Preparation of Three-dimensional Netlike Mesoporous Alumina Membrane

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Netlike mesoporous alumina membrane with layers of controllable pore size is fabricated by anodization and following chemical etching. All the nanochannels in this mesoporous membrane are connected together. By adjusting the anodization conditions, a series of mesoporous alumina membrane can be successfully prepared.

Mesoporous solids are very important as catalysts and sorption media. However, the size distribution of pores in ordinary mesoporous materials, such as silica, is wide.[1] It is well known that the mesoporous materials with narrow-sized distribution of pores are more effective than those with large-sized distribution of pores.[2] It was an important achievement that a mesoporous solid with uniform channels (MCM-41) was synthesized by means of a liquid-crystal templating mechanism.[3] However, the fabrication of mesoporous solids with larger pore diameter is still a challenge, and considerable efforts have been devoted to this field. Recently, self-assembly technique was used for fabricating mesoporous material such as three-dimensional (3-D) supramolecular porphyrin and oxide porous mesostructure.[4,5]

Porous anodic alumina membrane has been studied for many years,[6–10] and the alumina membrane with dense arrays of straight channels can be obtained by a two-step anodization process.[11] Anodic alumina membrane with parallel Y-branched channels can be fabricated by the way of reducing the anodizing cell voltage by a factor of 0.71 in the anodization process.[12] Anodic alumina membrane was used widely as template for nanomaterial preparation. The pores in ordinary anodic alumina membrane were parallel and isolated from each other. However, alumina membrane with 3-D nanopores was more desirable in many fields such as filtration and catalysis.

Here, we report a novel method to prepare a 3-D mesoporous alumina membrane with controllable pore size. The mesoporous anodic alumina membrane was fabricated by adjusting applied cell voltage in anodization process followed with chemical etching. Samples collected at different steps were characterized by a Sirion 200 field-emission scanning electron microscope (FE-SEM) operated at 5 kV.

Before anodization, high-purity aluminum foils (99.999%) were degreased in acetone. Subsequently, the aluminum foils were annealed at 450 °C for 4 h and then electropolished in a 10:90 volume mixture of $HClO_4$ and C_2H_5OH for 3 min.[13] Anodization was conducted under the designed periodic cell voltage as shown in Figure 1. The cell voltage–time curve starts with a decreased straight line from 60 to 30 V in 10 min (t_a) and then followed by a steep arise sine curve from 30 to 60 V in 30 s (t_b). The t_a segment of the voltage–time curve contains two different parts, one is the high voltage part (t_c) and the other is low voltage part (t_d). The straight main stem channels are formed during the high-voltage part (t_c), and then the main channels branch into several small channels during the low-voltage part (t_d). In this step both the length of the main channels and the branched channels can be adjusted by controlling the time t_c and t_d. And also the thickness of interchannel wall among the branched channels can be decided by t_d for the branched channels grow toward each other in time t_d. By choosing an appropriate t_d, the thickness of interchannel wall among branched channels can be very thin. In the period of time t_b, some branched channels can grow as thick as the main stem channels formed at the period of time t_c, which become the main stem channels again, and others will stop growing by a self-organized mechanism.[14] By means of these repeated process, a layer-by-layer structure can be formed in the alumina membrane.

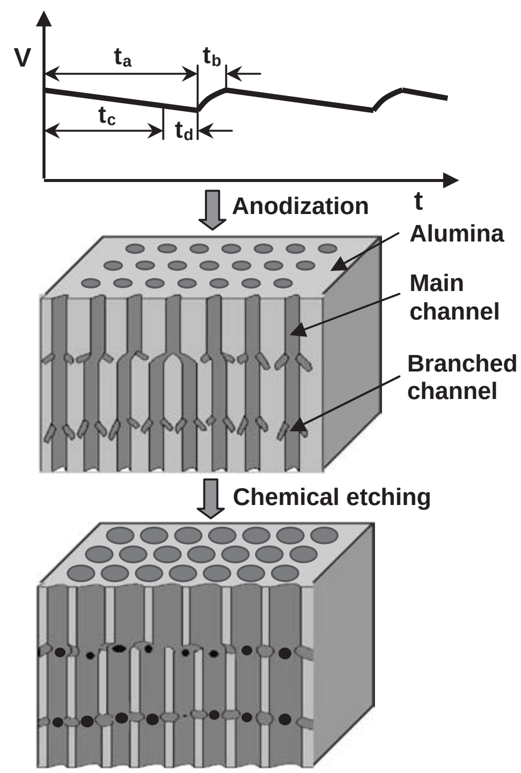

Figure 1. Schematic illustration of the synthetic process of the ordered netlike mesoporous anodic alumina membrane.

