# Alignment of Mesoporous Silica on a Glass Substrate by a Rubbing Method

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Alignment of hexagonal mesoporous silica particles was achieved by a simple rubbing method used for the alignment of liquid crystals on a very thin polyimide film coated on a silica glass substrate. Mesoporous silica was synthesized through the hydrolysis of tetraethoxysilane under acidic conditions in the presence of hexadecyltrimethylammonium chloride. The arrangement of the elongated particles was observed with their long axes parallel to the rubbing direction. The maximum aspect ratio of the particles reached ∼100. Both the elongation and alignment of the particles were not observed on the same substrate without the rubbing treatment. The hexagonal channel orientation was confirmed using in-plane X-ray diffraction and high-resolution scanning electron microscopy. The hexagonal mesoporous structure was retained over calcination in air and the adhesion of the particles onto the substrate was greatly improved.

## Introduction

Mesoporous materials synthesized through the reactions of inorganic species in the presence of surfactant assemblies have attracted worldwide attention since the discovery of FSM16[1,2] and MCM41.[3,4] A wide variety of mesophases with different compositions and structures have been obtained by the modification of the synthesis conditions including inorganic species, surfactants, and reaction conditions.[5−13]

These materials with the periodic mesoscaled spaces are expected to be applied to electrical and optical devices through the incorporation of various guest species.[14−18] However, since the most of these materials are powders, the control of the morphology,[19−21] especially film forming, is a key issue for practical applications. Several kinds of mesostructured film formation have been reported by spin coating,[22−26] dip coating,[6,27−30] and heterogeneous nucleation at interfaces.[31−39]

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In addition to film formation, the alignment of the mesochannels is another important issue. The growth of oriented hexagonal mesoporous silica film has been reported on mica and graphite substrates.[31,36,37] However, the overall channel alignment is not achieved and the domains with different channel orientations have been observed. On top of that, since both mica and graphite are not appropriate for practical use because of their cost, size limitation, and mechanically brittle properties, fully aligned mesoporous silica films on conventional substrates such as a glass plate have been desired.

Several groups have reported the formation of oriented hexagonal mesoporous silica films on glass and silicon substrates. Hillhouse et al. reported the oriented mesoporous silica film formation inside the glass capillary using a continuous-flow system,[40] and Trau et al. reported the patterning of oriented mesoporous silica using electro-osmotic flow within the microcapillaries.[41] Although the alignment was achieved, these methods require special apparatuses and restrict the substrate shapes or patterning sizes. Recently, Zhao et al. reported the axially oriented mesoporous silica film formation onto silicon wafers and glass slides by dip coating,[30] but the templating materials used in their experiments were limited to specialized nonionic surfactants such as block copolymers.

In this article, we report elongation and alignment of mesoporous silica particles grown on a very thin polyimide film coated on a silica glass substrate. The surface of the polyimide film was treated by rubbing which has been used for alignment of liquid crystals.[42] Standard cationic surfactant alkylammonium ions were used as a template. Placing the substrate simply in a reactant provides the alignment of elongated mesoporous silica particles parallel to the rubbing direction over the whole surface. The polyimide alignment film is thin enough to be removed by calcination with the macroscopic morphology unchanged. The hexagonal mesoporous structure is also retained over the calcination, and the uniaxial alignment of hollow mesoporous silica particles was achieved.

This result shows that the same technique as the alignment of liquid crystals can be applied to the alignment of mesoporous silica. This method is a new approach for obtaining oriented mesoporous structures and has the possibility to be applied for oriented mesoporous film formation onto a given substrate using standard alkylammonium templates.

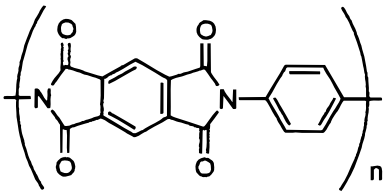

**Figure 1.** Ideal structure of the polyimide used in this study.

## Experimental Section

A polyimide precursor was spin-coated onto a clean silica glass substrate and baked at 200 °C to convert into a polyimide film.[43] The thickness of the polyimide film was about 5 nm as determined by ellipsometry. The polyimide film on the substrate was rubbed with a nylon buffing wheel. The ideal structure of the polyimide is shown in Figure 1.

