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Ordered SBA-15 Nanorod Arrays Inside a Porous Alumina Membrane

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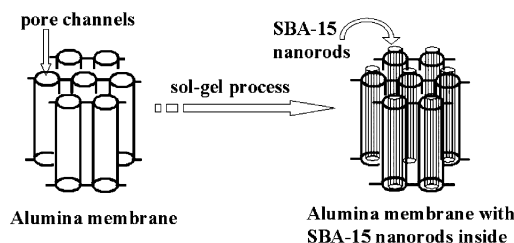
Mesoporous materials are a special type of nanomaterials with ordered arrays of uniform nanochannels. These materials have important applications in a wide variety of fields such as separation, catalysis, adsorption, advanced nanomaterials, etc.^{1–10} SBA-15 is by far the largest pore-size mesoporous material with highly ordered hexagonally arranged mesochannels, with thick walls, adjustable pore size from 3 to 30 nm, and high hydrothermal and thermal stability.^{11–15} It is expected to be useful in the synthesis of ultrafine nanorod arrays, protein separations, and highly efficient catalysis even just in its powder form.^{16–23} The potential widespread applications of SBA-15 warrant the need to synthesize orderly arranged, vertical, and industrially suitable SBA-15 nanorod arrays. So far, much attention has been paid to controlling the channel arrangement of mesoporous materials; however, the obtained channels normally lie in the plane of the substrate.^{24–26}

Porous alumina membranes have ordered and vertical one-dimensional (1D) channel structures. These membranes have stimulated a lot of interest in the scientific community for the growth of monodisperse and ordered 1D nanostructures within their pores, which serve as limiting templates.^{27–31} Until now, many nanorod arrays have been synthesized using porous alumina membrane as growth-limiting template.^{32–35} However, the pore sizes of alumina membrane are in the range of dozens of nanometers to several hundreds of nanometers, which limits its applications in the fabrication of nanodevices and bioseparation of small molecules. How to combine the advantages of the two types of materials to form a membrane with fine, vertical mesochannels with a size of about a few nanometers is of much importance and would provide wider applications in nanodevice fabrication, biomacromolecule separations, and more extensive applications in many other fields.

Herein, we report for the first time the synthesis of mesoporous material (SBA-15) nanorod arrays inside an ordered porous alumina membrane through a simple sol–gel method. The formed SBA-15 nanorods have been arranged to form hexagonal arrays by the limitation of pores of alumina membrane, and their diameters are in the range of 170–220 nm, in agreement with the pore sizes of the alumina membrane we used. These SBA-15 nanorods themselves have ordered hexagonal mesochannels with a channel size of about 6 nm, which is the typical pore size of SBA-15. Thus, the synthesized alumina membrane with mesoporous SBA-15 inside combines the advantages of porous alumina membranes and mesoporous SBA-15, providing fine and vertical mesochannels, parallel to the channels of the alumina membrane (Scheme 1). This composite membrane may serve as a new and efficient mold and find wider applications in nanodevice fabrication and biomacromolecule separation.

The synthesis of SBA-15 is similar to a published procedure³⁶ using Pluronic P123 (EO₂₀PO₇₀EO₂₀, M_{av} = 5800, Aldrich) and tetraethyl orthosilicate (TEOS, 98%, Aldrich) under acidic condi-

Scheme 1. Structures of Alumina Membrane and Alumina Membrane with SBA-15 Nanorods Inside



tions. For the synthesis of SBA-15 nanorod arrays inside a porous alumina membrane, a piece of porous alumina membrane was put in the middle of a sol solution⁶ of mesoporous SBA-15 composition at room temperature (about 25 °C) for 20 h. During this period, the sol infiltrated the pores of alumina membrane and changed to gel. A small amount of liquid paraffin wax to a thickness of 1 mm was put on the gel and then heated at 60 °C for 20 h. After that, the liquid paraffin was removed, and then the alumina membrane was calcined at 540 °C in air for 6 h. Some of the samples were ground for characterizations.

The mesoporous structure of the obtained sample was confirmed by powder small-angle X-ray diffraction (XRD) (See Supporting Information). Three diffraction peaks can be indexed as (100), (110), and (200) reflections, respectively, associated with *P6mm* hexagonal symmetry with (100) plane spacing of 9.30 nm. This pattern is just like the typical small-angle XRD pattern of SBA-15 powder,^{11,23} indicating the formation of SBA-15 inside the porous alumina membrane. The small-angle XRD of the sample has also been done in the plane of the alumina membrane with SBA-15 nanorods. There are no distinct peaks in the small-angle XRD pattern, which means that there are no ordered mesochannels parallel to the membrane plane.

