm. The TiO_2 nanotube arrays were prepared in a cylindrical electrochemical reactor (60 mm diameter by 60 mm height). A titanium foil ($15 \times 33 \times 0.25$ mm) was used as anode and a platinum foil ($25 \times 25 \times 0.1$ mm) was used as cathode. The current density in the cell was varied between 10 and 30 mA cm^{-2} for the Ti foil. The electrolysis time was set at 30 min. During the anodization, the electrolytes were stirred using a magnetic stirrer. After the treatment, the samples were rinsed in ultrapure water, dried at room temperature and characterized.

The structural and morphological conditions of the TiO_2 nanotubes were characterized using an environmental field-emission scanning electron microscope (PHILIPS FEI XL-30 SEM) operating an accelerating voltage of 20 kV. The scanning electron microscope was capable of energy dispersive X-ray spectroscopy (EDX).

The literature reports the use of various electrolytes for the fabrication of TiO_2 nanotubes [4,11–20]. However, these anodization experiments were carried out under constant-voltage conditions (potentiostatically) and, as a result, the current densities changed greatly during electrolysis (e.g. from 15 to 28 mA cm^{-2} [19]). Mor et al. [20] reported that, for a fixed HF concentration and anodization potential, the dimensions of the tube varied with respect to voltage and HF concentration. These phenomena may suggest that current density plays a significant role in nanotube formation with respect to pore size and morphology. Therefore, a galvanostatic anodization method was used in this work.

During anodization, hydrogen bubbles were produced on the cathode surface. In the aqueous solution, these bubbles become relatively large, and remain on the electrode surface until they have sufficient buoyancy to break free from the surface. Unfortunately, the formation of relatively large bubbles causes a fluctuation of the current density. However, smaller bubbles are formed and break free from the surface when methanol is added to the solution [21]. Consequently, methanol was added to the electrolyte solution in this study to reduce the hydrogen bubble size and the current density

was carefully controlled. The surface tension of water and pure methanol at 303.15 K and atmospheric pressure are 71.40 and 21.71 mN m^{-1}, respectively [22]. Therefore, the reduced bubble size may be due to a reduction in surface tension that results from methanol addition to the electrolyte solution.

During anodization, the visual color of the TiO_2 layer changed from purple to blue, yellow, red and light green during the initial 10–15 min. The visual color change may be attributed to the increasing thickness of TiO_2, and may suggest the formation of TiO_2 nanotubes. Using EDX analysis, the approximate Ti:O atom ratio was determined to be 1:2.

The effect of current density on the fabrication of TiO_2 nanotubes was investigated using a HF concentration of 1 wt.%, an electrolysis time of 30 min and a methanol volume fraction of 50%. These conditions were chosen from preliminary experiments using electrolysis times of 30–60 min, HF concentrations of 1–2 wt.% and a current density of 10 mA cm^{-2} using variable methanol water mixtures. Figure 1 shows SEM images of surface structures that were obtained with for current densities of 10–30 mA cm^{-2}. For current densities of 10 mA cm^{-2} (Fig. 1(a)), the inner diameter of TiO_2 nanotubes was very small, ~30 nm. As the current densities increased, the inner diameter of the TiO_2 nanotubes increased from 30 to 145 nm, as illustrated in Figure 1(b)–(d). Figure 2 shows the relation between the current density and the mean inner diameter of TiO_2 nanotubes. The error bars are the observed standard deviation of the nanotube diameter, which is based on the observation of 400 nanotubes of SEM images taken from different locations on a sample.