The mesoscopic silica formation was performed through the hydrolysis of silicon alkoxide in the presence of surfactants under the acidic conditions as reported by Yang et al.[31] TEOS (tetraethoxysilane, $(C_2H_5O)_4Si$) was mixed with an acidic cationic surfactant CTACl (hexadecyltrimethylammonium chloride, $CH_3(CH_2)_{15}N(CH_3)_3Cl$) solution, and the mixture was stirred for 2 min at room temperature and transferred into a Teflon vessel. The molar ratio was TEOS:CTACl:$H_2O$:HCl/0.10:0.11:100:7.0. The substrate described above was held horizontally in the mixture using a Teflon holder with the rubbed polyimide surface downward. To obtain a good alignment, the surface of the substrate was covered with another silica glass with a 0.2∼1 mm spacing. The vessel was sealed at 80 °C for 1 week for the formation of the mesoporous silica particles. After the reaction, the as-synthesized sample was washed with distilled water and dried in air. The calcination of the sample was conducted under an air atmosphere in a muffle furnace at 540 °C for 10 h at a rate of 2 °C $min^{-1}$.

The morphology of the sample was observed with a scanning electron microscope (SEM) (Hitachi S-900) after a Pt coating. For the high-resolution SEM observations, the same sample was prepared onto a polished silicon (100) substrate and observed without a metal coating. The mesoporous structure was elucidated by X-ray diffraction (XRD) (Rigaku RAD-2R) using Cu Kα radiation with a graphite monochromator. A grazing angle in-plane XRD study[44] was performed on a X-ray diffractometer equipped with a 4-axes goniometer (Rigaku ATX-G) with a parabolic multilayer mirror as the primary beam condenser. Cu Kα radiation from a copper rotating anode was used for the experiment. The alignment of the mesochannels was also confirmed by the direct observations by high-resolution SEM.

## Results and Discussion

Figure 2a shows the low-magnification SEM image of the as-synthesized mesoporous silica sample on the rubbing treated polyimide film coated on a silica glass substrate. The alignment of the long particles was observed. The direction of the long axis of each particle is identical to the rubbing direction. Although the length and width of the particles had a wide distribution, the maximum aspect ratio of the fiberlike particle reached ∼100. The thickness of the particles was 0.2∼0.3 $\mu$m. Most of the as-synthesized mesoporous silica on the polyimide-coated substrates without a rubbing treat-

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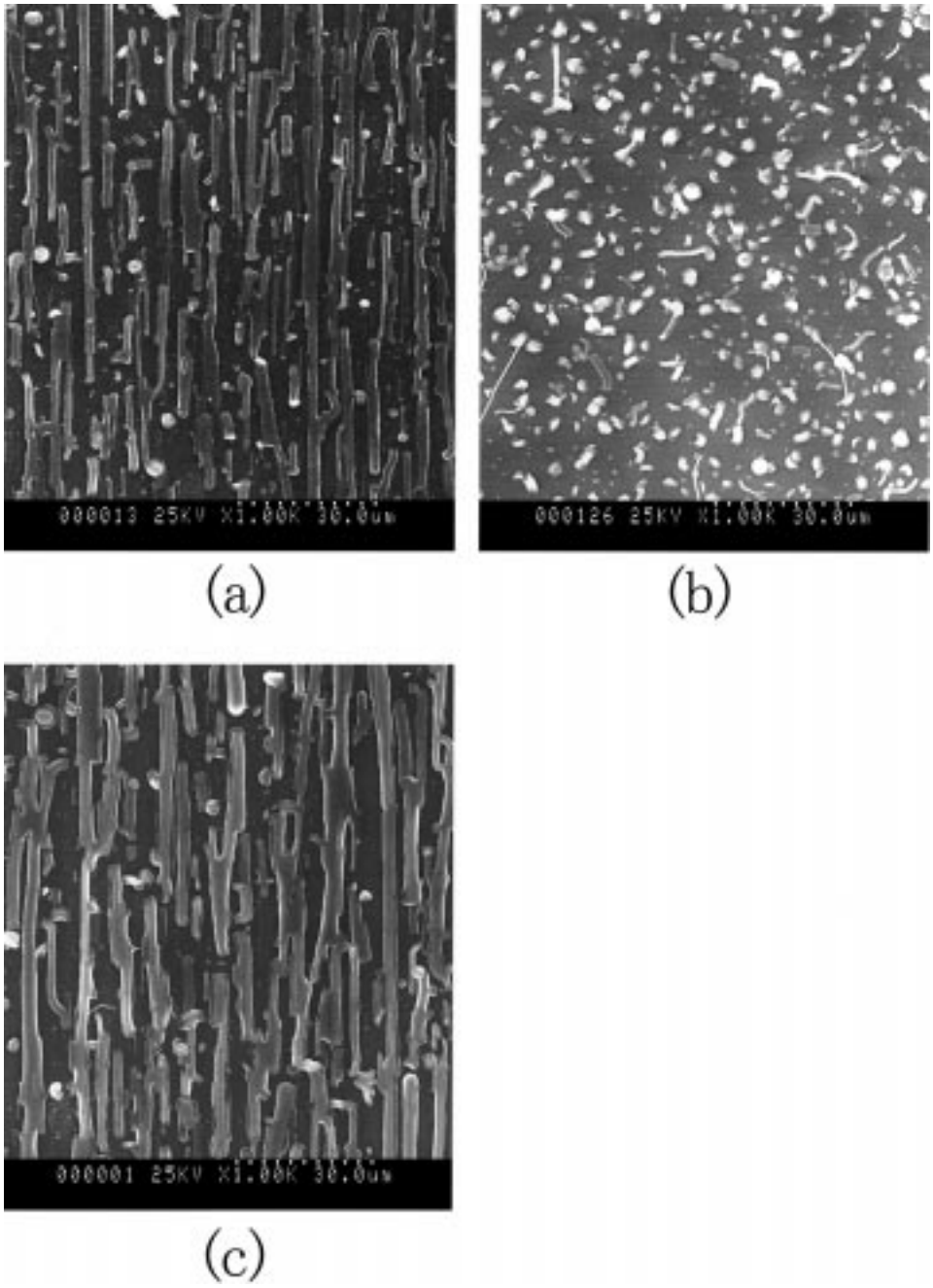