The product morphology was obtained by scanning electron microscopy (SEM). Figures 1a and 1b display the side view SEM images of the alumina membrane with SBA-15, evidently showing that uniform nanorods are grown inside the pores of the alumina membrane. The diameters of the nanorods range from 200 to 250 nm. Top view SEM images (Figures 1c and 1d) more clearly show that a number of nanorods grew inside the hexagonally arranged pore arrays of alumina. These results clearly indicate that ordered SBA-15 nanorod arrays formed inside the channels of the alumina membrane.

The product was further characterized by transmission electron microscopy (TEM) to observe the mesoporous structures. Figures 2a and 2b are typical TEM images of the obtained product, clearly showing that the nanorods have parallel-arranged channels with a periodic spacing of ~9 nm, which is the typical spacing of SBA-15 and also equal to the (100) plane spacing obtained from the small-angle XRD pattern. The pore diameters of the mesochannel of SBA-15 nanorods are about ~6 nm, which is the typical pore size of SBA-15 mesostructures. The diameters of these SBA-15

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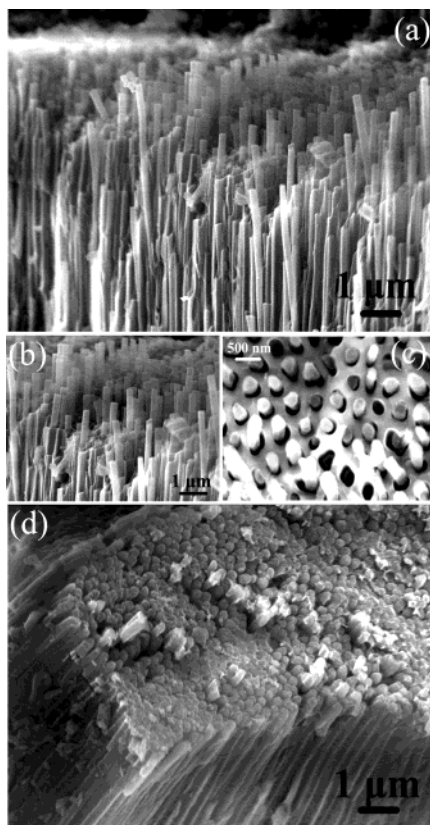


Figure 1. SEM images of the obtained alumina membrane with SBA-15 inside. (a, b) Side view SEM images. (c, d) Top view SEM images.

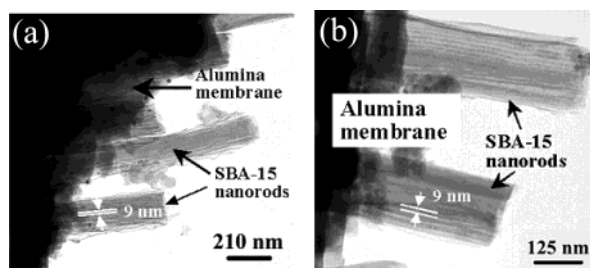


Figure 2. TEM images of the obtained sample.

nanorods are in the range of 170–220 nm, which is consistent with the pore sizes of the alumina membrane we used and at the same time confirms the limiting function of the alumina membrane in the synthesis of SBA-15 nanorod arrays. From TEM observation, almost all the observed rodlike grains have the parallel-arranged mesochannels parallel to their growth direction ($> 90\%$). This means that the SBA-15 nanorods grown inside the porous alumina membrane have a mesochannel orientation perpendicular to the alumina membrane. It is obvious that the TEM results are consistent with those obtained from small-angle XRD and SEM characterizations and further confirm the formation of the SBA-15 nanorod arrays in the pores of alumina membrane that are used as a template.

In summary, we report a simple method for the synthesis of SBA-15 nanorod arrays inside the commercially available porous alumina membrane. The formed SBA-15 appears to have vertical channels, parallel to those of the porous alumina membrane. The alumina membrane with SBA-15 inside thus has the advantages of porous alumina membranes and mesoporous material and may be useful for extending the applications of mesoporous materials in nanodevice fabrication and biomacromolecule separation.

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Supporting Information Available: Small-angle XRD pattern of the obtained sample. See any current masthead page for ordering information and Web access instructions.

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