Electronic Supplementary Information

Vapor phase synthesis of mesoporous silica rods within the pores of alumina membrane

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Experimental

Materials: Tetraethyl orthosilicate (TEOS), phosphoric acid (85 wt%), hydrochloric acid (35~37 wt%) and ethanol (99.5 wt%) were obtained from Wako Pure Chemical Industries, Ltd. Hexadecyltrimethylammonium bromide (CTAB) was obtained from Tokyo Chemical Industry (TCI). Pluronic P123 was obtained from BASF. Pluronic F127 was obtained from Sigma-Aldrich. All the chemicals were used as received without any further purification. Anodic alumina membranes (AAMs) (Membrane diameter is ca. 47 mm, thickness = ca. 60 μm. Here, the pore diameter is ca. 100 nm in one side (the corresponding thickness is ca. 1μm), the other side pore diameter is ca. 200 nm (the corresponding thickness is ca. 59 μm)) were obtained from Whatman. During the whole experiment, the Milliq-Ultra-Pure-Water system treated water was used.

Synthesis of porous alumina membrane with mesoporous rods: CTAB, P123 and F127 were used as surfactants for mesostructured directing agents. Typically, a certain mass of corresponding surfactant (1.2 g for CTAB, 1.5 g for P123 and 1 g for F127) was dissolved into 5 g 0.2 M HCl aqueous solution. One piece of AAM was set on an ordinary membrane filtration apparatus and 1 mL above prepared surfactant aqueous solution was poured onto the AAM. Then, aspiration were applied by using an aspirator (Ulvac, Model MDA-15), so that the surfactant solution penetrated into the columnar alumina pores. After all the surfactant solution had completely penetrated into the alumina pores, the aspiration was further maintained for several seconds. Hereafter, the AAM with surfactant solution was put into a closed polytetrafluoroethylene (PTFE) vessel, into which 0.25 mL TEOS for each piece of AAM with surfactant solution was added in advance. The closed PTFE vessel was placed into 373 K oven to carry out vapor-deposition hydrolysis process for 2h. Finally, the surfactant was removed by calcination at 823 K for 5 h. For sample nomination, AAM-MS-C, AAM-MS-P and AAM-MS-F represent AAM with mesoporous silica using C (CTAB), P (P123) and F (F127) as mesostructure directing agents, respectively. After the acidic removal of AAM, the above sample names are correspondingly changed into MS-C, MS-P and MS-F, respectively.