**Figure 2.** Low-magnification SEM images of (a) the as-synthesized mesoporous silica sample formed on the rubbing-treated polyimide film, (b) the as-synthesized mesoporous silica sample formed on the untreated polyimide film, and (c) the calcined mesoporous silica sample formed on the rubbing-treated polyimide film. The polyimide film was coated on a silica glass substrate. The long axis of each mesoporous silica particle is identical to the rubbing direction.

ment were small disklike particles (Figure 2b). Figure 2c shows the low-magnification SEM image of the calcined mesoporous silica sample grown on the substrate with a rubbing treatment. The calcination caused no morphological alteration on the arrangement of mesoporous particles.

The XRD pattern of the as-synthesized sample is shown in Figure 3a. Two diffraction peaks were observed at $2\theta = 2.3°$ and 4.7°, which were assigned as (100) and (200) planes of the hexagonal mesoporous structure, respectively, judging from the high-resolution SEM images that will be discussed later. The lack of a (110) diffraction peak indicates that the mesochannels run parallel to the substrate surface. The degraded XRD peak at a slightly higher $2\theta$ angle for the calcined sample (Figure 3b) confirms the retention of the structure, while it indicates the shrinkage and the disordering of the hexagonal structure. The observed mesostructural change was caused by the condensation of residual hydroxyl groups in the wall over the calcination.

Since the retention of the total mesoporous structure over the calcination is evident from the SEM images and the XRD patterns described above, the following characterizations were conducted for the as-synthesized samples which show a higher structural ordering.

The characterization by in-plane X-ray diffraction was conducted to show the alignment of the mesochannels over the whole substrate. Since only the structural information parallel to the film surface is obtainable,

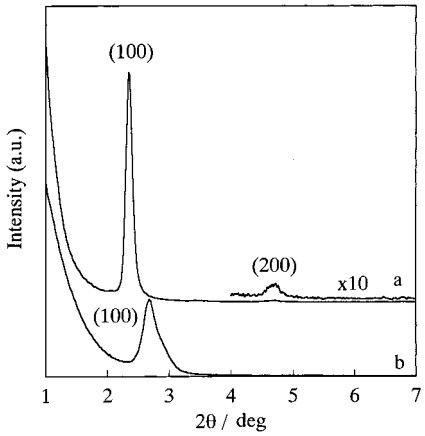


**Figure 3.** XRD patterns of mesoporous silica formed on the rubbing-treated polyimide film: (a) as-synthesized sample and (b) calcined sample.

