



High-density NiTiO₃/TiO₂ nanotubes synthesized through sol–gel method using well-ordered TiO₂ membranes as template

Dong Fang^a, Kelong Huang^{a,*}, Suqin Liu^a, Zhiping Luo^b, Xiaoxia Qing^a, Qiguang Zhang^a

^a College of Chemistry & Chemical Engineering, Central South University, Changsha 410083, People's Republic of China

^b Microscopy and Imaging Center, Texas A&M University, College Station, TX 77843, USA

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ABSTRACT

Free-standing and well-ordered TiO₂ membranes were prepared by two-step anodization in F⁻-containing ethylene glycol electrolytes at voltage of 60 V. It was found that the ordering of TiO₂ membranes was significantly improved after the second anodization process. The initially closed bottom side of TiO₂ membranes was opened through chemical etching to obtain two-end opened TiO₂ membranes. Using the two-end opened membranes as template, dense NiTiO₃/TiO₂ nanotubes were successfully prepared for the first time by a sol–gel method. The microstructure and morphologies of the samples were characterized by scanning and the transmission electron microscopy techniques.

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1. Introduction

The TiO₂ nanotube materials have been widely studied due to their potential technological applications in lithium batteries [1,2], solar cells [3], and photocatalysis [4]. The TiO₂ nanotube growth on titanium (Ti) under anodic bias in electrolytes has been an object for over a decade [5]. At least two different electrolytes were reported so far, the aqueous electrolyte [6–8] and non-aqueous organic electrolyte [9] respectively, yielding two distinguishable morphologies [10–12]. The mechanisms of the nanotubes formation have also been discussed previously by Yasuda et al. [13,14].

Towards the application of nanomaterials, as porous alumina membranes have relatively regular structure with concentrated size distributions in pore diameter and interpore spacing, they have been utilized as nanofilters to selectively filtrate nanomaterials, drug separation, as well as a host or template for nanodevices, such as magnetic, electronic, or optoelectronic devices [15]. On the other hand, well-ordered anodic titanium dioxides (ATO) also have potential applications as the porous alumina membranes. In addition, fabricating well-ordered ATO would provide clues for better understanding the formation mechanism of the anodization [16]. Efforts have been made to fabricate highly ordered nanoporous TiO₂ membranes by several groups [17–19].

Recently, ternary oxides containing titanium and transition metals, such as MTiO₃ (M = Ni, Pb, Fe, Co, Cu and Sr), are increasingly recognized as chemical or electrical materials because of their outstanding catalytic, ferroelectric, piezoelectric, pyroelectric, dielectric, and photoelectric properties [20–23]. Several methodologies, such as sol–gel [24], hydrothermal [25], sputtering [26], co-precipitations [27], solid-state reactions [28], and polymeric precursor method [29] have been proposed for synthesising crystalline MTiO₃ powders. While, MTiO₃ fabricated by these methods usually require complex equipments and complicated operation procedures. On the other hand, the traditional way to produce MTiO₃ using solid reaction produces large MTiO₃ particles with uncontrollable morphologies, due to their inherent problems such as high reaction temperature and heterogeneous solid phase reactions.

In the present work, we first attempt to fabricate well-ordered free-standing ATO membranes with ideal hexagonal ordering using the two-step anodization process. Second, two-end opened ATO membranes are obtained by chemical etching. Finally, high-density NiTiO₃/TiO₂ nanotubes are prepared by the sol–gel method on the two-end opened ATO template. Electron microscopic characterizations confirm the formation of NiTiO₃/TiO₂ nanostructures.

2. Experimental procedures

2.1. Preparation of TiO₂ nanotubes

Titanium (Ti) foils (99.6% purity, 0.3 mm thick) were degreased by sonication in acetone, isopropanol and methanol, respectively. This procedure was followed

* Corresponding author.

E-mail addresses: klhuang@mail.csu.edu.cn (K. Huang), luo@mic.tamu.edu (Z. Luo).

by rinsing with deionized water and then drying in a nitrogen stream. The electrochemical setup consisted of a two-electrode configuration with graphite as counter electrode. All anodization experiments were carried out at room temperature in glycol solution. The anodic titania was grown at a voltage of 60 V for 48 h. Afterwards, the whole samples were transferred into 95% of ethanol solution for ultrasonic agitation for several minutes. After removing the anodic oxide layers using ultrasonic agitation, the textured Ti substrate was anodized again under the same conditions as the first anodizing step.

2.2. Preparation of NiTiO₃/TiO₂ nanotubes

Before using free-standing ATO membrane, the bottom closed side of the membrane was chemically etched using a 5 wt% NH₄F-1 M H₂SO₄ solution for 15 min, to obtain two-end opened ATO membrane [30]. Then the two-end opened ATO membrane was immersed into the sol for 10 h under relative vacuum ambience. For the sol fabricating, nickel nitrate was used as the cationic source, and citric acid and alcohol as the monomers to form the polymeric matrix. Therefore, the Ni(NO₃)₂ was added to dissolve into a mixture of citric acid and alcohol solution, with molar ratio of Ni²⁺ to citric acid as 1:2, and then the solution was heated at 70 °C to distill out excess alcohol. Finally, the two-end opened ATO membrane was placed in a furnace and annealed at 450 °C for 2 h under atmosphere.

