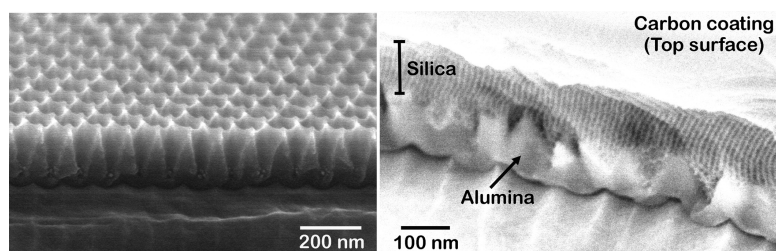


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Evolution of Standing Mesochannels on Porous Anodic Alumina Substrates with Designed Conical Holes

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Abstract: We report the formation of standing mesochannels simply by spin-coating a precursor solution onto a PAA (porous anodic alumina) substrate with designed conical holes, utilizing exactly the same precursors and reaction conditions that form two-dimensional (2D) hexagonal mesoporous SBA-15-type films. When the aspect ratios of the conical holes are lower, the sponge-like mesopores are generated within the conical holes. Such a formation of sponge-like mesostructures truly acts as a trigger for the evolution of perpendicularly oriented and tilted mesochannels. On the other hand, when the PAA substrates with high-aspect cones are used, the mesochannels are stacked like a doughnut within the conical holes, which leads to parallel orientations of the mesochannels in the continuous film region.

1. Introduction

The self-organization of molecules is currently receiving attention because of its potential for applications in the development of the next generation of nanoarchitected materials. Mesoporous materials created by the self-organization of surfactants and inorganic species have attracted enthusiastic interest as a key material in nanotechnology since their discovery in the early 1990s.¹ Ordered mesoporous materials with various morphologies, including powders, monoliths, spheres, rods, fibers, and films, have been reported so far.² In particular, mesoporous films with regular mesoporous structures and high surface areas have attracted much attention because of their potential applications to various optical and electronic devices.^{3,4} Several kinds of unique and ordered mesostructures (e.g., lamellar, 2D hexagonal, 3D hexagonal, 3D bicontinuous cubic

structures) with various compositions have been designed. Among them, the 2D hexagonal mesoporous structure ($p6mm$) composed of hexagonally packed mesochannels has been utilized as a host material for the encapsulation of functional molecules and for the fabrication of metal nanowires with unusual properties.

Mesoporous films have been prepared either by evaporation-induced self-assembly (EISA)³ or by hydrothermal deposition, which is based on the heterogeneous nucleation and growth of mesostructured silica seeds.⁴ In general, mesochannels in 2D hexagonally ordered mesoporous films run parallel to the substrate, but mesoporous films with perpendicular mesochannels should offer different properties. At this point, various attempts (e.g., the nanophase separation of eutectic materials,⁵ the microphase separation of block copolymers,⁶ the use of modified surfaces,⁷ the confined effect,⁸ the application of

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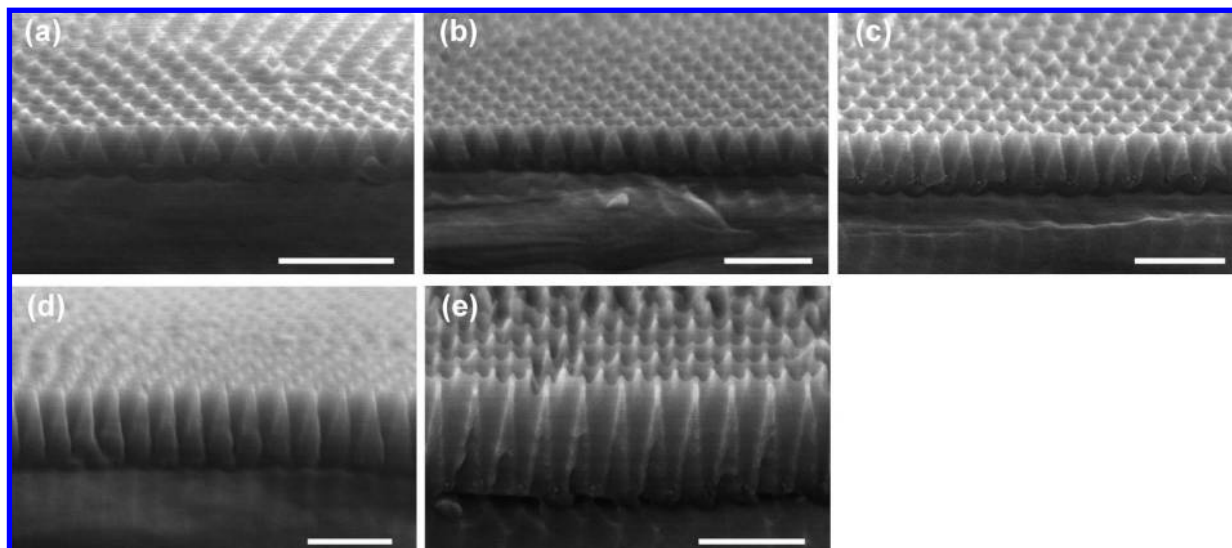