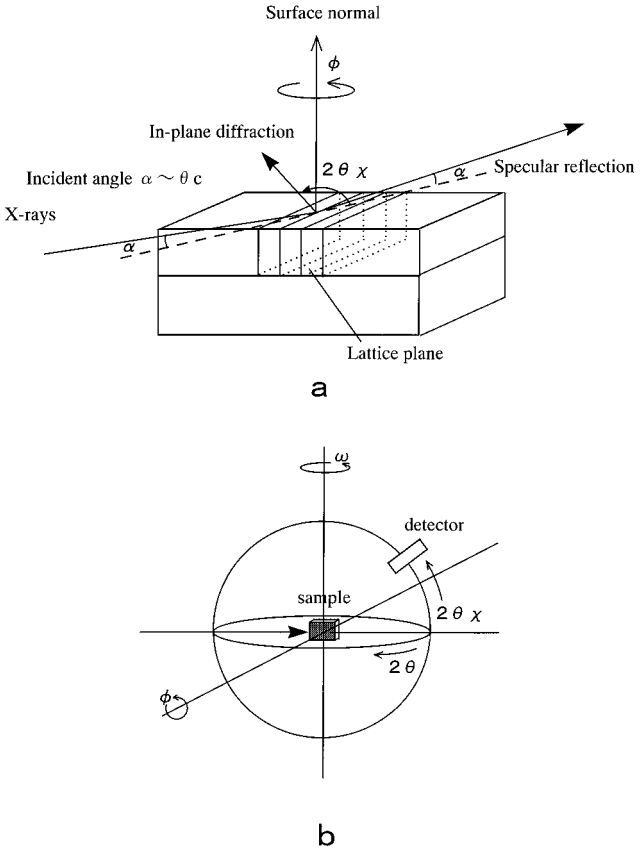


**Figure 4.** (a) The geometry of the in-plane X-ray diffraction and (b) the 4 axes ($\omega$, $\phi$, $2\theta$, $2\theta\chi$) of the goniometer used for in-plane diffraction measurement.

direct evidence for the alignment of the mesochannels in the film is not available using conventional $\theta-2\theta$ measurements. In-plane X-ray diffraction is caused by the lattice plane normal to the film surface when the X-ray is incident to the sample surface at a grazing angle around the total reflection angle. The geometry of the in-plane diffraction and the four axes of the goniometer are illustrated in Figure 4a,b, respectively. The sample rotation angle ($\phi$) dependence of the in-plane diffraction peak intensity directly reflects the hexagonal channel orientation in the film plane.

Figure 5 is the $\phi-2\theta\chi$ scan profile measured with the incident angle 0.2°. The sample was set with the rubbing direction parallel to the incident X-ray. A broad peak

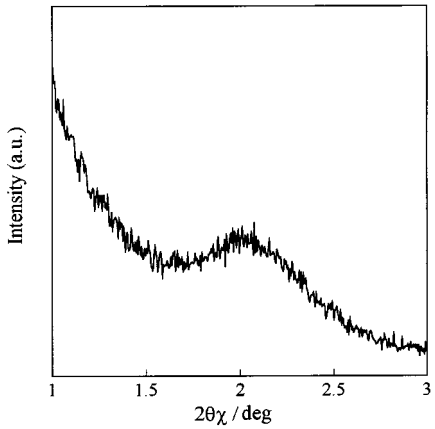


**Figure 5.** $\phi-2\theta\chi$ scan profile of the in-plane XRD obtained for the as-synthesized mesoporous silica formed on the rubbing-treated polyimide film on a silica glass substrate. The spacing corresponding to this diffraction peak is identical to the center-to-center distance of the mesoporous silica.