After anodization, the samples were etched in a 5 wt % aqueous phosphoric acid solution at 40 °C. After etching for a certain time, the alumina barrier among all the branched channels can be dissolved while the walls among the main channels remain, for the thickness of walls between the branched channels is thinner than those between the main channels. Finally, the desired 3-D

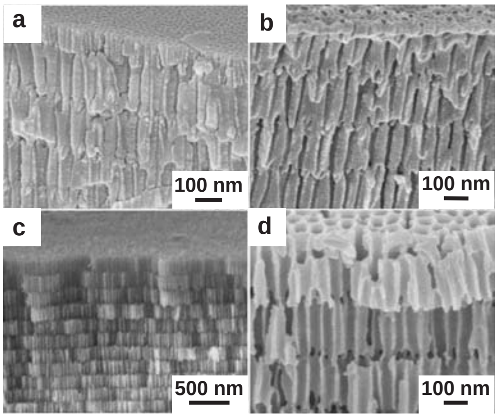

Figure 2. The FE-SEM image of the sample before chemical etching (a). After chemical etching in acid solution for 8 min (b). Low and high magnification of the sample after chemical etching for 15 min (c), (d). $t_a = 10$ min.

netlike mesoporous alumina membrane was fabricated successfully.

Figure 2 shows the FE-SEM images of the sample prepared with t_a of 10 min. Figure 2a is the image of sample before chemical etching in the last step. The alterative main channel layer and branched channel layer can be clearly observed, and the length between every adjacent layer is about 200 nm. Figure 2b shows the sample after chemical etching for 8 min. From Figure 2b we can see that all the channels are enlarged but still isolated from each other. The FE-SEM images of Figures 2c and 2d show low and high magnification of sample after chemical etching for 15 min. It can be seen that the remaining interchannel wall was very thin and that a 3-D netlike mesoporous structure was formed. In this netlike structure, the diameter of the main channel is about 50 nm, and the diameter of branched channel perpendicular to the main channel is between 20 to 50 nm. It can also be seen that all the channels in the alumina membrane are connected together after the chemical etching.

Since the length of the layer in this membrane corresponds to the time t_a, and since the diameter of the nanochannel can be modulated by the etching time, the type and concentration of the electrolyte, we can fabricate a series of netlike mesoporous alumina membranes by adjusting the anodization conditions. For example, we prepared another sample with the same method mentioned above but t_a of 20 min. Figure 3 shows the results observed from this sample, and it is evident that a same 3-D structure with layers of connected inner channels was formed. Comparing Figure 3 with Figure 2, we can find that the length of the layer is proportional to the t_a in anodization process.

In summary, we have successfully developed a practical method to fabricate the 3-D netlike mesoporous anodic alumina membrane with series of channel diameters and membrane sizes. The controllable experiments allow one to tailor the mesoporous structure formed in alumina membrane. For attractive properties of alumina matrix, this netlike mesoporous alumina membrane is expected to be important in those fields such as filtration, catalysis, and optoelectronics.

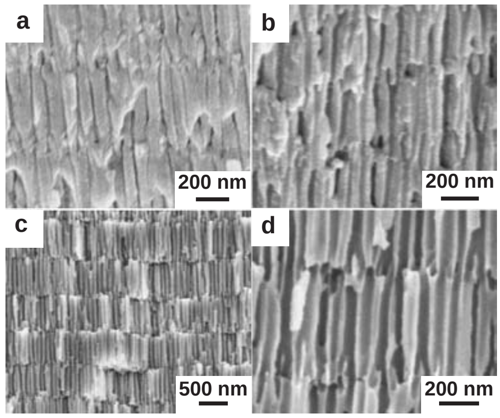

Figure 3. The FE-SEM image of the sample before chemical etching (a). After chemical etching in acid solution for 8 min (b). Low and high magnification of the sample after chemical etching for 15 min (c), (d). $t_a = 20$ min.

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