Figure 1. Cross-sectional SEM images of the PAA substrates with the conical holes with different aspect ratios. The height of the conical holes was varied from (a) 100 nm to (b) 115 nm, (c) 160 nm, (d) 245 nm, and (e) 325 nm, respectively. Aspect ratios were (a) 1.00, (b) 1.15, (c) 1.60, (d) 2.45, and (e) 3.25, respectively. Scale bar is 300 nm.

electric and magnetic fields,⁹ and ternary surfactant systems¹⁰) to generate perpendicular alignments of mesochannels have been reported. However, these previous systems had several problems, including the limitation of morphologies to monoliths and platelets, complex preparation conditions, and the requirement of precise control of the pore size and film thickness.

In this paper, we report the successful formation of standing mesochannels simply by spin-coating a precursor solution onto a PAA film with conical holes. The formation of standing mesochannels is thought to be based on an “oriented growth” mechanism induced by sponge-like structures formed within conical holes. In other words, the presence of the sponge-like mesostructures truly acts as a trigger for the evolution of perpendicularly oriented and tilted mesochannels. Here, we demonstrate the critical effect of nanoarchitected substrates on mesochannel orientations by using several types of PAA films with different aspect ratios. This is a unique approach for the orientation control of the self-organization of surfactants, utilizing the intrinsic mutual interaction of surfactants without the application of forced manipulations, such as magnetic and electric processing. Very recently, it was proved that the presence of the standing mesochannels (including tilted mesochannels) can contribute effective diffusion of guest species into the film, from the detailed investigation on vertical connectivity and accessibility of mesochannels to the outside by measuring a positronium time-of-flight.¹¹ Therefore, we strongly believe that our new class of films represents a significant breakthrough in mesoporous materials science and could lead to a vast range of applications, such as highly

Table 1. Preparative Conditions of the PAA Substrates Having Conical Holes with Different Aspect Ratios

PAA substrates (aspect ratios)	repeated times of anodization step	anodization time (s) (anodization time at the first step (s))	pore widening time (s)
substrate A (1.00)	4 times	20 (25)	720
substrate B (1.15)	4 times	25 (30)	720
substrate C (1.60)	4 times	40 (50)	720
substrate D (2.45)	4 times	55 (65)	720
substrate E (3.25)	7 times	50 (60)	470

sensitive chemical sensors, highly selective separation, and ultrahigh-density magnetic recording media.

2. Experimental Section

2.1. Preparation of PAA Substrates Having Conical Holes with Different Aspect Ratios. PAA substrates with conical holes and different aspect ratios were prepared by a multistep anodization and leaching process, which is described as follows. A pure aluminum was electrochemically polished in a solution composed of perchloric acid and ethanol. The aluminum was then washed in ethanol and pure water. For the anodization, a carbon electrode was used as the cathodic electrode. The aluminum was anodized at 40 V in a 0.3 M oxalic acid solution at 16 °C. Long-period anodization steps were performed for 10 h each to produce a hexagonally ordered PAA. The alumina layer was then dissolved in a mixed solution of 6 vol % phosphoric and 1.8 wt % chromic acids.

