Facile unidirectional alignment of mesochannels in a mesoporous silica film on a freshly cleaved mica surface†

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The alignment of mesochannels in a mesoporous silica film on a freshly cleaved mica surface, prepared by an evaporation-induced self-assembly process, is unexpectedly found to be unidirectional with the narrowest directional distribution.

Transparent mesoporous silica films prepared on substrates through self-assembly of surfactants are interesting nanomaterials[1–7] due to their potential applications to optical and electronic devices. The macroscopic control of in-plane alignment of tubular mesochannels in two-dimensional (2D) hexagonal mesoporous silica films is important for the applications including molecular-scale devices. By incorporating guest species, such films can show macroscopically anisotropic properties due to guest species confined in the aligned mesochannels. There has been some research on successful alignment control by using external fields (*e.g.* shear flow, magnetic and electric fields),[2,3] confined spaces on lithographically patterned substrates,[4,5] and substrates with surface anisotropies (*e.g.* rubbed polyimide and photo-induced polymer films).[6,7] Such aligned mesochannels provide anisotropic properties by incorporating guest species, such as dyes, polymers, and nanowires.[8] However, these methods for the alignment of mesochannels require complex and time-consuming processes, which has suppressed the research on the applications of mesoporous silica films with uniaxially aligned mesochannels.

One possible way to align mesochannels is the use of crystal surfaces. The epitaxial growth of mesochannels on a crystal surface results in the preferred alignment.[1,9] Mesoporous silica films, prepared by hydrothermal deposition, are formed on mica, graphite, and Si(110) surfaces.[1,9] The properties of the surfaces including hydrophilicity influences the alignment of mesochannels. Mesochannels formed on mica and graphite are not aligned to one direction because both surfaces have hexagonal symmetry, leading to the formation of triaxially aligned mesochannels.[1] The mesochannels on the Si(110) surface with a 2-fold axis are aligned to one direction. However, the alignment distribution is broad.[9] Consequently, the facile and strict control of mesochannels has not been achieved so far despite its high necessity for the next step toward the application of mesoporous silica films.

Here we report the facile control of mesochannels with the narrowest directional distribution in mesoporous silica films prepared by the evaporation-induced self-assembly (EISA) process on a freshly cleaved mica surface. We have accidentally discovered the alignment of mesochannels, which are uniaxially aligned over an entire film.

Muscovite mica (ideal formula, $K_2Al_4(Al_2Si_6O_{20})(OH)_4$) was obtained from Furuuchi Chemical Co. and is denoted here as mica. (The structure is shown in the ESI, Fig. S1†) Mica was carefully cleaved just prior to the reaction by using tweezers to create fresh and flat surfaces because the higher roughness of the surface, formed by forceful cleavage, induced the formation of triaxially aligned mesochannels. The mesoporous silica film was prepared by a dip-coating method using nonionic surfactant Brij 56 (polyoxyethylene 10 cetyl ether). (The experimental procedure is described in the ESI.†)

The mesoporous silica film prepared on thinly cleaved mica is optically transparent (Fig. 1A inset). The optical microscopic image of the film, taken under a transmission mode, is shown in Fig. 1A.† The characteristic texture in the optical micrograph of the film, which is normally observed for the films with aligned mesochannels,[6] was reproducibly found. Interestingly and importantly, the characteristic texture is aligned in one direction over an entire film. The alignment direction of the mesochannels did not depend on the withdrawal direction of mica substrates. Two freshly cleaved surfaces provided basically the same direction of the characteristic texture. (Fig. 2A) The texture grew from ~30 s after the dip-coating (see ESI, Movie S1†), indicating the controlled alignment at the very early stage.

The peak of the conventional θ–2θ scanning XRD and TEM image are consistent with the 2D-hexagonal mesoporous structure with a period of $d_{01} = 4.0$ nm. (see ESI, Fig. S2†).

The alignment of the mesochannels was quantitatively estimated by using grazing incident in-plane XRD.†[3,5–7,9] Fig. 1B shows the in-plane radial (ϕ–$2\theta\chi$) scanning profiles of the mesoporous silica film. The diffraction peaks assigned to ($\bar{1}1$) and ($\bar{2}1$) were observed when the direction of characteristic texture in the optical micrograph was set parallel to the incident X-rays at $2\theta\chi = 0°$ (solid curve), but no diffraction peaks were observed at low angles when the direction of characteristic texture was set perpendicular to the incident X-rays (dotted curve). The peak assigned to ($\bar{1}1$) does not contribute to the XRD profile under the ideal ϕ–$2\theta\chi$ scanning geometry, but the finite divergence angle of the X-ray beam, which is comparable to the small diffraction angle of the