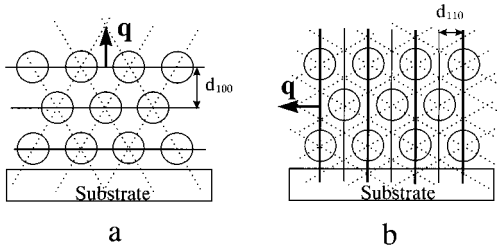


**Figure 6.** The arrangement of the mesopores in the sample and diffraction vector **q**: (a) conventional $\theta-2\theta$ scan and (b) in-plane diffraction. The structural information parallel to the diffraction vector can be obtained in each measurement.

centered at $2\theta\chi = 2.0°$ was observed. The spacing was determined to be 4.3 ± 0.6 nm from the full width at half-maximum of the diffraction peak. Considering the existence of a strong (100) diffraction peak in the $\theta-2\theta$ XRD pattern (Figure 3), ⟨100⟩ is parallel to the diffraction vector **q**. The pore arrangement in each particle can be illustrated as Figure 6a. In this pore arrangement, the lattice planes observed by the in-plane diffraction should be parallel to (110) (Figure 6b). Since the (110) spacing is calculated to be 2.2 nm from the $d_{100}$ spacing, the diffraction peak observed at $2\theta\chi = 2.0°$ was assigned as ($^1/_2$ $^1/_2$ 0) of the surface structure. Because the penetration depth of the grazing incident X-ray is very shallow in this measurement, this in-plane diffraction is caused by the surface thin layer. This is considered to be the reason that the diffraction corresponding to the center-to-center distance of the hexagonal mesoporous structure which is absent in the bulk powder sample was observed.

When the position of the detector is fixed at $2\theta\chi = 2.0°$, the sample was rotated around the $\phi$-axis. The periodic variation of the diffraction intensity was observed as shown in Figure 7. The interval of the two peaks is 180°, which shows that the mesochannels are aligned along the axis over the whole plane.

Figure 8a,b shows the low-magnification and the high-magnification images of the as-synthesized mesoporous silica particle formed on a silicon substrate, respectively. The rubbing-treated polyimide film was similarly coated on the silicon substrate. The stripes with a ∼4 nm interval were observed at the edge of the elongated

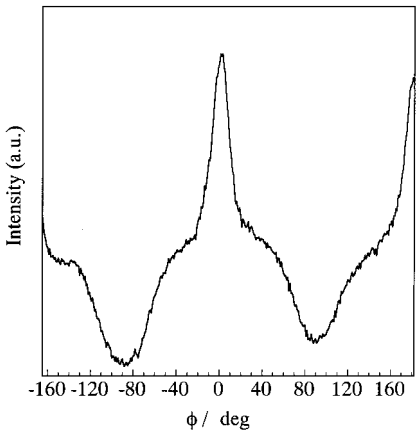


**Figure 7.** $\phi$-scan profile of the in-plane XRD obtained for as-synthesized mesoporous silica formed on the rubbing-treated polyimide film. The variation of the diffraction intensity with a 180° interval shows the axial orientation of the mesochannels.

particle along its long axis. The stripes were observed in each particle on the sample. This is direct evidence of the alignment of the hexagonal mesochannels.

Although the rubbing method is a common process for the fabrication of a liquid-crystal display, the precise origin of the alignment on the rubbed substrate has not yet been completely understood.[42] It is considered that a number of physical and chemical effects are responsible for the phenomena such as the morphological effect of the microgroove or orientation of the polymer chain.

In the formation of the mesoporous silica with a wide variety of shapes, the polymerization and growth of a silicate liquid-crystal seed are considered to be included.[33−35] The alignment of the mesoporous silica particles and the mesochannels in this study shows the validity of the technique used for thermotropic liquid-crystal alignment, indicating similar alignment mechanisms between thermotropic liquid crystals and mesoporous silica.

To distinguish the morphological effect which is considered to be included in the orientation mechanism of the liquid crystal on the rubbing-treated polymer, an obliquely deposited film of silicon monooxide (SiO) was used instead of a rubbed polyimide film. An SiO evaporated film has a column-like structure, and thermotropic liquid crystals are also well-aligned on the obliquely evaporated SiO layer. For the alignment of the liquid crystals on obliquely evaporated SiO, only the morphological effect is considered to be responsible.[42] However, the alignment of mesoporous silica using the obliquely evaporated SiO layers was unsuccessful in this study for the 10° and 30° evaporation angles. This indicates that the alignment of the silicate liquid crystal cannot be achieved only by the morphological effect. The microscopic alignment potential of the substrate surface, that is, molecular-scaled interactions between the substrate surface and the silicate liquid-crystal seed, is considered to be essential.

