Continuous Mesoporous Silica Films with Highly Ordered Large Pore Structures**

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Mesoporous silica films can be grown at solid–liquid and liquid–vapor interfaces through an interfacial silica–surfactant self-assembly process,[1–8] and more recently, the formation of continuous mesoporous silica films by sol-gel dip-coating has been reported by Lu et al.[9] All of these films were formed using acidic conditions,[10] and low molecular weight surfactants. Many of them are granular and have 2-dimensional (2D) hexagonal structures with pore channels aligned within the substrate plane, an orientation that does not provide the easy accessibility to the substrate, as required for many separation and catalysis applications.[2–9] Few reports have been published on mesoporous films that might have accessible pores.[6,9,11] Furthermore, these films generally have quite small pore sizes (~20 Å) and relatively low porosities (<60 %).[4,6,9]

Here we report the formation of continuous mesoporous silica films with large periodic cage and pore structures using low-cost commercially available poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers and poly(ethylene oxide) non-ionic surfactants[12–15] as the structure-directing agents in conjunction with dip-coat processing.[9] These structures can be made with either continuous channel or ordered cage arrays. The films exhibit highly ordered and oriented large periodic mesostructures, which can be 3D cubic ($Im\bar{3}m$, $Pm\bar{3}m$ space group), hexagonal ($P6_3/mmc$, $p6mm$) structures with variable pore sizes (34–90 Å) and porosities to 75 %. These films exhibit high thermal stability upon calcination at 450 °C and are crack-free when the thickness is less than 1 μm. The relatively large porosities of the films result in dielectric constants (k = 1.45–2.1) that are very low.

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The mesoporous silica films are deposited by dip-coating on polished (100) silicon wafers and glass slides. The coating solutions are prepared by the addition of an ethanol solution of PEO-PPO-PEO triblock copolymers or alkyl poly(ethylene oxide) oligomeric non-ionic surfactants to silica sol-gels made by an acid-catalyzed process[10,14,15] with stirring for 2 h at room temperature. The silica sol-gels are prepared by heating the mixture of a calculated amount tetraethoxysiliane (TEOS), ethanol, water, and HCl at 50–80 °C for 1 h. Besides ethanol, other organic solvents, such as methanol, 1,4-dioxane, tetrahydrofuran (THF), CH_3CN, and propanol, can be used as the solvents. The silica films are transparent and continuous with smooth surfaces and mesoscopic structures (Fig. 1). The thickness of the film can be uniform and varied from 300 nm to several hundred micrometers by adjusting the coating solution concentration or dip-coating rate (~10 cm/min). Higher concentrations of the coating solution result in thicker films.

Figures 2a and b show X-ray diffraction (XRD) patterns of as-deposited and calcined films prepared by using triblock copolymer $EO_{20}PO_{70}EO_{20}$ species as the structure-directing agents. Shown for comparison in Figure 2c is the XRD pattern of a bulk mesostructured sample synthesized using the same triblock copolymer in a strong acid medium.[15] As shown in Figure 2a, five XRD peaks are observed at a low angle of $2\theta \sim 0.4$–5°, which can be indexed as (100), (200), (300), (400), and (500) reflections of a highly ordered hexagonal ($p6mm$) mesostructure with a large unit cell (a = 105 Å).[14,15] Compared to the bulk sample (Fig. 2c), the (110), (210), (220), and (310) reflections in Figures 2a and b are missing, suggesting that the film has a highly oriented 2D hexagonal mesostructure with its pore channels aligned parallel to the substrate plane. This is similar to films of SBA-3 prepared using low molecular weight cationic surfactant species.[2,3]