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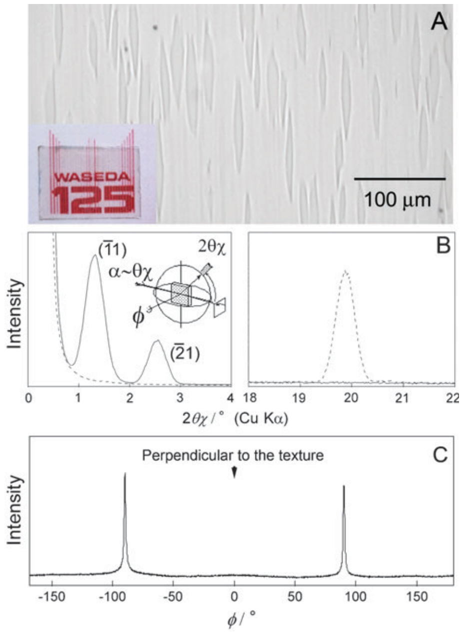

Fig. 1 (A) Optical micrograph image of the mesoporous silica film on a mica surface taken under a transmission mode. Inset: the appearance of the film. (B) In-plane ϕ–$2\theta\chi$ scanning profiles. The solid and dotted curves are recorded under the geometry in which the incident X-ray is set parallel and perpendicularly to the characteristic texture at $2\theta\chi$ = 0°, respectively. Inset: scanning axes of the in-plane XRD geometry. (C) In-plane ϕ scanning profile of the film recorded for the diffraction peak at $2\theta\chi = 1.3°$. The sample size is *ca.* 2 × 2 cm.

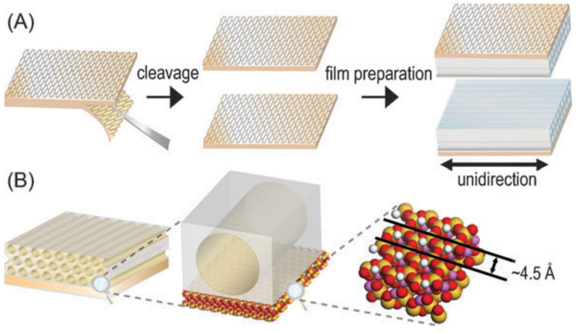

Fig. 2 Illustration of the alignment of mesochannels. (A) Two freshly cleaved surfaces provide basically the same direction of the mesochannels. (B) The mesochannels are aligned perpendicularly to the one axis of (110), (1$\bar{1}$0), and (020) of mica. The crystal image of mica was created by using Materials Visualizer (Material Studio software, Accelrys Inc.). Color spheres; red = O, yellow = Si, pink = Al, purple = K, and white = H. A quarter of SiO_4 are replaced with AlO_4 tetrahedra.

mesoporous material, results in the appearance of the peak in the diffraction profile.[6] This anisotropic in-plane XRD patterns show a strong anisotropy in the mesoporous structure. The peak was observed at ~20° (d = ~4.5 Å) only when the X-ray is set perpendicularly to the characteristic texture and is assigned to (110), (1$\bar{1}$0), or (020) of mica that are equivalent planes in the ideal structure, showing that the mesochannels are aligned perpendicular to these planes over an entire film. (Fig. 2B)

The structure of the film deviates from the ideal 2D-hexagonal structure because of the preferential structural shrinkage along the direction of film thickness. The deviation can be estimated to be ~34% from the $d_{01} : d_{\bar{2}1}$ ratio (1.73 for the ideal 2D-hexagonal structure).[6]

The distribution of the in-plane alignment of the mesochannels can be quantitatively estimated by measuring the ϕ scanning profile (in-plane rocking curve). Fig. 1C shows the ϕ scanning profile recorded for the diffraction peak at $2\theta\chi$ = 1.3° of the film. Strong and sharp diffraction peaks were observed when the direction of characteristic texture was set parallel to the incident X-rays, showing that the mesochannels are aligned to one direction. It should be noted that the full-width at half-maximum (FWHM) of the peaks was estimated to be ~1.6° which is narrowest if compared with all those reported previously (magnetic field; ~20°,[3] lithographically patterned substrate; ~3.6°,[5] rubbed polyimide film; ~3.0°,[7] and Si(110) surface; ~26°[9]). These results indicate the successful formation of the 2D-hexagonal mesoporous silica film with strictly aligned mesochannels on a mica surface.

On the other hand, we observed that the broad peaks in the ϕ scanning profile of the mesostructured silica film prepared by hydrothermal deposition method (denoted as the hydrothermal film, the experimental procedure is shown in the ESI.†), suggesting the different alignment mechanism of the present case (see ESI, Fig. S3†). The FWHM of the peaks was estimated to be ~32°, showing a very broad directional distribution of mesochannels, as reported previously.[1] The hydrothermal film is thought to be formed *via* adsorption of surfactant molecules to assemble because the surfactant : water molar ratio is low (Brij 56 : H_2O = 0.0011 : 1.0), near the critical micelle concentration (CMC). Tubular micelles consisting of adsorbed surfactant molecules meandered at the intervals of a few nanometer,[10] resulting in the broad directional distribution of mesochannels.