The mesoporous silica formed on the rubbing-treated polyimide film was not a continuous film but an arrangement of separated elongated particles. The spaces between the particles are not cracks induced by a stress. This morphological feature indicates low nucleation density of the mesoporous silica on the polyimide film

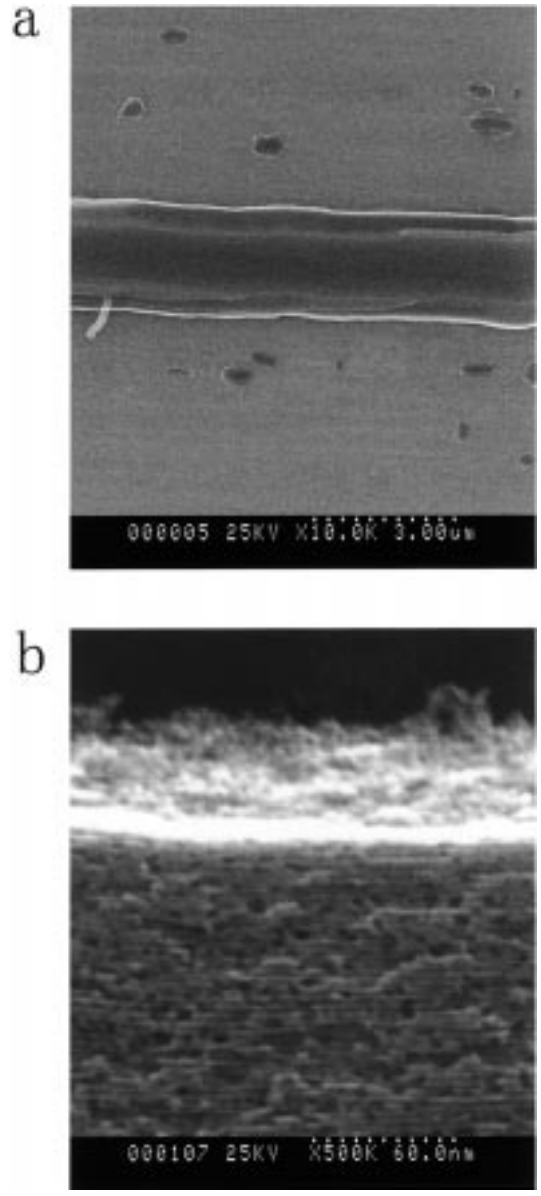


**Figure 8.** (a) Low-magnification and (b) high-magnification SEM images of the as-synthesized mesoporous silica formed on the rubbing-treated polyimide film on a silicon substrate. Mesochannels run parallel to the long axis of the elongated particle and the rubbing direction.

in these experimental conditions. The high uniaxial orientation and the large aspect ratios of the particles were achieved for the conditions where the nucleation density on the surface was low. For example, the density of the particles on the substrate was increased when the samples were prepared without the cover during the reaction. However, the order of the alignment was significantly failed. This incompatibility would be related to the surface energy of the polyimide surface. Since the alignment of liquid crystals is largely influenced by the surface energy of a substrate, the morphology of the mesoporous silica particles would also be affected. The improvement of the continuity, that is, a continuous film formation, is expected through changing the polymers, rubbing conditions, and so on.

The thickness of the polyimide layer is thin enough to be removed by the calcination in air without flaking the particles from the substrate. The adhesion of the particles onto the substrate was greatly improved

through calcination; the particles were easily removed from the substrate surface for the as-synthesized sample, while they were attached firmly onto the silica glass substrate after calcination. The partial bonding between the silica glass substrate surface and the mesoporous silica particle through the dehydration of silanol groups are considered to take part in the observed adhesive stability.

## Conclusions

Alignment of the mesoporous silica was achieved using a rubbing-treated polyimide film on a silica glass substrate and standard alkylammonium surfactants. The periodic variation of in-plane diffraction intensity along the $\phi$-rotation with an interval of 180° shows the alignment of mesochannels along the rubbing direction. The alignment was also confirmed by a direct observation by high-resolution SEM. The adhesion of the particles onto the substrate was greatly improved by calcination without destroying the microscopic and macroscopic structures.

This strategy to align the mesoporous silica onto a substrate using a rubbing method is useful because it will present a new method of making an axially oriented mesoporous silica film onto a glass substrate using common surfactants. Optimizing both the kind of polymers and the synthesis conditions will lead to the success of mesoporous silica film formation with fully aligned mesochannels.

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