

Synthesis of continuous mesoporous silica thin films with three-dimensional accessible pore structures

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Continuous mesoporous silica thin films with three-dimensional (3-D) accessible pore structures ($Pm3n$, $P6_3/mmc$ space groups) have been prepared by a dip-coating technique using cationic surfactants as the structure-directing agents in nonaqueous media under acidic conditions.

The integration of hydrogen bonding interaction at the organic/inorganic interface with organic/inorganic domain assembly and the use of sol-gel and emulsion chemistry in acidic media¹⁻⁴ has proven to be a general route for the easy processing of ordered mesoporous materials into desired morphologies.⁵⁻¹¹ Mesoporous silica thin films with highly ordered mesostructures have numerous potential applications in catalysis, sensors, separation, and opto-electric devices.⁴⁻¹¹ We have recently described how surfactant and non-aqueous cosolvents can be used to define mesophase structure,²⁻⁴ and to grow 3-D hexagonal mesostructured silica films at solid-liquid and liquid-vapor interface⁷ following the film growth procedures described by Yang *et al.*⁵ and Aksay *et al.*⁶ for 2-D hexagonal mesostructured silica thin films that have 1-D channel structures with the pore channels oriented parallel to the substrate surface. More recently, the formation of continuous supported cubic and 2-D hexagonal mesoporous silica thin films by sol-gel dip-coating using the above acid synthesis procedure¹⁻³ with addition of ethanol has been reported by Brinker and coworkers;¹¹ fine tuning of the conditions for film formation yields high quality, pinhole-free films with the desired thickness.¹¹

Here we report the formation by dip-coating¹¹ of continuous, stable mesoporous silica thin films with 3-D accessible pore structures using cationic surfactants. Large-head-group cationic surfactants such as $C_{16}H_{33}N(C_2H_5)_3Br$ (CTEABr) or gemini surfactants such as $C_{18}H_{37}N(CH_3)_2(CH_2)_3N(CH_3)_3Br_2$ (C_{18-3-1}) can be used as the structure-directing agent. The thin films exhibit highly ordered mesostructures, which can be 3-D cubic ($Pm3n$ space group) and 3-D hexagonal ($P6_3/mmc$) structures with high BET surface areas (up to $1500\text{ m}^2\text{ g}^{-1}$) and varying pore sizes (18–25 Å).

The mesoporous silica films were deposited by dip-coating on polished (100)-silicon wafers or glass sheets. The coating solutions were typically prepared by the addition of 0.78 g CTEABr cationic surfactant dissolved in 10 g ethanol (EtOH) to polymeric silica sols made by an acid-catalyzed process with stirring for 1 h at room temperature. The polymeric silica sols were prepared by heating a mixture of 2.08 g tetraethylorthoxysilane (TEOS), 5.5 g EtOH, 0.5 g water and 0.4 g (0.1 M) HCl at 70 °C for 1 h. To complete the polymerization of the silicate species and to further improve the thermal stability of the film, the as-deposited film was heated at 80 °C in de-ionized water overnight. After drying, the film supported on the silicon wafer was calcined in air at 500 °C for 4 h to remove the organic template.

Generally, supported silica films prepared using cationic surfactants, such as CTEABr, gemini C_{18-3-1} , and $C_{16}H_{33}N(CH_3)_3Br$ (CTAB), in nonaqueous solutions under acidic conditions are transparent and continuous (see Fig. 1a). The thickness of the film is uniform, and can be varied from 300

nm to several hundred micrometers by changing the coating solution concentration or the coating time.

Fig. 2 shows XRD patterns of as-deposited and calcined supported silica films prepared using cationic surfactants as the structure-directing agent. As-deposited film with CTEABr shows seven well-resolved diffractions peaks in the 2θ range 1–6° (Fig. 2a), suggesting that the as-deposited film has a highly ordered cubic ($Pm3n$) mesostructure with $a = 84.4\text{ Å}$. The XRD pattern remains the same as the film is rotated by 180°, suggesting that the film has an isotropic cubic mesostructure.

After calcination, the XRD pattern (Fig. 2b) of the cubic film shows that the cubic mesostructure is preserved with $\approx 3\%$ shrinkage ($a = 81.7\text{ Å}$). An additional two peaks indexed as (400), (332) are apparent, possibly due to different shrinkage along the 3-D directions. SEM and photomicroscopy images show that the calcined films with thicknesses $< 1\text{ }\mu\text{m}$ are not cracked. TEM images recorded along the [100], [210] and [111] orientations of calcined mesoporous silica films prepared using CTEABr surfactant (Fig. 2b–d) show well-ordered 3-D cubic arrays of mesopores and confirm that the silica film has a highly ordered 3-D cubic ($Pm3n$) mesostructure after calcination.

N_2 adsorption-desorption isotherms of calcined silica films show type IV curves without the hysteresis loop, a pore size of 20 Å, a pore volume of $0.54\text{ cm}^3\text{ g}^{-1}$, and a BET surface area of $1200\text{ m}^2\text{ g}^{-1}$ (Table 1).

