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Hydrothermal synthesis of aluminum oxy-hydroxide nanorod and nanotube arrays

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ABSTRACT

The aluminum oxy-hydroxide (AlOOH) nanorod and nanotube array are synthesized by hydrothermal treatment of the anodic aluminum oxide (AAO) membranes. This method might be a simple and efficient approach for fabrication of AlOOH nano-materials with controlled morphology. A possible mechanism on the hydrothermal growth is proposed and validated by the experimental results. The obtained AlOOH nanorod and nanotube arrays are anticipated to improve their performances as catalysts and absorbents and broaden their applications in the fields of biology and nanotechnology.

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1. Introduction

Aluminum oxy-hydroxide (AlOOH) is one of the most-important hydroxide materials, which has been widely used as vaccine adjuvants [1], adsorbents and catalysts for the chemical processes [2–4]. In the past decades, many methods were developed to fabricate the AlOOH nanostructures with different morphology, and the effect of morphology on the surface properties was exhibited [5–9]. However, up to present the AlOOH nanostructures with homogeneous and reproducible morphologies are still difficult to obtain in mass production. Therefore, finding a workable method is much important and necessary.

Anodic aluminum oxide (AAO) is a typical self-organized porous membrane material with highly ordered nanopore arrangement, which has been studied intensively for a long time [10,11]. Previously, the nanopores of AAO membranes were sealed hydrothermally to protect the aluminum-based materials from corrosion [12,13]. In 1962, the first theory on the AAO hydrothermal treatment was put forward by Hoar and Wood [14]. Afterwards, many fruitful studies were done [15–19]. Among these works, the report of Jha et al. on the synthesis of AlOOH nanofibers attracted our attention because of their morphology controllability [20,21]. Focused on this clue, the growth mechanism of AlOOH nanostructures by hydrothermal treatment of AAO membranes was investigated carefully, and the AlOOH nanorod and nanotube arrays with controlled morphologies were obtained successfully in recent years.

Our work provides new insight and understanding on the formation of the AlOOH nanorod and nanotube arrays by hydrothermal treatment of AAO membranes. We believe that the corresponding theoretical and experimental results would be of significant interest for catalysis, adsorbents, biomedical engineering, and nanotechnology.

2. Experimental

2.1. Fabrication of AAO membranes

High-purity aluminum sheets (99.99%) with a thickness of 0.4 mm were used as the starting materials. Prior to anodization, the aluminum sheets were degreased in acetone and ethanol for 15 min of ultrasonic cleaning, separately. Subsequently, the sheets were electropolished at 0 °C and 21 V in a 1:4 by volume mixture of perchloric acid and ethanol. Next, anodization was carried out under two different conditions:

I. 0 °C and 205 V in a 1 wt% phosphoric acid electrolyte with 0.01 mol/L aluminum oxalate (Alox) addition for 6 h [22].
II. 0 °C and 40 V in a 0.3 M oxalic acid electrolyte for 12 h [10].

After the first anodization, the AAO membrane was removed completely in a mixture of phosphoric acid (50 mL/L) and Cr_2O_3 (30 g/L) at 70 °C. Then, the second anodization was conducted at the same condition as above. Finally, two groups of AAO membranes

