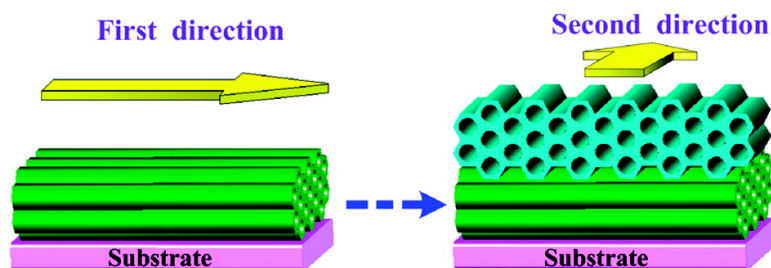


A Facile Method to Prepare Macroscopically Oriented Mesostructured Silica Film: Controlling the Orientation of Mesochannels in Multilayer Films by Air Flow

Bin Su, Xuemin Lu, and Qinghua Lu

J. Am. Chem. Soc., **2008**, 130 (44), 14356-14357 • DOI: 10.1021/ja8003254 • Publication Date (Web): 11 October 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



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

Bin Su, Xuemin Lu, and Qinghua Lu*

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, P.R. China

Received January 15, 2008; E-mail: qhlu@sjtu.edu.cn

Host–guest chemistry is considered to be a facile approach to designing new functional molecules or devices for different purposes. As an ideal candidate for host, mesoporous silica materials with macroscopically oriented hexagonally packed tabular mesochannels have received much attention in nanostructured host/guest composites. In these systems, a mesostructured silica film with the orientation controlled in three dimensions has been anticipated to have great potential in the design of devices in optics, microelectronics, etc.¹ Several methods have been advanced to fabricate oriented mesoporous films. However, the mesochannel orientation was solely controlled in a single direction over the whole film (in other words, the orientation of mesochannels was controlled in two dimensions). On the other hand, these methods show special requirements on supported substrate such as an anisotropic surface,² photolithographic silica,³ oriented polymer film,⁴ or a closed cell,⁵ which also limited their practical application. It would be more useful to design multilayered optical or microelectric nanodevices if the oriented mesochannels could be controlled in a desired direction or in three dimensions on any substrate.

To test this possibility to prepare such an oriented multilayered mesostructured silica film, we report here a facile method to freely control the orientation of mesochannels in a mesostructured silica film on a large scale. Based on this method, multilayered mesoporous silica films with a complex arrangement of controlled mesochannel orientations can be prepared. This method shows good control of the orientation of mesochannels in three dimensions and has no special requirement on the supported substrate, which is expected to form the basis of new applications.

Pluronic 123 (polyethylene oxide–polypropylene oxide–polyethylene oxide triblock copolymer (EO₂₀–PO₇₀–EO₂₀)) was used as the structure directing agent. A surfactant/silica composite film was prepared on a polymer substrate, PET film (7.5 × 2.5 cm), by employing a jet of hot, strong air flow. As standard procedure, a droplet of sol silica precursor solution was pipetted onto a PET film and then a hot, strong air flow was applied parallel to the substrate for 10 s to prepare a mesostructured film. The whole procedure is shown in Supporting Information Scheme S1. In the experiment, the speed and temperature of the air flow were controlled at 19.5 m/s and 70 °C, respectively. The resulting film was highly transparent and uniform with a thickness of ~600 nm (Table S1)

As verified by high-resolution TEM (HR-TEM), the mesochannels were packed in a hexagonal structure in the obtained mesostructured silica film (Figure S2). Powder X-ray diffraction (XRD) patterns of the mesostructured film shows that a diffraction peak appeared at $2\theta = 0.96^\circ$, assigned as (10) of the hexagonal structure. After removal of organic surfactant, the position of the (10) peak shifted to $2\theta = 1.16^\circ$ (Figure S3), indicating that the mesopores in the silica film shrank and became smaller.

