Supporting information

A Facile Method to Prepare Macroscopically Oriented Mesostructured Silica Film: Controlling the Orientation of Mesochannels in Multilayer Film by Air Flow

*Bin Su, Xuemin Lu, Qinghua Lu**

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University

No.800,Dongchuan Rd, Shanghai, 200240, P.R. China

Fax: +86-21-54747535

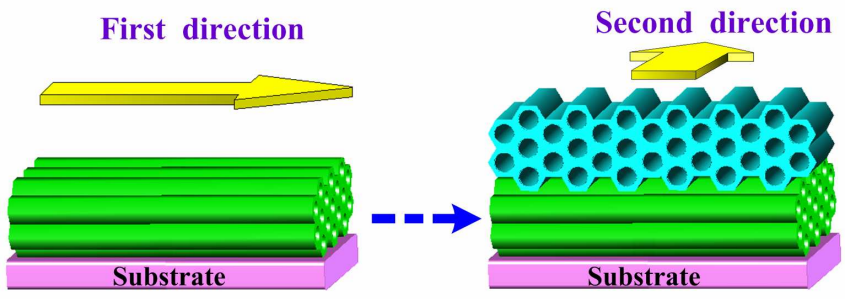
E-mail: qhlu@sjtu.edu.cn.

1. Preparation of mesostructured silica film by air flow

The preparation of mesoporous silica film was performed by hydrolysis of tetraethoxysilane [TEOS; $(C_2H_5O)_4Si$] in the presence of the surfactant P123 (polyethylene oxide–polypropylene oxide–polyethylene oxide triblock copolymer (EO_{20}-PO_{70}-EO_{20})) under acidic conditions. The molar ratio of the reactants was TEOS/P123/H_2O/HCl/EtOH =1:0.01:6.5:0.01:21. After stirring at room temperature for 3 h, the precursor solution was dropped onto a PET substrate (7.5 cm×2.5 cm) to spread a thin liquid sol-layer. A hot (70˚C) and strong (speed was 11.1–20.5 m/s) air flow parallel to the substrate was applied for 10 s to prepare mesostructured silica films. For multilayer film, a drop of silica sol was drop on the pre-prepared single layer film and treated again using air flow in a controlled direction. The whole procedure is shown in Scheme S1. After exposure in air for 3 h, transparent mesoporous silica films were obtained. The template of organic surfactant was removed using ethanol extraction for 48 h.[1]

To prepare multi-layer film, a drop of sol precursor was placed on as-synthesized film and air flow (19.5 m/s) parallel or perpendicular to the first flow direction was applied to form the second layer mesostructured film on the first layer of the as-synthesized film.

The speed of air flow was measured with a Pitot Type Flow Meter. The thickness of the film was observed by JEOL HR-SEM (JSM-7401F) at a voltage of 5 keV and by ellipsometry (W-VASE32TM, J.A. Woollam). Microscopic observations of the morphology were carried out using a Leica optical microscope.



Scheme S1: Schematic illustration of oriented SBA-15 mesostructured film prepared by the air flow approach.

2. Characterization of mesostructured silica film

The TEM micrographs were taken on a JEOL TEM-2100 operating at an accelerating voltage of 200 KeV. The specimen for the TEM observations was prepared as follows: first, two samples were glued face-to-face with epoxy resin and sawed into a piece with a thickness of 500 μm. Second, the piece was mechanically prethinned and polished with a disk grinder and a dimple grinder to produce a central region ~ 10 μm thick. Finally, the central region was milled with two Ar+ ion beams.

θ-2θ X-ray diffraction (XRD) patterns were collected with an X-Ray Polycrystalline Diffractometer using Cu Kα radiation (D8 ADVANCE, Bruker). In-plane XRD measurements were performed on a D8 Discover GADDS (General Area Detector Diffraction System, Bruker) using diffraction radiation.

3. Homogeneity of the film.

The homogeneity of the film can be divided into two parts: one is the orientation degree of mesochannels at different area of the film and the other is the thickness at different area of the film.

For the homogeneity of orientation degree, we employed in-plane XRD measurement to detect three area marked as A, B, C and the geometry were shown in Figure S1. FWHM and corresponding orientation degree was given in Table 1.

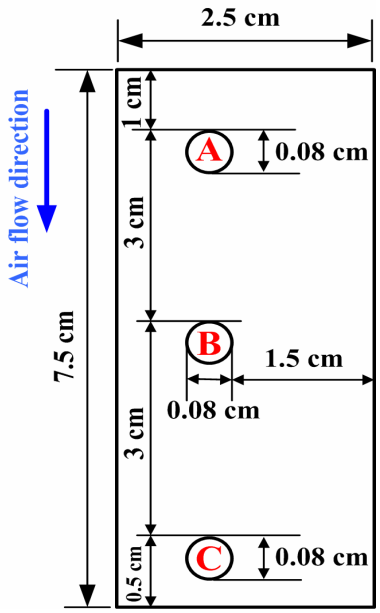


Figure. S1 The geometry of detected sample prepared by air flow at a velocity of 19.5 m/s.

The film was homogeneous in our sample (7.5 cm×2.5 cm) because the in-plane XRD was employed to detect the orientation degree of meoschannels from one edge to the other edge of the sample and the orientation degree was nearly the same (FWHM (full width at half maximum) only changed 0.2°).

Under the hot air flow, silica sol solution was quickly moved in desired direction and most of the excess solution was streamed out of the substrate, left only a thin, transparent and oriented mesostructured silica film. We checked the homogeneity of our obtained film in whole region (7.5cm x 2.5cm) by using ellipisometry and found that the thickness of the mesostructured film is very uniform.