Characterization: Scanning electron microscopic (SEM) images were obtained with a Hitachi-4300 field emission electron microscope (FE-SEM). In order to get a clear cross-sectional view, the alumina membrane was slightly etched by 10 wt% phosphoric acid solution for 1 h. The cleavage membrane was fixed on a SEM stage using carbon tapes and the SEM measurements performed after deposition of a thin Pt/Pd layer using an ion-sputter (Vacuum Device Inc., Model MSP-10, Japan). Small-angle X-ray diffraction (SAXRD) patterns were recorded by MAC Science/Bruker M21X diffractometer with Cu Kα radiation (45 kV and 250 mA). The scanning rate is 0.3° min^{-1}. In order to get clear XRD patterns, each sample for XRD measurement was carried out after the removal of AAM. Transmission electron microscopic (TEM) images were taken by a JEM-2000EX Ⅱ or Topcon EM-002B with an accelerating voltage of 200 kV. Samples for TEM were prepared by the following methods: 1. The AAM with mesoporous silica rods was immersed in 10 wt% phosphoric acid solution for 10 h to completely remove the alumina membrane. The obtained mesoporous silica fibers (powder) were dispersed in ethanol by ultrasonication, and then mounted on a Cu grid. 2. For the plan view of AAM with mesoporous silica rods, the samples were firstly prepared by dimple grinding then followed by Ar ion polishing. Nitrogen adsorption-desorption measurements at 77 K were carried out on Micromeritics ASAP 2020 porosimeters. Before measurements, the samples, which mass included the AAM, were degassed under 413 K for 10 h.
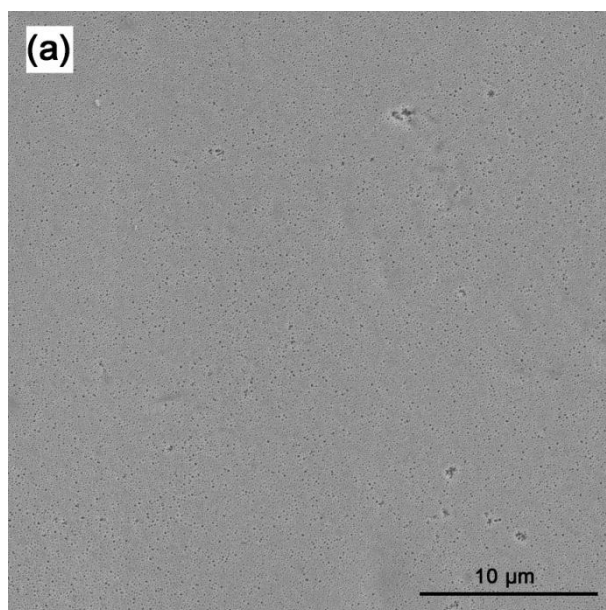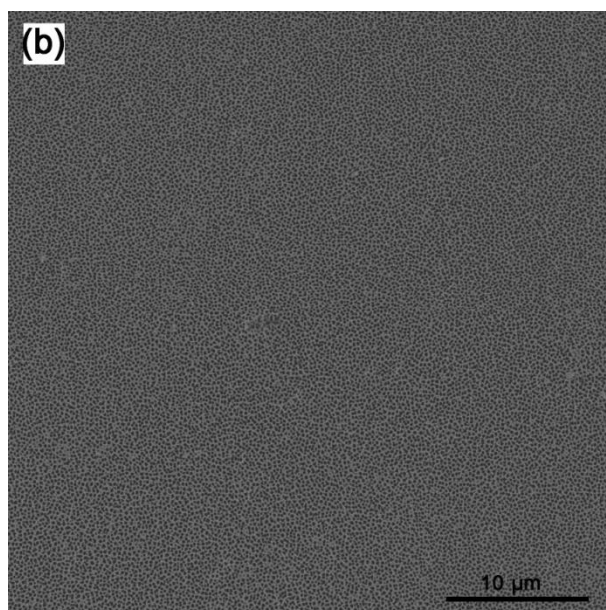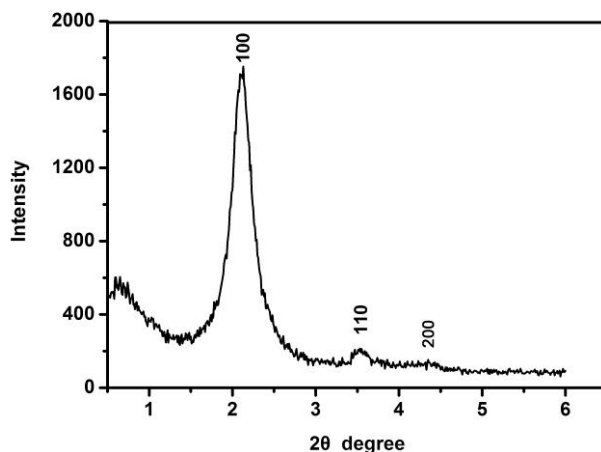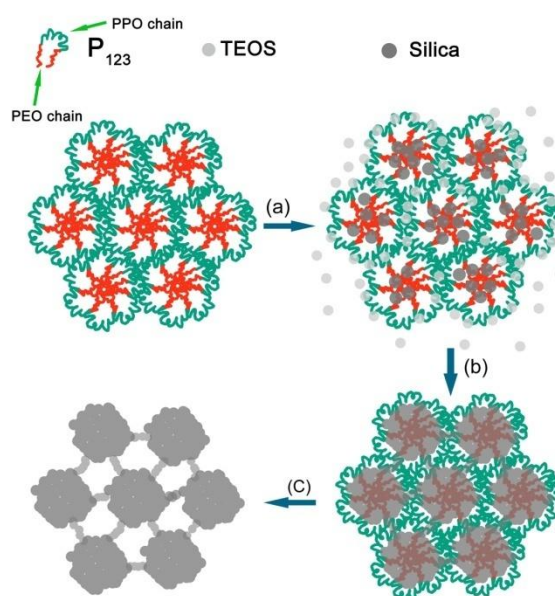
Figure 1. The plan view of the AAM-MS-C (a) 100 nm side and (b) 200 nm side. Rarely mesoporous silica layer or clusters can be seen.
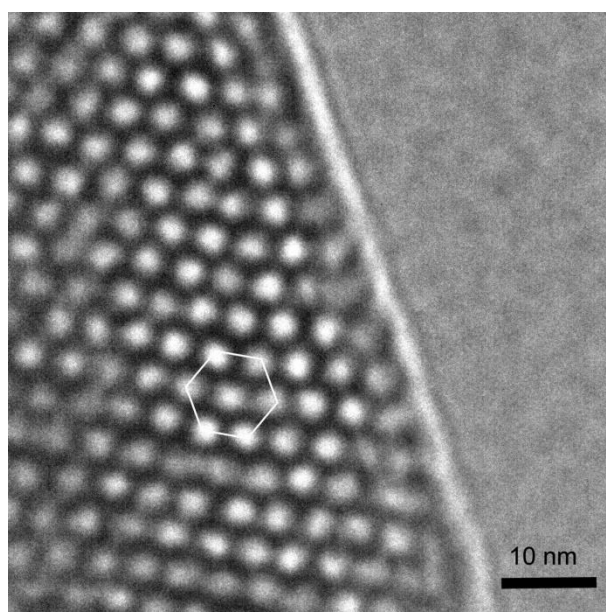

Figure 2. High resolution TEM image of MS-C. The image shows highly hexagonal ordered mesopores.
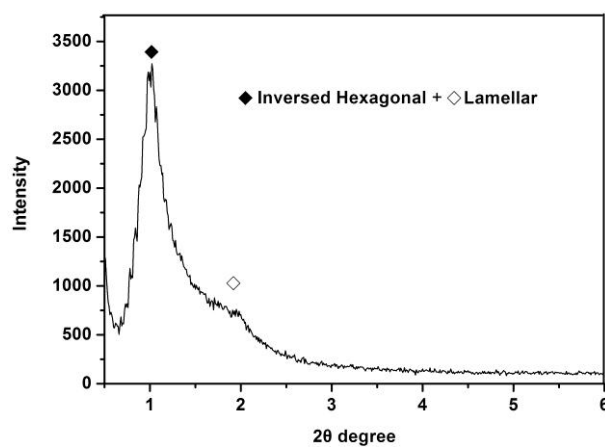
Figure 3. SAXRD pattern of MS-C. And the pattern is typical for hexagonal type.