To fabricate the conical pores on this substrate, repeated and alternating anodization and pore widening treatments were performed. Each anodization step was conducted at 40 V in a 0.3 M oxalic acid solution at 9 °C. After that, the holes were widened by immersion in a 5 vol % phosphoric acid solution at 30 °C. The preparatory conditions are shown in Table 1. For comparison, a PAA substrate with straight cylindrical holes was also prepared.

2.2. Coating of Mesoporous Silica Films on the PAA Substrate. A P123-based precursor solution was uniformly spread by spin-coating on the PAA film. To prepare the precursor solution, 5.2 g of tetraethyl orthosilicate (TEOS, purity 98%, Aldrich), 6.0 g of ethanol, and a 2.7 g of diluted HCl (pH 2) solution were mixed. After stirring for 20 min, 1.4 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, Aldrich) and 4.0 g of ethanol were added and stirred for 3 h. The

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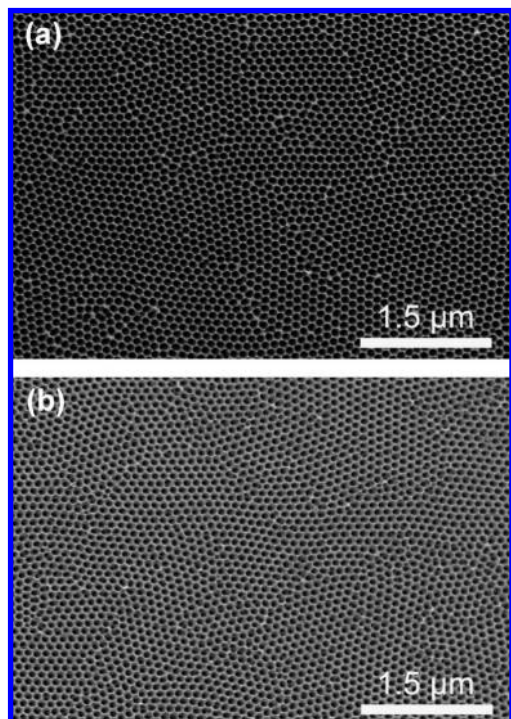


Figure 2. Top surface SEM images of the PAA substrates with the conical holes with different aspect ratios. Aspect ratios were (a) 1.60 and (b) 3.25, respectively.

as-prepared film was dried for 1 h at room temperature. After drying, the as-prepared film was calcined at 400 °C for 4 h.

3. Results and Discussion

Figure 1 shows the cross-sectional SEM images of the PAA substrates with conical holes with different aspect ratios. For all the PAA films, the distances between the neighboring holes were about 100 nm. The open pores of the conical holes were almost the same size (100 nm). The height of the conical holes varied from 100 to 115 nm, 160 nm, 245 nm, and 325 nm. The aspect ratios were 1.00, 1.15, 1.60, 2.45, and 3.25, respectively. The periodic honeycomb arrangement of the inverted conical holes was observable over the entire area (Figure 2). The domain size was measured to be micrometer scale. Consequently, the PAA substrates with different aspect ratios were prepared using an excellent anodization process. After coating with a mesoporous silica layer followed by calcination, continuous films with uniform thickness were coated on the PAA substrates. The silica layers were densely filled within the conical holes, as confirmed by the cross-sectional SEM images (Figure S1).

When the PAA substrate (substrate C) with an aspect ratio of 1.60 was used, all the mesochannels in the film clearly stood out, as was confirmed by a cross-sectional SEM image (Figure 3a, S2-a, and S2-b). On the top-surface of the film, the honeycomb arrangements of the uniform mesopores were clearly observed, indicating that the tubular mesochannels were passed through the outside (Figure 3b). In some domains (indicated by the arrows circles in the Figure 3b), the mesochannels were observed. However, there are honeycombs-like mesopores among the mesochannels, suggesting that mesochannels are tilted. The distance between the mesochannels was measured to be about 10 nm from Figure 3c. This value is similar as those of mesoporous silica films prepared by P123 molecules.^{9c,d} Both the cross-sectional (Figures 3a, S2-a, and S2-b) and the top-