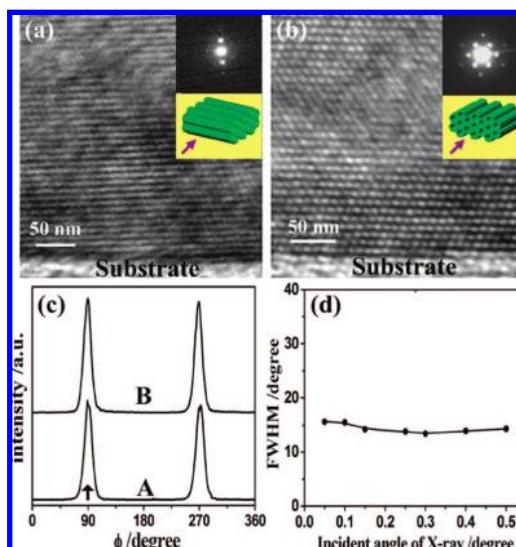


Figure 1. (a and b) Cross-sectional TEM images of the as-synthesized mesostructured silica film grown on substrate by air flow. The sample was sliced along (a) and across (b) the air flow direction. Inset: Selected area electron diffraction pattern of the mesostructured silica part; (c) Φ -Scanning in-plane XRD pattern of as-synthesized silica film (profile A) and after removal of organic surfactant (profile B); the arrow shows the air flow direction. (d) Relationship between fwhm and the angle of incident X-rays.

The packing state of the mesochannels relative to the substrate was directly visualized by HR-TEM. Figure 1a is the TEM image obtained in the direction along the air flow direction, and Figure 1b is that obtained in the direction across the air flow. We can clearly see that the mesochannels are aligned parallel to the supported substrate and along the direction of hot air flow. In-plane XRD was further employed to characterize the orientation of mesochannels in the as-synthesized silica film. Moreover, for homogeneous investigation, three different points were selected (Figure S1) and the correspondent in-plane XRD results were listed in Table S1. Each detected area was $0.08 \times 0.08 \text{ cm}^2$ according to the equipment's handbook. Figure 1c shows a typical in-plane XRD profile of silica film, and two diffraction peaks were observed at Φ values of 90° and 270° . The value of the full width at half-maximum (fwhm) was only 12.8° , corresponding to an orientation degree of 92.9% . After removal of organic surfactant, the orientation degree was almost unchanged with $\text{fwhm} = 12.2^\circ$, corresponding to an orientation degree of $\sim 93.2\%$. This result shows that the mesochannels have a uniform orientation in the direction parallel to the air flow.

The orientation uniformity of mesochannels along the normal of the as-synthesized silica film was also investigated by using the in-plane XRD at varied incident angle mode. Under this mode, the

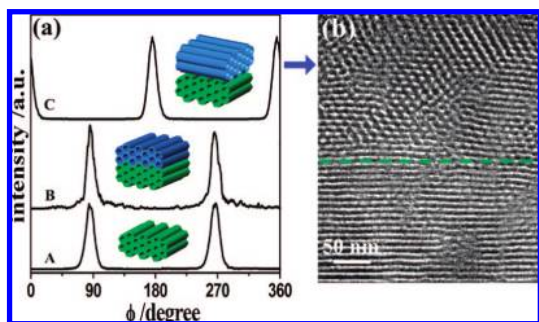


Figure 2. (a) Φ -Scanning in-plane XRD pattern of as-synthesized single-layer mesostructured silica films (A); double-layer treated films with the second flow direction parallel (B) and perpendicular (C) to the initial direction of the air flow. (b) Cross-sectional TEM image of perpendicular array of mesochannels in perpendicularly treated silica film; the green line in (b) marks the boundary of perpendicular mesochannels.

distribution of the mesochannels in the inner part can be detected by increasing the incident angle of X-rays. Figure 1d shows the relationship between the orientation degree of the mesochannels and the incident angle of X-rays. The deviation in orientation between the inner and top portion was only 2° , almost invariable with the increasing incident angle of the X-rays, indicating that the mesochannel orientation is very uniform along the direction normal to the mesoporous film.

The orientation of mesochannels was attributed to the interaction between the high speed air flow and the sol solution. Air flow with high speed leads to rapid motion of the droplet on the substrate in a preferred direction,⁶ 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 tetraethyl orthosilicate 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. This speculation was further proved by the effect of the speed of air flow on the final orientation of mesochannels (Table S2).

Taking into account the fact that the mesochannel orientation is only affected by the air flow direction, it could be anticipated that a multilayered film with different mesochannel orientations in different layers may be prepared by adjusting the direction of air flow; that is to say, the mesochannel orientation can be controlled in three dimensions. To make such a film, another drop of sol-gel precursor was placed on top of the first air-flow treated film. Then a jet of air flow at the same speed was applied in a certain direction. An SEM image of the cross section of the resultant mesoporous silica film proved that the thickness of the film was $\sim 1.1 \mu\text{m}$, about two times that of the first treated film. If the directions of the two steps were fixed to be parallel to each other, a slight increase in orientation degree from 92.9% (fwhm = 12.6°) to 93.6% (fwhm = 11.6°) was found. If the direction of the second step was set perpendicular to the first step, a perpendicular configuration of mesochannels was obtained, as shown in Figure 2a. Three diffraction peaks appear at 0° , 180° , and 360° , indicating that the array of mesochannels in the second layer was perpendicular to that of the previous layer and, from the fwhm, their orientation degrees were almost invariant. The perpendicular array of mesochannels