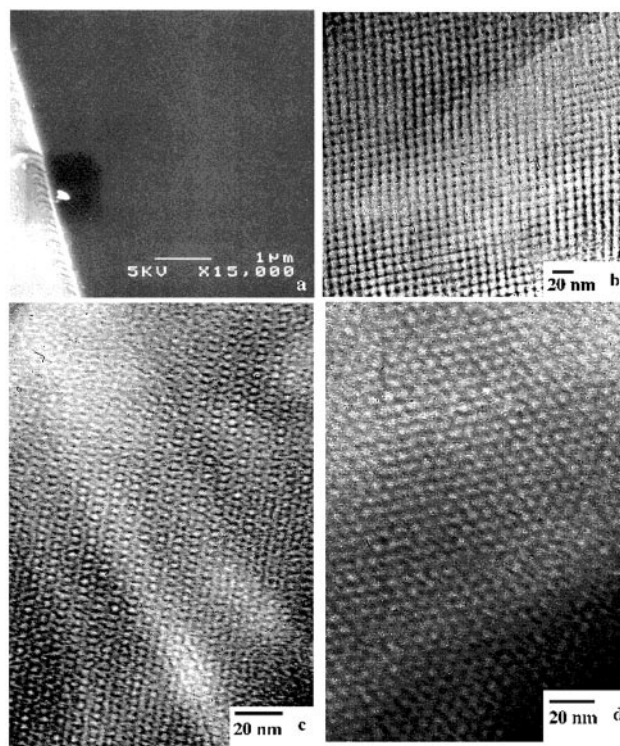


Fig. 1 a, SEM image of as-deposited 3-D cubic mesoporous silica film prepared using CTEABr surfactant. b–d, TEM images of calcined cubic mesoporous silica film with orientations: b, [100] plane; c, [210] plane; and d, [111] plane.

Table 1 Physicochemical properties of mesoporous silica thin films reported in this paper. In each pair with the same surfactant, the second entry was prepared with a high concentration of HCl or a low concentration of surfactant

Surfactant	Phase	Unit cell parameter/Å	Pore size ^a /Å	BET Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹
C ₁₆ H ₃₃ N(C ₂ H ₅) ₃ Br	cubic (<i>Pm3n</i>)	<i>a</i> = 81.7	20	1200	0.54
C ₁₆ H ₃₃ N(C ₂ H ₅) ₃ Br	hexagonal (<i>p6mm</i>)	<i>a</i> = 40.8	18	1080	0.92
C ₁₈ H ₃₇ N(CH ₃) ₂ (CH ₂) ₃ N(CH ₃) ₃ Br ₂	hexagonal (<i>P6₃/mmc</i>)	<i>a</i> = 44.7 <i>c</i> = 74.0	24	1500	0.86
C ₁₈ H ₃₇ N(CH ₃) ₂ (CH ₂) ₃ N(CH ₃) ₃ Br ₂	hexagonal (<i>p6mm</i>)	<i>a</i> = 44.0	25	1160	0.81
C ₁₆ H ₃₃ N(CH ₃) ₃ Br	hexagonal (<i>p6mm</i>)	<i>a</i> = 43.9	24	740	0.67
C ₁₆ H ₃₃ N(CH ₃) ₃ Br	hexagonal (<i>p6mm</i>)	<i>a</i> = 38.2	19	1490	0.76

^a After calcination at 500 °C in air, the pore sizes were calculated by using BJH analysis from the adsorption branch of the isotherms.

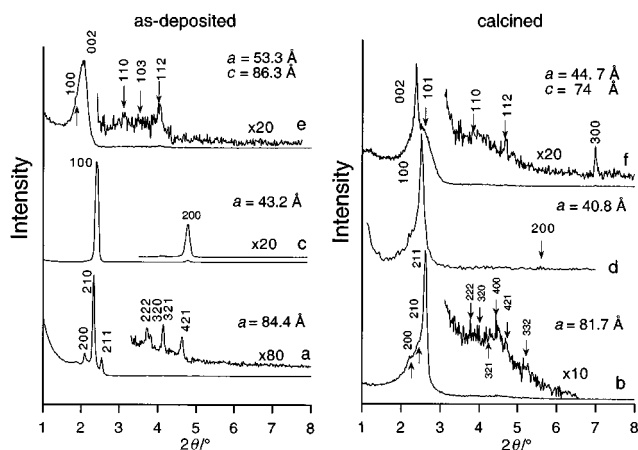


Fig. 2 XRD patterns of a, as-deposited and b, calcined 3-D cubic (*Pm3n*) mesoporous silica thin film prepared using CTEABr surfactant; c, as-deposited and d, calcined 2-D hexagonal mesoporous silica thin film prepared using CTEABr surfactant; e, as-deposited and f, calcined 3-D hexagonal mesoporous silica film prepared using gemini C₁₈₋₃₋₁ surfactant.