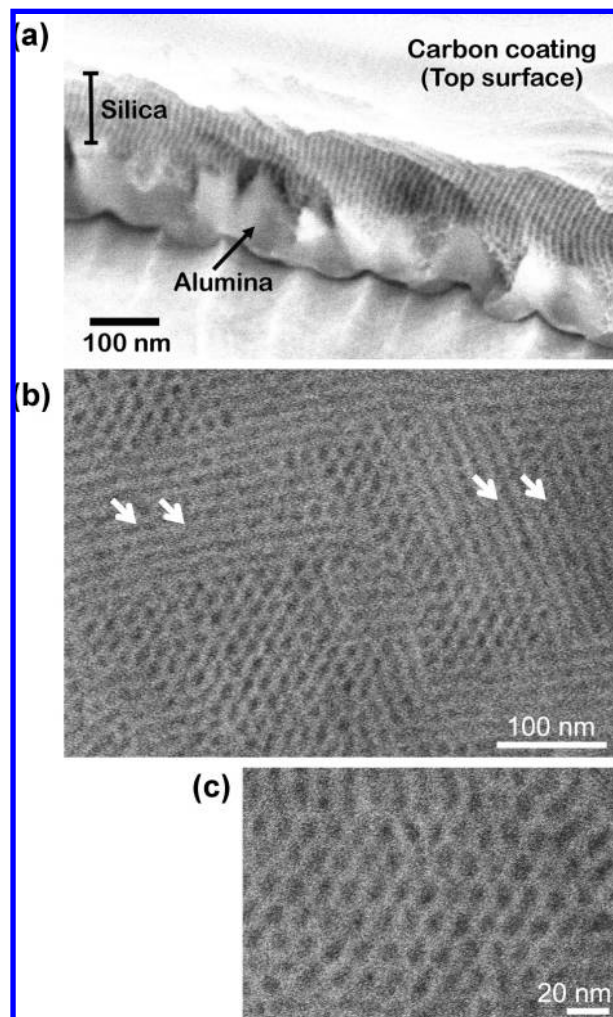


Figure 3. Highly magnified SEM images of mesoporous silica film on the PAA substrate (substrate C). (a) Cross-sectional SEM image. The top surface of the film was coated by carbon. (b) Top-surface SEM images. Mesochannels with honeycomb-like mesopores are indicated by the arrows. (c) Enlarged SEM image.

surface SEM images (panels b and c of Figure 3) can nicely support the presence of perpendicular orientations.

From the cross-sectional TEM images, tilted mesochannels were observable in some domains (Figure 4a). The domain boundaries were clearly highlighted. From TEM observations over a wide area, the distribution of the alignment degree was calculated. More than 70% of the mesochannels were tilted, and the other mesochannels directly faced the substrate.

Although cross-sectional TEM and SEM are important tools for the direct visualization of the alignment of mesochannels in films, the images provide only local information. In order to confirm the macroscopic information on the alignment of mesochannels, a conventional θ - 2θ scanning XRD measurement was carried out (Figure 5). For comparison, the XRD profiles of a mesoporous silica film prepared on a flat substrate showed two intense peaks corresponding to (10) and (20) diffractions of a well-ordered 2D hexagonal structure. On the other hand, the XRD profiles of the film prepared on the PAA substrate had no peaks; the two intense peaks corresponding to (10) and (20) diffractions had completely disappeared. Generally, the conventional θ - 2θ XRD measurement provides only structural information