was further verified by HR-TEM as shown in Figure 2b. The arrangements of mesochannels in adjacent layers are obviously perpendicular to each other in both microregions and the whole film. Because the direction of the second air flow can be set independently, the configuration of mesochannels in the mesoporous silica film can be freely designed. Multiple treatments can also be applied to prepare multilayer films with a controlled configuration by simply modifying the air flow direction. This feature will be very attractive for the application of mesoporous films in many fields.

In conclusion, we found a rapid and simple method to prepare oriented mesoporous silica films by hot air flow. The mesochannels in such a mesoporous silica film were oriented along the air flow direction with a uniform distribution of the orientation degree both whole plane and along the direction normal to the thin film. A complex arrangement of mesochannels in mesoporous film and, thus, the control of orientation in three dimensions can also be obtained by multistep treatment. Most importantly, this method presented here gives a choice in deposited substrate and can be applied onto a wide range of materials. Besides PET film, we applied this method to other substrates, such as glass, silicon, polyimide film, and even a metal aluminum substrate, and oriented mesostructured silica films were also obtained. Furthermore, it is also possible to carry out such a procedure on a curved substrate. We anticipate that this method has significant potential for the application of mesostructured silica film in many fields.

Acknowledgment. The authors acknowledge financial support from the National Science Foundation of China (60577049, 20874059), “973” project (2009CB930400), “Nano Project” (0652nm017) of Science and Technology Commission of Shanghai Municipal Government, and Shanghai Leading Academic Discipline Project (No. B202).

Supporting Information Available: Experimental procedures, characterization of the as-synthesized silica film, orientation uniformity of mesochannels along the film normal, effect of air flow speed on the orientation degree of the mesochannels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Molenkamp, W. C.; Watanabe, M.; Miyata, H.; Tolbert, S. H. *J. Am. Chem. Soc.* **2004**, *126*, 4476–4477. (b) Angelos, S.; Johansson, E.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 2261–2271. (c) Martini, I. B.; Craig, I. M.; Molenkamp, W. C.; Miyata, H.; Tolbert, S. H.; Schwartz, B. J. *Nat. Nanotechnol.* **2007**, *2*, 647–652.
- (2) (a) Yang, H.; Kuperman, A.; Coombs, N.; Mamiche-Afara, S.; Ozin, G. A. *Nature* **1996**, *379*, 703–705. (b) Lu, Y. F.; Ganguli, R.; Drewien, C. A.; erson, M. T.; Brinker, C. J.; Gong, W. L.; Guo, Y. X.; Soye, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364–368. (c) Brezesinski, T.; Antonietti, M.; Smarsly, B. M. *Adv. Mater.* **2007**, *19*, 1074–1078.
- (3) (a) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674–676. (b) Rice, R. L.; Arnold, D. C.; Shaw, M. T.; Iacopina, D.; Quinn, A. J.; Amenitsch, H.; Holmes, J. D.; Morris, M. A. *Adv. Funct. Mater.* **2007**, *17*, 133–141. (c) Wu, C. W.; Ohsuna, T.; Edura, T.; Kuroda, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5364–5368.
- (4) (a) Fukumoto, H.; Nagano, S.; Kawatsuki, N.; Seki, T. *Adv. Mater.* **2005**, *17*, 1035–1039. (b) Kawashima, Y.; Nakagawa, M.; Ichimura, K.; Seki, T. *J. Mater. Chem.* **2004**, *14*, 328–335. (c) Kawashima, Y.; Nakagawa, M.; Seki, T.; Ichimura, K. *Chem. Mater.* **2002**, *14*, 2842–2844. (d) Miyata, H.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 1609–1614. (e) Miyata, H.; Kuroda, K. *Adv. Mater.* **1999**, *17*, 1448–1452. (f) Miyata, H.; Kawashima, Y.; Itoh, M.; Watanabe, M. *Chem. Mater.* **2005**, *17*, 5323–5327.
- (5) Hillhouse, H. W.; Okubo, T.; van Egmond, J. W.; Tzapatsis, M. *Chem. Mater.* **1997**, *9*, 1505–1507.
- (6) Woolley, A. T.; Kelly, R. T. *Nano Lett.* **2001**, *1*, 345–348.

JA8003254