Figure 4 Shematic illustration of the formation mechanism of reversed hexagonal mesostructure by reversed hexagonal micellar network. (a) TEOS vapor is introduced into the PPO chain area due to the relative hydrophobicity, and then TEOS gradually diffuse into PEO area and simultaneously hydrolyze into silica under HCl catalysis, (b) after the completion of silica condensation, the mesostructured hybrid composite is obtained, and (c) the surfactant was removed by calcination.
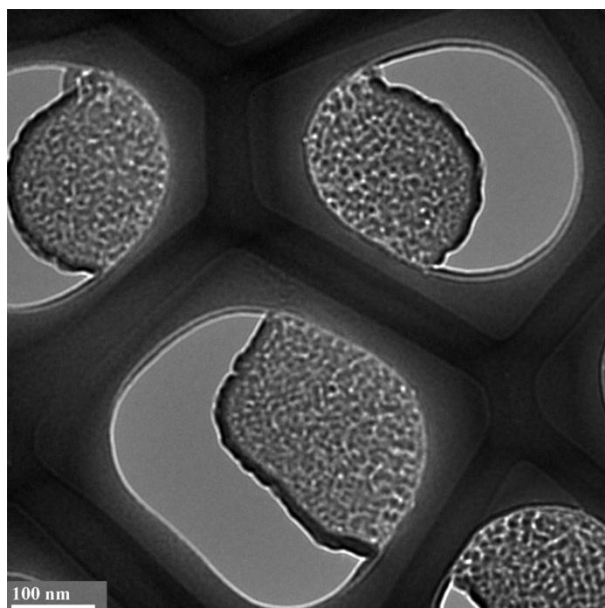
Figure 5 TEM plan-view image of AAM-MS-P. The reversed hexagonal mesostructure collapsed due to lack of a sufficiently strong three-dimensional network,[1] and the collapse should happen during the Ar ion polishing process.

Figure 6. SAXRD pattern of MS-P. Here, mesostructure dominantly is inversed hexagonal and also there is some lamellar.[2]
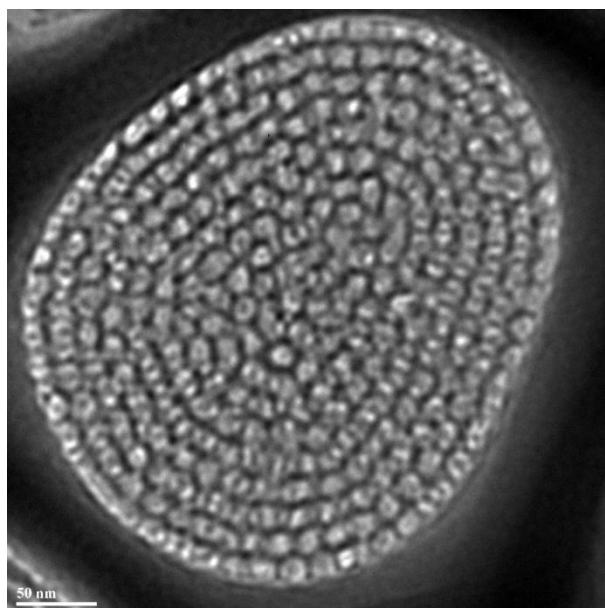
Figure 7 TEM plan-view image of AAM-MS-F along the [111] direction.[3]
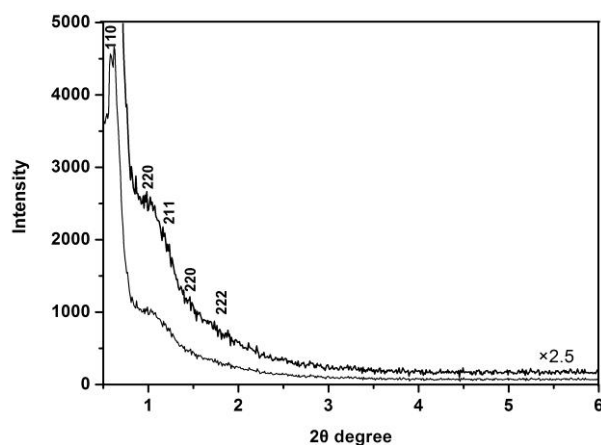
Figure 8. SAXRD pattern of MS-F. The pattern well match that of $Im\bar{3}m$.[4]

Reference

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