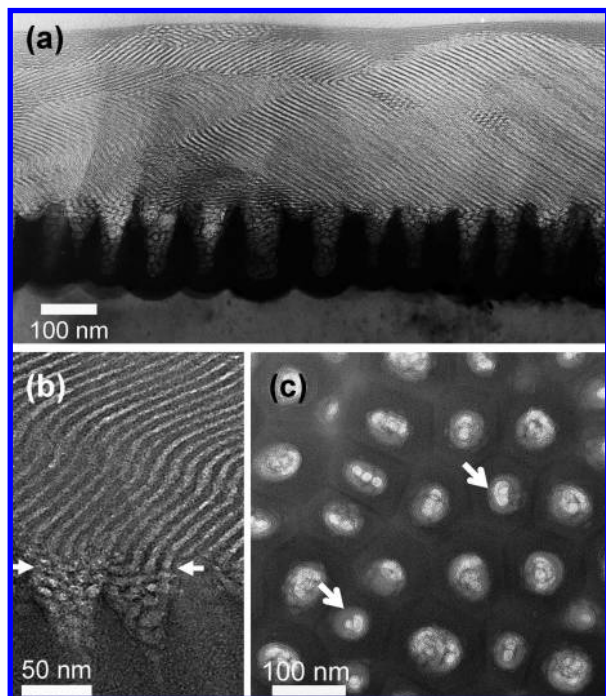


Figure 4. TEM images of mesoporous silica film on the PAA substrate (substrate C). (a) Cross-sectional TEM image over the entire area of the film. (b) Highly magnified TEM image of the interface between the continuous film region and the substrate with the conical holes. (c) TEM image of the sponge-like mesopores inside the conical holes.

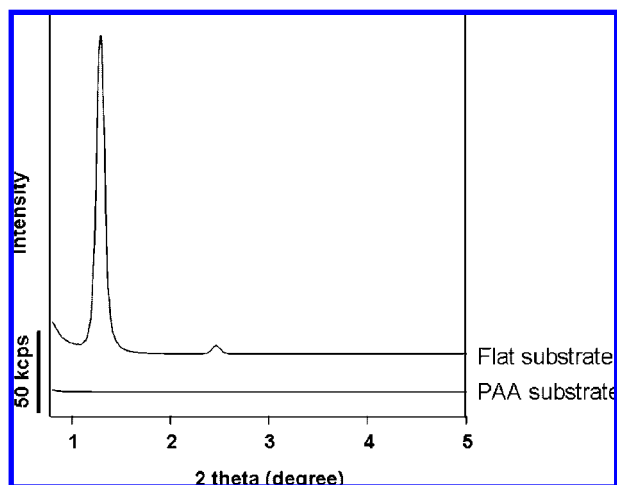


Figure 5. Low-angle XRD patterns of mesoporous silica films on flat substrate and the PAA substrate (substrate C).

parallel to a substrate.¹² Therefore, the absence of peaks in a low-angle range suggested that all the mesochannels were induced along the direction perpendicular to the substrate; in other words, no mesochannels were oriented parallel to the substrate. Another possibility is that the absence of peaks may be derived from the formation of a mesostructure with a lower ordering. However, from the TEM and SEM images (Figures 3, 4, and S2), only straight mesochannels of highly ordered 2D hexagonal structures were formed in the continuous film region. No formation of disordered mesoporous

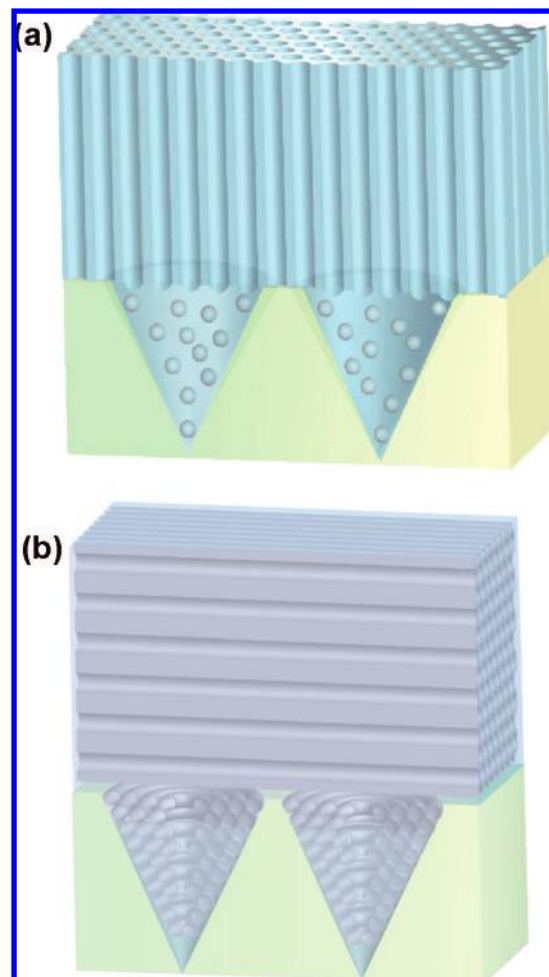


Figure 6. Schematic model of “oriented growth”. (a) Perpendicularly oriented mesochannels induced by the disordered mesopores within the conical holes. (b) Parallel oriented mesochannels induced by the circularly packed mesochannels within the conical holes.

structures was observed. Therefore, it is concluded that the peaks had disappeared because the tubular mesochannels were tilted or oriented perpendicular to the substrate.