3-D cubic mesoporous silica thin films can be grown on the substrate over a range of reaction compositions: the ratios can be 1 TEOS : 0.12–0.37 CTEABr : 4.4–8.9 H₂O : 0.0004–0.004 HCl : 10–60 EtOH at room temperature. Unlike aqueous media synthesis [in which CTEABr only favors forming cubic (*Pm3n*) silica mesostructures under strongly acidic conditions¹], in nonaqueous solution, higher concentrations of HCl result in the formation of 2-D hexagonal (*p6mm*) silica films confirmed by XRD patterns (Fig. 2c,d) and TEM images. N₂ adsorption measurements show the calcined film to have a pore size of 18 Å, a pore volume of 0.92 cm³ g⁻¹, and a BET surface area of 1080 m² g⁻¹ (Table 1).

The 3-D hexagonal mesostructured silica film formed using C₁₈₋₃₋₁ over a range of compositions (1 TEOS : 0.13–0.27 C₁₈₋₃₋₁ : 4.4–11 H₂O : 0.0002–0.002 HCl : 10–60 EtOH) at room temperature shows two strong diffraction peaks with *d*-spacings of 46.2 and 43.2 Å, and three weak peaks with *d*-spacings of 30.7, 24.4, 22.5 Å (Fig. 2e). The XRD pattern can be indexed in the 3-D hexagonal space group *P6₃/mmc* with *a* = 53.3, *c* = 86.3 Å. After calcination, the XRD pattern (Fig. 2f) shows four peaks in the 2θ range 1–8°, which can be indexed as (002), (101), (112) and (300). TEM measurements further confirm that the silica film prepared using C₁₈₋₃₋₁ has a highly ordered 3-D hexagonal mesostructure. N₂ adsorption–desorption isotherms show that the calcined films exhibit type IV curves without the hysteresis loop, a narrow pore size distribution at a mean value of 24 Å, and a BET surface area of 1500 m² g⁻¹ (Table 1).

While in aqueous synthesis, C₁₈₋₃₋₁ surfactant favors formation of only 3-D hexagonal SBA-2,³ in nonaqueous media lower concentrations of C₁₈₋₃₋₁ surfactant and higher concentrations of HCl yield a hexagonal (*p6mm*) oriented silica film with pore channels parallel to the substrate plane. On the other hand,

oriented 2-D hexagonal silica films (Table 1) can also be formed through the use of CTAB as the structure-directing agent over a wide range of compositions (1 TEOS : 0.05–0.42 CTAB : 0.8–2 H₂O : 0.0004–0.04 HCl : 10–100 EtOH). The 2-D hexagonal mesostructure is preserved upon changing the concentration of CTAB surfactant and HCl, but the *d*(100) spacing decreases linearly from 40.8 to 34.5 Å with increase of the concentration of CTAB and HCl. Based on N₂ adsorption measurements, the pore sizes (19–24 Å) of the silica film are also variable with concentration of CTAB and HCl (Table 1). These results suggest that the formation of the silica film occurs with an S⁺X⁻I⁺ self-assembly pathway¹ and that CTEABr surfactants have large head group and favor the formation of the 3-D cubic (*Pm3n*) mesophase.³ Higher HCl concentration results in stronger interaction between inorganic and organic species and favors the formation of the 2-D hexagonal mesophase.

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Notes and references

- Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176; *Nature*, 1994, **368**, 317.
- S. Schacht, Q. Huo, Voigt-Martiniq and G. D. Stucky, *Science*, 1996, **273**, 768.
- Q. Huo, D. I. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147; Q. Huo, R. Leon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.
- D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548, *J. Am. Chem. Soc.*, 1998, **120**, 6024; D. Zhao, P. Yang, Q. Huo, B. F. Chmelka and G. D. Stucky, *Curr. Opin. Solid State Mater.*, 1998, **3**, 111; Q. Huo, D. Zhao, J. Feng, K. Weston, S. K. Buratto, G. D. Stucky, S. Schacht and F. Schüth, *Adv. Mater.*, 1997, **9**, 974.
- H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara and G. A. Ozin, *Nature*, 1996, **379**, 703; H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *Nature*, 1996, **381**, 589; H. Yang, N. Coombs, O. Dag, I. Sokolov and G. A. Ozin, *J. Mater. Chem.*, 1997, **7**, 1755.
- I. A. Aksay, M. Trau, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger and S. M. Gruner, *Science*, 1996, **273**, 892.
- S. H. Tolbert, T. E. Schäffer, J. Feng, P. K. Hansma and G. D. Stucky, *Chem. Mater.*, 1997, **9**, 1962.
- M. Ogawa, *Chem. Commun.*, 1996, 1149; *J. Am. Chem. Soc.*, 1994, **116**, 7941.
- J. E. Martin, M. T. Anderson, J. G. Odinek and P. P. Newcomer, *Langmuir*, 1997, **13**, 4133.
- R. Ryoo, C. H. Ko, S. J. Cho and J. M. Kim, *J. Phys. Chem. B*, 1997, **101**, 10610.
- Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, J. C. Brinker, W. Gong, Y. Guo, H. Soye, B. Dunn, M. H. Huang and J. I. Zink, *Nature*, 1997, **389**, 364.