To elucidate the orientation of the films, a pole-figure XRD pattern (Fig. 2d) of the uncalcined film was obtained by rotating the film horizontally with respect to the X-ray beam through the 360° from the coating direction. This 2D XRD pattern shows that the intensities of the (200) and (300) peaks substantially change as function of the angle between the X-ray beam and the coating direction of the film. When the angle is 90°, the intensity is at minimum. The coordinate frame is schematically indicated in Figure 2e. In this x–y (film plane–X-ray beam plane) frame, two strong and narrow scattering peaks along y are observed. This is the result expected for a 2D hexagonal ($p6mm$) structure with its pore channels aligned along the coating direction.[12,16] The scanning electron microscopy (SEM) image in Figure 1a of the as-deposited film shows striations on a 10 nm length scale that are consistent with alignment of the cylindrical aggregates along the dip-coating direction. In addition, atomic force microscopy (AFM) images of the as-synthesized 2D hexagonal film confirm that the widths of these periodic film striations are approximately 100 Å. These results are consistent with the XRD

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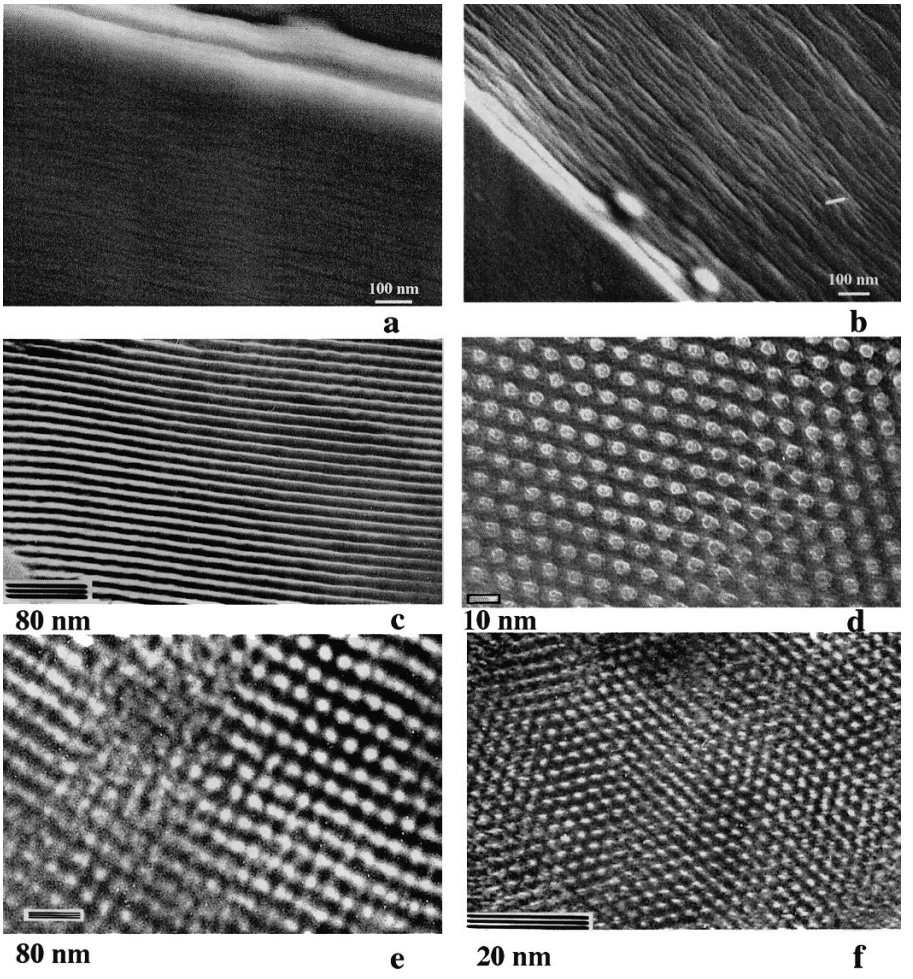