The formation of standing mesochannels is thought to be based on an “oriented-growth” mechanism induced by sponge-like structures formed within conical holes, as was directly observed by TEM observation (Figures 4 and S3-a). In other words, each 1D mesochannel seems to grow epitaxially from sponge-like mesopores within conical holes. The size of the sponge-like mesopores is in close agreement with that of the 1D-mesochannels. Probably, the P123 chains tend to be lying near the interface, as indicated by the arrows (Figure 4b), due to the presence of the sponge-like mesopores, which force the liquid crystal into a conformation that is normal to the substrate during solvent evaporation (Figure 6a). Therefore, the formation of the sponge-like mesostructures truly acts as a “trigger” for the evolution of perpendicularly oriented and tilted mesochannels.

For a more thorough understanding of this possible mechanism, the PAA substrates with different aspect ratios were used for the preparation of mesoporous silica film. By the same procedure, SBA-15-type mesoporous silica layers were coated on the PAA substrates. Figure 7 shows cross-sectional TEM images of the mesoporous silica film on the PAAM substrate

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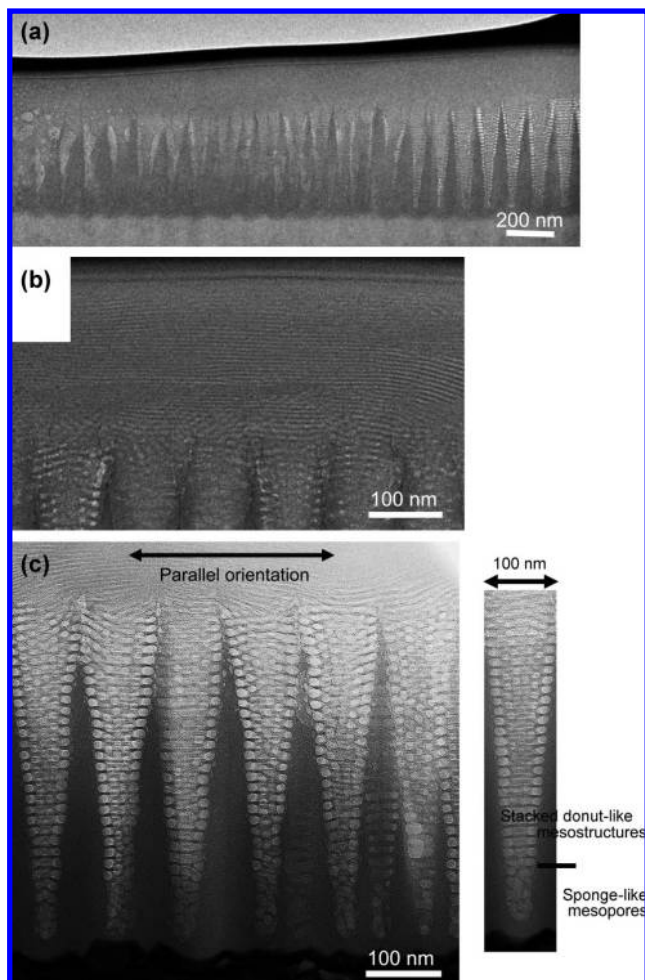


Figure 7. Mesoporous silica film on the PAA substrate (substrate E). (a) Low-magnification TEM image of cross section. (b) Enlarged TEM image of the interface between the continuous film region and the conical holes. (c) Highly magnified TEM image of the stacked donut-like mesostructures inside the conical holes.

(substrate E) with high aspect ratios (3.25). It was clear that the tubular mesochannels were circularly packed within the conical holes throughout the area; however, sponge-like mesopores were generated at the bottom (Figure 7c). At the interface between the film and conical holes, the mesochannels tended to be oriented parallel because their orientations were strongly induced by the circularly packed mesochannels within the conical holes (Figure 7c). Therefore, in the continuous film regions, almost all mesochannels were oriented parallel to the substrate (Figure 6b). The same phenomena were observed for the PAA substrate (substrate D) with an aspect ratio of 2.45 (Figure S4-a).