Table S1. FWHM, orientation degree and thickness of different area in the film

	FWHM (°)	Orientation degree (%)	Thickness (nm)
Area A	12.9	92.8	600
Area B	12.8	92.9	610
Area C	13.0	92.8	610

*Values of the FWHM were calculated from the Φ-scanning profile in the in-plane measurement.

4. Packaging state of mesochannels in the mesostructured silica film

The packaging state of mesochannels was firstly detected by using high resolution TEM. The sample was collected from the sol solution same to prepare mesostructured silica film. From Figure S2, we can found that the mesochannels was packaged in hexagonal phase.

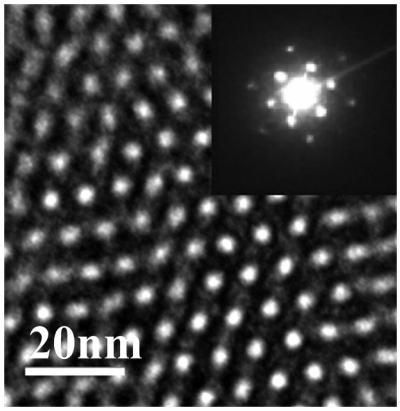


Figure S2. TEM image of mesostructured silca film. The powder was scratched from the as-synthesized silica film and collected to copper net for TEM detection. The inner image was the electron diffraction pattern of the corresponding region.

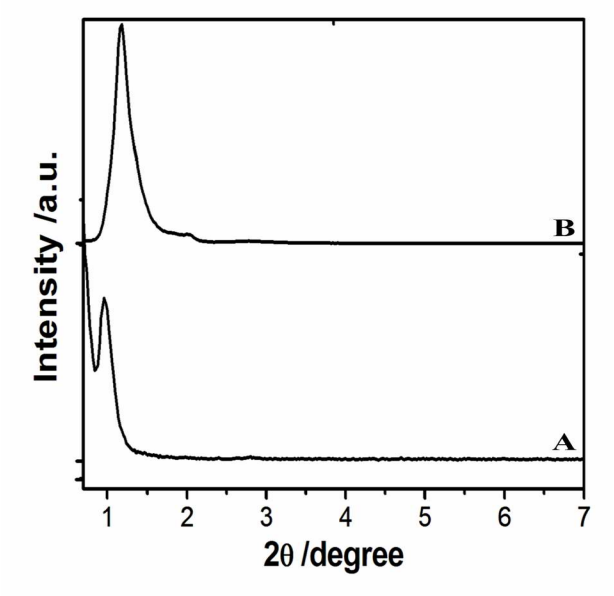


Figure S3. Powder XRD pattern of as-synthesized mesostructured silica film by air flow (A) and that after removal of organic surfactants (B)

Figure S3 shows powder X-ray diffraction (XRD) patterns of the mesostructured films. The diffraction peak of the as-synthesized mesostructured film appeared at 2θ=0.96°, assigned as (10) of hexagonal structure. After removal of organic surfactant, the position of the (10) peak shifted to 2θ=1.16°, indicating that the mesopores in the silica film shrank and became smaller. The (11) peak, which is generally present in hexagonally packed silica film, was not seen in Figure S3. In a previous

report by Hillhouse et al.,[2] this phenomenon occurs when the mesochannels are aligned parallel to the substrate. However, it is difficult to be certain of the exact orientation of the mesochannels based only on the absence of the (11) peak because the possibility of coexisting orientations that are perpendicular or inclined to the substrate cannot be excluded.

5. Effect of the air flow speed on the final orienting degree of mesochannels in the as-synthesized silica film

The mechanism of mesochannel orientation is thought to be as follows. Air flow with high speed leads to rapid motion of the droplet on the substrate in a preferred direction, generating great shear force in the liquid layer. Simultaneously, in this case, with evaporation of ethanol under hot air flow, organic surfactants in the sol silica precursor could be enriched and form abundant tubular-shaped micelles with the TEOS molecules organizing and attaching to the outer surfaces of the micelles. Under the shear force induced by high speed air flow, the micelles were anisotropically arranged along the air-flow direction. Hereby, we speculate that the orientation degree should be related to the shear force, which was proved by investigation of the influence of the speed of air flow on the degree of orientation. Table S2 shows the orientation degree of the mesochannels under different air speeds. When the air speed was 11.1 m/s, the FWHM maintained a value of 17.3˚ corresponding to an orientation degree of 90.4%, and with increasing air speed, the value of the FWHM decreased and finally arrived at a constant level. The result that a high velocity of air flow leads to a narrow orientation of mesochannels was in accord with our analysis.

Table S2. Relationship between the FWHM and the velocity of air flow

Air speed (m/s)	FWHM (°)*	Orientation degree (%)
11.1	17.3	90.4
17.7	15.2	91.6
18.1	14.0	92.2
19.5	12.8	93.0
20.5	13.3	92.1

*Values of the FWHM were calculated from the Φ-scanning profile in the in-plane measurement.

References

[1] Hua, Z. L.; Shi, J. L.; Wang, L.; Zhang, W. H. *J. Non-crystal Solids.* **2001**, *292*, 177-183.

[2] Hillhouse, H. W.; Egmond, J. W.; Tsapatsis, M.; Hanson, J. C.; Larese, J. Z. *Micro. Meso. Mater.* **2001**, *44-45*, 639-643.