In the EISA film reported here, the domains of quasi lyotropic liquid crystals' (LLC) mesophase gradually grow during the solvent evaporation process because the surfactant : water molar ratio is relatively high (Brij 56 : H_2O = 0.016 : 1.0). It is known that the mesochannels in EISA films formed on hydrophilic substrates do not meander at a scale of several tens of nanometre,[11] probably because large energy is necessary for the quasi LLC domains to warp. The quasi LLC can be aligned on the anisotropic surface through the interactions between quasi LLC and the mica surface, resulting in the formation of strictly aligned mesochannels. Also, the EISA method was applied at room temperature. Smaller molecular motion of surfactants on the substrate can be favourable for the strictly aligned mesochannels to avoid the disarrangement of micelles due to larger motion at higher temperature.[7]

The mesochannels in both the hydrothermal and EISA films were uniaxially aligned although the alignments of many adsorbed substances were reported to be triaxially aligned.[1,12] For the uniaxial alignment, the reduced chemical and physical adhesion is important. Brezesinski *et al.* reported the three-dimensional (3D) cubic mesoporous titania film with a single-crystal-like mesostructure on a 3D-cubic mesoporous ceria film.[13] They proposed that the low physical and chemical adhesion between titania and ceria films is crucial for the formation of single-crystal-like mesostructure. The high hydrophilic–hydrophobic contrast between the ceria and titania films, which is defined by the differences in contact angle, suppresses the physical adhesion. The mesoporous structure on the ceria layer reduces the chemical adhesion because of decreased contact interfaces due to surface mesopores. Such a reduced physical and chemical adhesion induces the rotational mobility of the mesostructured domains of mesoporous titania.

In our present case, the hydrophilic–hydrophobic contrast between the mesoporous silica film and mica is high because mica has a highly hydrophilic property[14] and the contact angle of the bare silica film is 75°.[13] The density of protons, formed by ion exchange of potassium ions under the presence of water,[15] on the mica surface is low. Therefore, each domain of mesostructured silica can easily rotate on the mica surface. With the reaction time, the domains grow, hit each other, and subsequently move uniaxially like a shear flow process, resulting in the formation of uniaxially aligned mesostructure.

At the same time, the mesochannels are aligned perpendicularly to one axis of (110), $(1\bar{1}0)$, and (020) of mica through the interactions between protons on the mica surface and quasi LLC, as reported previously.[1] The fact that the directions of mesochannels on both of the freshly cleaved surfaces are basically the same hints at the mechanism of selection of one specific axis out of three. The hand-operated cleavage should cause some anisotropic defects and, in particular, formed steps may influence the direction of mesochannels. The cleaved process provides a sort of symmetrical step with positive and negative patterns. Such surface steps, consisting of single mica layer of ~ 1 nm at the thinnest part, are formed through the collapse of siloxane bonds along the perpendicular and parallel axes to the (110), $(1\bar{1}0)$, and (020) of mica.[16] Silanol groups are generated along the surface steps by reactions between the broken siloxane bonds and probably atmospheric water.[16] The atomically aligned silanol groups on the edge of the steps should influence the alignment of mesochannels through the interaction with surfactants, which is consistent with the effect of OH-terminated Si surfaces.[9] It is known that nanoscale surface steps, such as grooves prepared by a rubbing treatment of polyimide, influence the alignment of mesochannels by a sort of confined effect.[17] In fact, the higher roughness of the surface induces the formation of triaxially aligned mesochannels. Therefore, not only the protons on the mica surface, which is predominant with alignment, but also the anisotropic surface steps should become a determining factor in the final alignment direction of mesochannels. The combination of this effect with the tendency of unidirectional orientation described in the preceding paragraph can explain the present findings.

In summary, we have succeeded the facile and strict alignment control of mesochannels in mesoporous silica films on a freshly cleaved mica surface. The mesochannels were aligned perpendicularly to one axis out of three of mica with a very narrow directional distribution. The formation of strictly controlled mesochannels was induced by the following three factors; the formation of quasi LLC during the solvent evaporation, the presence of structurally defined surface of mica, and reduced chemical and physical adhesion between mesostructured silica films and mica surface. This strategy will lead to the development of preparation of host-materials for optical, electronic, and optoelectronic materials. Future works on various crystal surfaces will lead to the clear solution of the formation mechanism, probably resulting in the formation of films with various compositions including non-siliceous oxides, organosilicas, and metals.

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