Using PAA substrates (substrates D and E) with high aspect ratios (2.45 and 3.25), the mesochannels were stacked like a doughnut within the conical holes. In fact, the cross-sectional SEM image (Figure S3-b) showed that the stripes derived from the mesochannels were oriented parallel to the substrate, leading to parallel orientations of the mesochannels in the continuous film region. On the other hand, when the aspect ratios were lower (substrates A, B, and C), the sponge-like mesopores were generated within the conical holes, as confirmed by the cross-sectional TEM (Figures 4c and S4-d) and SEM images (Figures S3-a). Such a formation of

sponge-like mesostructures truly acts as a trigger for the evolution of perpendicularly oriented and tilted mesochannels (Figures 4b, S2, S4-b, and S4-c).

The reason that the sponge-like mesopores were generated within the low-aspect conical holes is still unclear. It has been previously reported that hexagonally ordered mesochannels were circularly packed within straight channels of the PAA membranes due to the confined effect. The following formation mechanism has been proposed by Wu and Stucky et al.: (1) As water and ethanol evaporate, the PAA straight channels provide a significant solvent concentration gradient in the channel direction. (2) The order–disorder transition is carried out, leading to the creation of the ordered mesophase and disordered phases. (3) As the solvent evaporation continues, the circularly packed mesophase is formed along the channel axis.^{8c} However, when the degree of confinement is tightened (i.e., a very confined space smaller than 30 nm), a transition is observed in the mesopore morphology from a coiled cylindrical to a spherical cage-like (i.e., sponge-like) geometry.^{8e} No circularly packed mesochannels were observed.^{8e}

In the present system using conical holes, the sponge-like mesopore regions were thought to be generated due to the very confined space near the vertex point of the inverted conical cones. In the case of the low-aspect conical holes, the channel lengths are, of course, short. Therefore, the sponge-like mesopores are thought to be induced over the entire conical cones by a sponge-like mesopore region near the cone vertex. As another possibility, each cone has only one open pore, unlike the previous PAA membranes with two open pores. This makes sufficient solvent evaporation more difficult, leading to sponge-like mesopores near the cone vertex. In other words, the silica condensation reaction would be terminated before the order–disorder transition (i.e., before the complete solvent evaporation.). Actually, the circle mesopores with different sizes were confirmed by the TEM images. Large circle mesopores were also formed, indicated by the arrows (Figures 4c and S4-d), because the unevaporated ethanol molecules were incorporated in the core of the self-assembled P123 micelles. On the other hand, the high-aspect cones have sufficient length for transition to the circularly packed mesochannels. Consequently, the mesostructures and orientations of mesochannels within the conical holes were strictly dependent on the aspect ratios of the conical holes used.

In another experiment, the PAA substrate with straight holes (open hole size: 100 nm, height: 300 nm) was used (Figure S5-a). As described above, it has been reported that circularly packed mesochannels were generated in straight channels of PAA membranes. As expected, within the straight holes, similar circularly packed mesochannels was formed, though large mesochannels were partially formed, indicated by the arrows (Figure S5-b) due to the incorporation of the unevaporated ethanol molecules in the core of the self-assembled P123 micelles. The circularly packed mesochannels led to the parallel orientation of the mesochannels in the continuous film region. From these results, the present of the conical holes with low aspect ratios is vital for the formation of the standing mesochannels.

4. Conclusion

We report the successful formation of standing mesochannels simply by spin-coating a precursor solution onto a PAA film

with conical holes. The standing mesochannels were successfully generated by utilizing an oriented growth mechanism induced by sponge-like structures formed within conical holes with low aspect ratios. This work demonstrates the importance of the nanoarchitecture of substrates for perpendicularly oriented mesochannels. In the future, by optimizing the nanoarchitecture of the substrate surface, further enhanced perpendicular orientation should be realized. This new class of films represents a significant breakthrough in mesoporous materials science and could lead to a vast range of applications, such as highly sensitive chemical sensors, highly selective separation, and ultrahigh-density magnetic recording media.

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Supporting Information Available: Detailed characterizations of the films prepared by using several types of the PAA substrates with the different aspect ratios and shapes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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