The overall reactions for the anodization of titanium can be represented as follows:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{1}$$

$$Ti + O_2 \rightarrow TiO_2 \tag{2}$$

Initially, an oxide layer forms on the surface of titanium as a result of the above reactions. In the presence of fluoride ions, the oxide layer dissolves locally [12,19,23] and a nanotube is created from small pits that are formed in the oxide layer. These pits are created from the following reactions between TiO_2 and HF:

$$TiO_2 + 4H^+ + 6F^- \rightarrow TiF_6^{2-} + 2H_2O \tag{3}$$
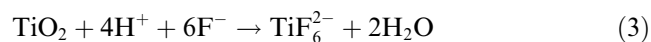
This chemical dissolution reduces the thickness of the oxide barrier layer at the bottom of the pits and allows the electrochemical etching process to continue (field-assisted oxidation and dissolution). If the chemical dissolution rate is too large or too small, the TiO_2 nanotubes cannot be formed. At the bottom of the pits, both the chemical dissolution and the electrochemical etching take place. The oxide layer at the bottom of the pits is relatively thin; and the thin layer, in turn, increases the electric field intensity, resulting in further pore growth. In addition, chemical dissolution removes the top of the shallow pore column and this forms the unanodized metallic region between the pores. The channels formed in these regions separate the pores from each other. The electrochemical process rate depends mainly on the current density of anodization.
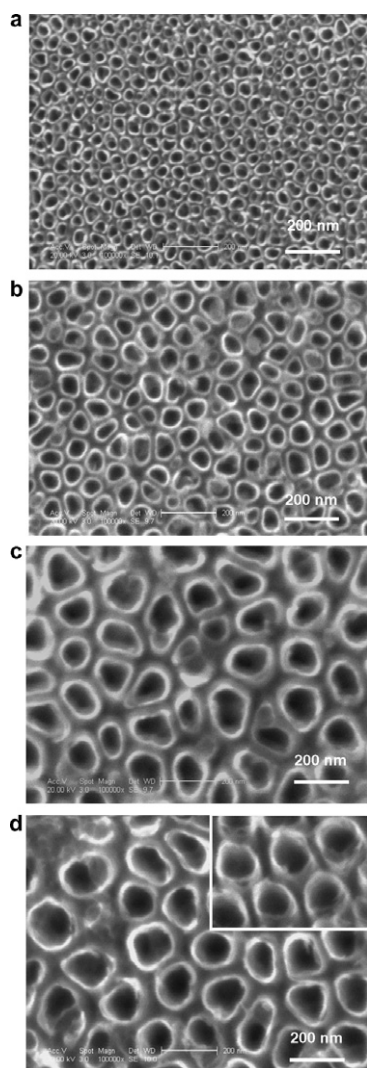
Figure 1. SEM images of the TiO$_2$ nanotubes obtained with different current densities in a methanol and water mixture (50 vol.% methanol, 1 mass% HF) for an electrolysis time of 30 min and these current densities: (a) 10 mA cm^{-2}, (b) 15 mA cm^{-2}, (c) 20 mA cm^{-2} and (d) 30 mA cm^{-2}.
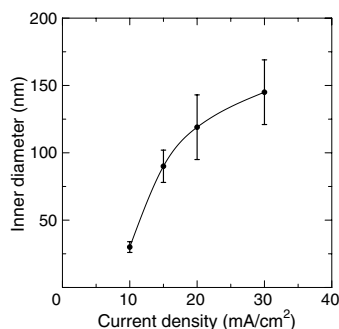
Figure 2. Relation between the current density and the inner diameter of TiO$_2$ nanotubes under the same conditions as for Figure 1.

Different TiO$_2$ nanotubes pore sizes are produced under different current densities, because this impacts the electrochemical etching rate. As the current density increases, the electrochemical etching rate, power and

electric field intensity (which is required to maintain the current density in the curved surface of the pore) are all increase. These effects appear to cause pit widening before the formation of channels that form separate pores.

The influence of methanol content in the electrolyte on the fabrication of TiO$_2$ nanotubes was investigated at a current density of 10 mA cm^{-2}. The nanotube number density (number per square centimeter) and the pore diameter are summarized in Table 1. As discussed above, when methanol was not present the current density was hard to control precisely, especially for higher current densities. Although the nanotube number density is almost the same for oxidation that is carried out in 50 vol.% methanol in water, it was difficult to produce uniform nanotubes when water alone was used. The variability in nanotube diameter can be seen in the relative standard deviation (RSD) in the nanotube diameter and the shape, which is not shown or reported here. As shown in Table 1, the RSD is larger for the nanotubes that were formed in water.

