1D Mesostructured Silica Materials

Template Synthesis of Uniform 1D Mesostructured Silica Materials and Their Arrays in Anodic Alumina Membranes**

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Mesostructured materials are useful in many fields such as in catalysis, separation, sensors, and optical materials. Since the pioneering work by Mobil scientists,[1] template synthesis has been extensively used to prepare mesostructured materials from several to tens of nanometers long.[2] Hereafter the mesostructured materials have been processed into various macroscopic morphologies such as spheres[3,4] and thin films.[5,6]

Besides, 1D mesostructured materials are interesting because of their hierarchically organized structure and potential applications such as waveguides and laser materials. Mesostructured silica fibers have been grown in a two-phase system.[7,8] They can also be prepared by spinning.[9] Mesostructured silica tubes have been obtained at an aqueous–oil (or air) interface.[8d,e,10] Recently, "tubules-within-a-tubule" hierarchical silica tubes were prepared by acidification induced membrane curvature.[11] However, if the acidification rate is fast, microparticles are unavoidably formed. It remains a challenge to control the diameter and aspect ratio of 1D mesostructured materials.

Well-distributed tubular porous media such as porous anodic alumina membranes have been extensively used as templates to prepare uniform 1D materials with controlled diameter and aspect ratio.[12] Recent work has shown the method's simplicity in preparing polymer nanotubes from polymer melts or solutions by a preferential wetting mechanism.[13] It is important to render the 1D materials a hierarchical structure.

Herein we report the preparation of 1D hierarchically mesostructured silica materials and their arrays in porous anodic alumina membranes. Silica nanotubes and nanofibers can be obtained by varying the pore-wall wettability. Both the interior cavity of the tubes and the mesopores can be used as mesocontainers to incorporate active components forming 1D nanocomposites.

The alumina membrane used became transparent after being immersed in the sol for 5 min, which means the pores were completely filled. After the sol–gel process induced by solvent evaporation, 1D mesostructured silica materials formed in the pores and arranged in an ordered array. When the alumina membranes without modification were used, silica preferentially coated the pore wall resulting in the formation of nanotubes. After the removal of the surfactant by calcination and the alumina with hydrochloric acid, long uniform silica nanotubes and their ordered arrays were obtained (Figure 1a and b). The interior cavity is clearly discerned in the broken nanotubes (inset Figure 1b). The sheath thickness is 50 nm, and the cavity diameter is 150 nm. The sheath became thinner by lowering the sol concentration. The as-prepared silica before calcination is also tubular, thus confirming that the interior cavity does not originate from contraction during calcination. The sheath thickness was less influenced by prolonging the immersion time, which is in contrast to that previously reported.[12] It is time consuming to prepare silica fibers by using the unmodified alumina

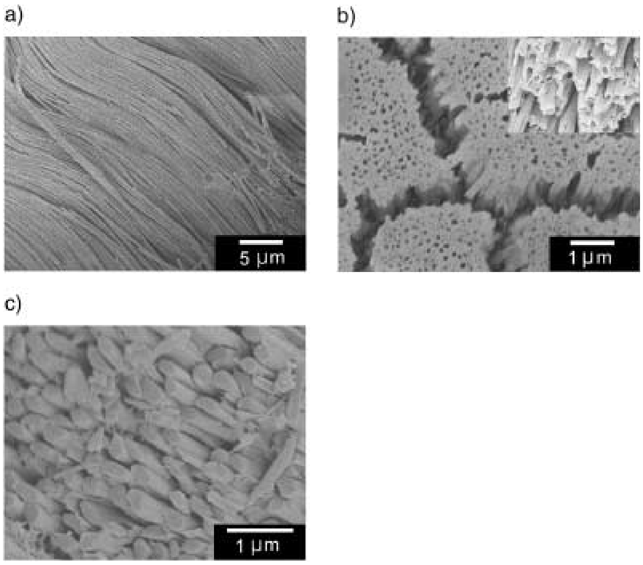

Figure 1. Scanning electron micrographs of 1D mesostructured silica materials and their arrays after being calcined at 450 °C for 3 h. a) Side and b) top views of the mesostructured silica tubular arrays prepared in the porous alumina membrane. c) Top view of the mesostructured silica fibril arrays prepared in the hydrophobically modified porous alumina membrane.

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membrane because the membrane has to be immersed in the sol and undergo the whole bulk sol–gel process for a few days. As an alternative, we have developed a new method to prepare solid mesostructured-silica nanofibers and their arrays by exposing the sol-filled hydrophobically modified alumina membrane[14] to air. The diameter of the resulting nanofiber is about 250 nm (Figure 1c). The process time is substantially reduced from days to hours.