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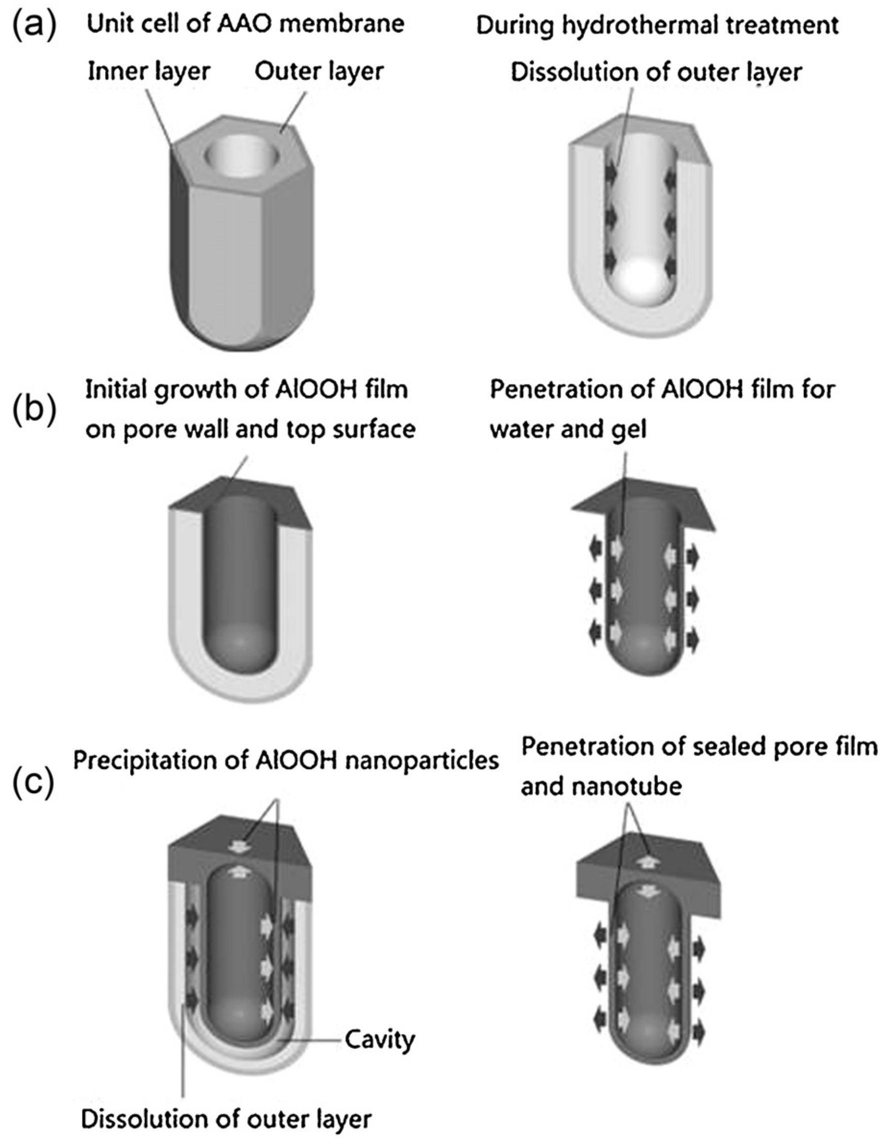

Scheme 1. The proposed dissolution–precipitation process during the hydrothermal treatment.

with interpore distance of 490 nm (Group I) and 100 nm (Group II) were obtained.

2.2. Synthesis of AlOOH nanorod and nanotube array

For fabrication of the AlOOH nanorod and nanotube arrays, the as-prepared AAO membranes were immersed in 5 wt% phosphoric acid at 30 °C for 0–3 h to widen the pores. Then, the hydrothermal treatment was executed. The membranes were transferred to a 500 mL Teflon-lined stainless-steel autoclave, which was heated in an airflow electric oven at 100 °C, 120 °C and 150 °C for 3 h, separately. After the autoclave cooled down naturally to the room temperature, the remaining aluminum was dissolved in a saturated $CuCl_2$ solution. Subsequently, the AAO membranes were put into a tailor-made holder with the bottom surface exposed to the chemical solution of 0.06 mol/L tri-sodium citrate [$C_6H_5O_7Na_3 \cdot 2H_2O$] for 40–80 min at 80 °C to remove the barrier layer [20].

The morphology of the obtained membranes was examined by field-emission scanning electron microscopes (Nova NanoSEM 430, LEO1530 VP and Hitachi S4800).

3. Results and discussion

As shown in Scheme 1, the AAO membranes are made up of numerous hexagonal unit cells, and each unit cell is comprised of two layers. The inner layer is a hexagonal thin walled tube, called "skeleton", which is relatively pure and dense alumina. The outer layer is a thick walled tube and its chemical composition is anhydrous alumina with acid contamination. During the hydrothermal process, the outer layer is dissolved to form the $Al(OH)_3$ gel [23]. As the $Al(OH)_3$ is much less stable, the following chemical reaction can occur at relatively low temperature [24,25]:

$$Al(OH)_3 \rightarrow AlOOH + H_2O \quad (1)$$

At the initial stage of the hydrothermal treatment, the AlOOH nanoparticles will precipitate simultaneously on the pore wall and the top surface of the AAO membranes to form a film. Noteworthily, this film is permeable, allowing the penetration of water and gel by diffusion. Thus, the repeated dissolution–precipitation can continue to proceed.

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