In addition, when the methanol concentration was increased to 90 vol.% the number density decreased. As illustrated in Figure 1(a), the nanotubes fabricated in 50 vol.% methanol were tightly packed. When the methanol concentration was more than 80 vol.%, the TiO$_2$ nanotubes density changed drastically. Figure 3 shows

**Table 1.** TiO$_2$ nanotube number density and diameter[a]

Electrolyte[b]	Number density[c] ($\times 10^8$/cm^2)	Inner diameter[d]	
		Mean value (nm)	RSD (%)
Water	356 ± 29	38 ± 7	18
50 vol.% Methanol	394 ± 33	30 ± 4	14
90 vol.% Methanol	148 ± 16	53 ± 7	13

[a] Anodization processes were performed with current density of 10 mA cm^{-2} for 30 min.
[b] All electrolytes contained 1 wt.% HF.
[c] The TiO$_2$ nanotube number density and its relative standard deviation were calculated from six SEM images taken from different locations of a sample.
[d] The nanotube inner diameter and its relative standard deviation were calculated from about 400 nanotubes of SEM images taken from different locations of a sample.
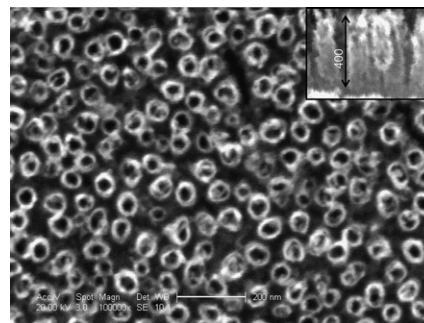
Figure 3. SEM images of the TiO$_2$ nanotubes anodized with a current density of 10 mA cm^{-2} in a methanol and water mixture (90 vol.% methanol, 1 mass% HF) for an electrolysis time of 30 min. Under these conditions, the length of fabricated nanotubes was shown to be about 400 nm from cross section.

an SEM image for the TiO_2 nanotubes that were fabricated in 90 vol.% methanol and Table 1 reports the number density. The pore diameter of nanotubes that were fabricated in the HF solution containing 90 vol.% methanol was 53 ± 7 nm. The space between nanotubes that were fabricated using 90 vol.% methanol increased by approximately 300% as compared with those fabricated using 50 vol.% methanol. The increased spacing between the nanotubes could be useful for obtaining patterned nanomaterials. The length of the nanotube arrays was approximately 400 nm. These results are similar to the results reported using a fluorinated DMSO and electrolyte ethanol mixture [18].

The reason for the decreased number density in this work could not be clarified completely. A large methanol content in the electrolyte may affect the formation of Ti and F hydrate complexes [12,18]. In the case of low methanol content, the chemical dissolution quickly removes the Ti corrosion products and this produces numerous nanotubes. On the other hand, the high methanol content slows the dissolution rate and this results in the formation of fewer nanotubes.

In conclusion, the influence of current density and solution conditions on the fabrication of uniform TiO_2 nanotubes was investigated. As the current density of the Ti foil increased from 10 to 30 mA cm^{-2}, the pore size of TiO_2 nanotubes increased from 30 to 145 nm. Consequently, different tube diameters could be produced by controlling the current density. An important advantage is that any form of titanium surface (sheets, foils, sputtered layers) can be treated using a quick and low-cost method to create a TiO_2 nanotube layer, and a good electrical connection would exist between the nanotubes and the Ti surface. This could form the basis for a number of interesting applications (e.g. catalysts and sensors). However, for some applications isolated nanotubes may be essential and this can be achieved by increasing the methanol content of the electrolyte solution.

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