The ordered arrays were easily broken into 1D individuals by ultrasonication. As shown in Figure 2a, uniform mesopores of about 12 nm in diameter are hexagonally arranged over the whole nanotube sheath. The pore size decreases to 8–9 nm in diameter after calcination at high temperature above 600 °C. The ordered structure is preserved even at 900 °C. For the nanofibers, the center area looks dark with the ordered porous structure discernable at the edge (Figure 2b) with the diameters of the pores being about 7 nm. The *d* spacings of the mesostructures in the silica tubes and fibers (see Supporting Information) are 12.3 nm and 9.8 nm respectively, which are consistent with TEM observations. The difference in the sizes of the pores found in the tubes and in the fibers is likely to be related to the pore-wall wettability and the sol–gel starting sites. Hexagonally ordered pores can also be found in the whole longitudinal ultra-microtomed sections of the tubes and fibers (see Supporting Information). Circular structures are found in the ultra-microtomed cross sections (Figure 2c, d), which is similar to the mesostructured fibers reported.[8b–d] The fingerprint-like structure (Figure 2c) results from the deformation of the concentric circular structure of the nanotubes owing to the stress during microtoming. The nanotubes and nanofibers have high specific surface areas and large pore volumes,[15] thus indicating the mesopores are interconnected. With an increase in surfactant concentration,

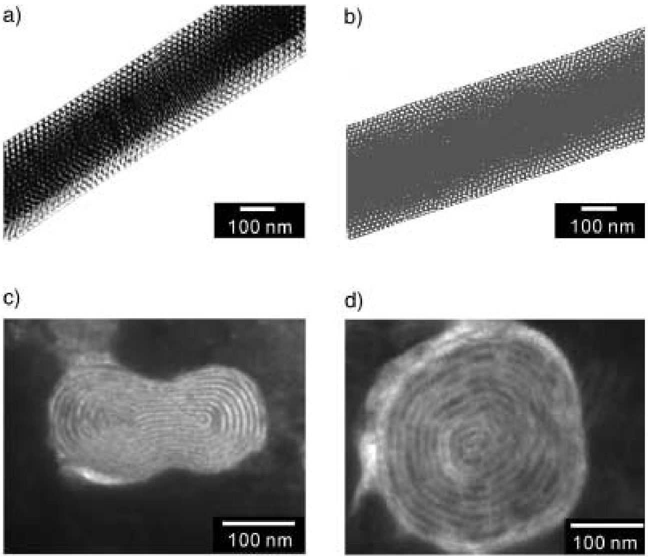

Figure 2. Transmission electron micrographs of the 1D mesostructured silica materials after being calcined at 450 °C for 3 h. a) b) Side views of the mesostructured silica nanotube and nanofiber prepared at Pluronic F-127/TEOS (wt/wt 1:3.2) by using the porous alumina membrane and the hydrophobically modified alumina membrane, respectively. c) d) Ultramicrotomed cross-sections of the same mesostructured silica nanotube (a) and nanofiber (b).

some morphologies of coexisting pores and stripes, and parallel stripes along the longitudinal tube axis are found (see Supporting Information). If the surfactant concentration is decreased by 20 %, the mesopores are disordered.

The alumina membrane with the pore wall that has been coated with mesostructured silica tubes becomes a new well-distributed tubular membrane. A variety of 1D materials can be prepared in the new membrane, thus forming 1D mesostructured silica-sheathed core hierarchical composites and their arrays. As an example, mesoporous silica-sheathed titania nanofibers and their arrays were prepared to demonstrate the methodology. The alumina membrane filled with mesostructured silica tubes was immersed in pure tetrabutyltianate (TBT) in a sealed system for 12 h at ambient temperature. After the sol–gel process was complete, the surfactant was removed by calcination at 450 °C and the silica nanotubes (Figure 1b) had become solid nanofibers similar to those of Figure 1c. A TEM image of the product (Figure 3a) shows the black interior. The area selected electron-diffraction pattern indicated that the anatase phase was formed. The composite-fiber edge is smooth and the ordered mesoporous structure preserved. When the composite was calcined at high temperature, for example 600 °C, the titania transformed into coexisting crystals of anatase and rutile, and contracted remarkably. The interior titania nanofibers could slip out of the broken shorter tubes (see Supporting Information), whilst the mesoporous structure of the sheath kept the same appearance as that before the loading of the titania (Figure 2a). This finding confirms that titania predominantly forms in the interior cavity of the silica nanotubes. When a membrane coated with mesoporous silica nanotubes after calcination was used, titania was formed both in the interior cavity and in the mesopores of the silica sheath (Figure 3b). Many 1D nanocomposites based on silica nanotubes and nanofibers may be prepared by incorporating functional components into the mesopores.[16]