2.3. Materials characterization

The samples were characterized by scanning electron microscopy (SEM, JSM-6360LV) and transmission electron microscope (TEM, JEM-2100). For the SEM, a thin Au layer (~3 nm) was evaporated on the sample surface to form a conductive film for the observation. For the TEM, a small piece of the template with NiTiO₃ nanoparticles was immersed into 1 ml water, which was broken into fine pieces using ultrasonication, and then a drop of the solution was placed onto a Cu grid covered with carbon support film. Quantitative measurements of electron diffraction (ED) intensities were made using ELD program [31,32] in Crisp package [33], and the simulations of powder ED patterns were performed using the Reflex module in Materials Studio, Version 5.0, by Accelrys.

3. Results and discussion

In the initial stage of the anodization, the degree of the ordering at the surface of the ATO is low, since the surface of the starting material is relatively rough at the micrometer scale. As a result, holes develop randomly. To improve the ATO ordering on the surface, two-step anodization is exercised. This process involves two

separate anodization procedures, as sketched in Fig. 1. Starting from the Ti film with rough top surface (Fig. 1a), the first anodization process is a long-period anodization to form the highly ordered dimple configuration at the TiO₂/Ti interface using the electrochemical anodization of Ti foil at 60 V (Fig. 1b). Subsequently, the textured Ti substrate was obtained after removing the ATO membrane using ultrasonic agitation in 95% of ethanol solution (Fig. 1c). Then the textured Ti substrate was anodized again under conditions identical to the first anodizing step, in which a way an ordered holes array throughout the entire oxide layer was generated in this process (Fig. 1d). Using ultrasonic agitation, the free-standing and well-ordered ATO membrane, with ideally hexagonal ordering, could be peeled off from the Ti substrate.

In the ATO membrane prepared by the first anodization, as shown in the SEM image of the top surface in Fig. 2(a), the ordering areas are limited, with evident gaps exist between them, and the degree of hexagonal ordering is also limited. Fig. 2(b) shows the Ti substrate after removing the TiO₂ membrane, which exhibits relatively flat dimpled surface, acting as the starting material for the second anodization.

By the second anodization, free-standing and well-ordered ATO membrane was produced, as shown in Fig. 3. Its average pore diameter (d_p) is about 115 nm as measured from its top surface (Fig. 3a), and the length of the membrane is about 158.3 μm as revealed from the cross-sectional view in Fig. 3(b). Fig. 3(c) is the SEM image of the bottom side of the film, depicting that the nanotubes are completely closed at this end. Fig. 3(d) shows an image of the free-standing well-ordered ATO membrane taken using an ordinary digital camera, with the dimensions of the membrane about 2.0 × 2.0 cm².

In order to fabricate NiTiO₃ inside the well-ordered ATO membrane, as shown in Fig. 4, the well-ordered ATO membrane (Fig. 4a) was soaked in 0.5 wt% NH₄F-1 M H₂SO₄ solution to obtain the two-end opened ATO membrane (Fig. 4b) [30]. Afterwards, the two-end opened ATO membrane was immersed in the sol under relative vacuum ambience so that the sol could get into the tube during this process (Fig. 4c). The membrane was then taken out from

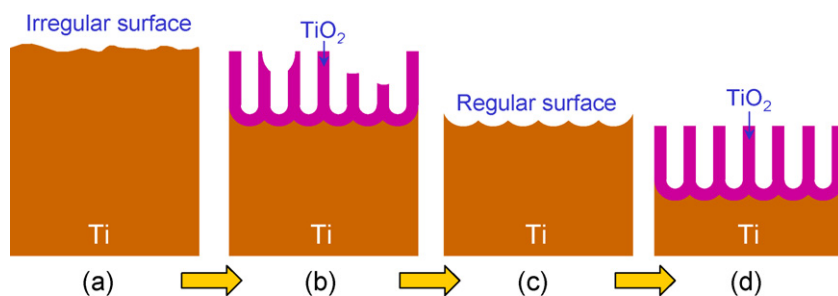


Fig. 1. Two-step anodization process. (a) Starting material with irregular surface; (b) formation of TiO₂ nanotubes after the first anodization; (c) regular dimpled surface after removing the TiO₂ nanotubes by the first anodization; (d) formation of well-ordered TiO₂ nanotubes after the second anodization.

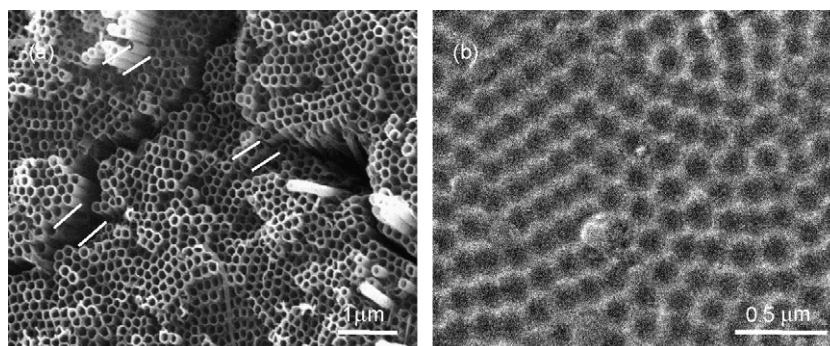


Fig. 2. SEM images of (a) top surface of porous TiO₂ membrane formed by the first-step anodization, and (b) titanium substrate surface after removing the TiO₂ membrane.

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