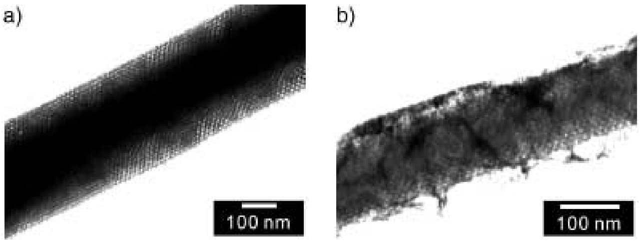

Figure 3. Transmission electron micrographs of the calcined (450 °C) mesostructured silica-sheathed titania composite nanofibers prepared by using the porous alumina membranes coated with different nanotubes. a) With surfactant/silica nanotubes. b) With mesoporous silica nanotubes.

In summary, 1D mesostructured silica materials and their ordered arrays have been prepared in anodic alumina membranes. By adjusting the wettability of the alumina pore wall, nanofibers and nanotubes are prepared in a controlled way. Both mesopores and tubular cavities can be incorporated with functional materials forming 1D hierarchical nanocomposites and their arrays.

Experimental Section

1D mesostructured silica materials and their arrays: Anodic alumina membranes (Anodisc 47) about 60 μm thick were purchased from Whatman International Ltd. The average pore diameter was 250 nm as specified. They were hydrophobically modified with octachlorosilane by heating to reflux at 60 °C for 3 h under decreased pressure.[14] A block copolymer Pluronic F-127 ($EO_{106}PO_{70}EO_{106}$) was purchased from BASF and used as received. A typical preparation process was given to form a silica–surfactant sol. Pluronic F-127 (1.0 g) was dissolved in ethanol (2.3 g) followed by the addition of nitric acid (0.54 g 0.3 $mol L^{-1}$)to the stirring mixture. Tetraethyl orthosilicate (TEOS; 3.2 g) was added to the mixture, which was stirred for 2 h at room temperature forming the sol. Two typical anodic alumina membranes before and after modification were then immersed in the sol for 12 h to ensure complete infiltration. After the membranes had been taken out from the sol, the residual sol on the membrane surface was completely scratched away. The sol–gel process was undertaken in air for 2 h followed by the aging at 60 °C for 1 h. The silica filled alumina membranes were calcined at 450 °C for 3 h to remove the surfactant. Alumina membranes were dissolved in hydrochloric acid (5 $mol L^{-1}$) at 60 °C and the residual product was washed with a large amount of water. 1D materials were obtained by ultrasonication.

Mesostructured silica-sheathed titania nanofibers: The alumina membrane filled with mesostructured silica tubes was immersed in pure TBT in a sealed system at ambient temperature for 12 h, the TBT swollen composite was then exposed to a moist atmosphere about 90 % relative humidity at 25 °C for 48 h to allow the TBT sol–gel process. The surfactant was removed by calcination at 450 °C for 3 h.

Characterization: JEOL JSM-6700F field emission scanning electron microscope at the acceleration voltage of 3 kV was used to record the morphology. The mesostructured silica materials were suspended in ethanol after ultrasonication for 15 min. A drop of the suspension was placed on a carbon-coated copper grid for transmission electron microscopy observation using JEM-100CX with EDX apparatus at the acceleration voltage of 75 kV. Ultramicrotomed sections were obtained by cutting the mesostructured samples embedded in copper followed by ion milling. A JEOL JEM-2010 electron microscope at the acceleration voltage of 200 kV was used to observe the section morphology. Rigaku D/max-2500 wide angle goniometer was used to measure the interpore distance of the samples. Nitrogen adsorption isothermal was performed on a Micromeritics OMNISORP 100CX porosimeter.

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[15] The silica nanotube (Figure 2 a) has a BET specific surface area of 420 $m^2 g^{-1}$ and pore volume of 0.59 $cm^3 g^{-1}$. The nanofiber (Figure 2 b) has a BET specific surface area of 453 $m^2 g^{-1}$ and pore volume of 0.42 $cm^3 g^{-1}$.

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