Fig. 1. a,b) SEM micrographs of a) as-deposited and b) calcined hexagonal (*p6mm*) mesoporous silica films prepared using amphiphilic $EO_{20}PO_{70}EO_{20}$ block copolymer structure-directing agents. c,d) TEM images recorded along the c) [110] and d) [100] zone axes of a calcined hexagonal (*p6mm*) mesoporous silica film prepared using $EO_{20}PO_{70}EO_{20}$ triblock copolymer species. e,f) TEM images recorded along the e) [110] and f) [100] zone axes of a calcined cubic ($Im\bar{3}m$) mesoporous silica film prepared using the triblock copolymer $EO_{106}PO_{70}EO_{106}$ species. The SEM images were obtained on a JEOL 6300-F microscope. The TEM micrographs were recorded on a JEOL 2010 electron microscope operating at 200 kV. The samples were detached from the substrates and dispersed as a slurry in acetone, then deposited and dried on a holey carbon Cu grid.

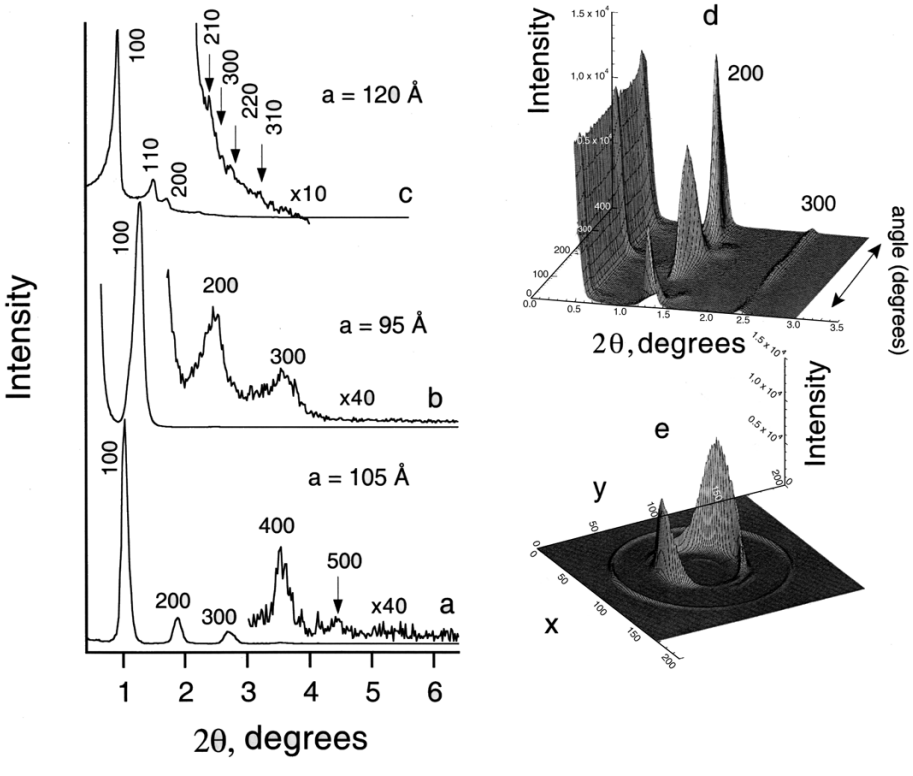

Fig. 2. XRD patterns of a) as-deposited and b) calcined hexagonal (*p6mm*) mesoporous silica films prepared using amphiphilic triblock copolymer $EO_{20}PO_{70}EO_{20}$ species, and c) a bulk sample of hexagonal SBA-15 prepared using the same block copolymer at 40 °C, as described in [15]. 2D XRD patterns of the as-synthesized hexagonal silica film are shown in: d) recorded by rotation of the film plane starting from coating direction, and e) for different directions of the X-ray beam with respect to the film frame. The XRD patterns were acquired on a Scintag PADX diffractometer using Cu Kα radiation; 2D XRD patterns were recorded on Philips X'Pert Powder Diffractometer.

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measurements, and demonstrate that the 2D hexagonal mesostructured silica–$EO_{20}PO_{70}EO_{20}$ film has a high degree of orientational order.

To increase the degree of polymerization of the silica framework and further improve the thermal stability of the film, the as-deposited films were heated in deionized water at 80 °C overnight.[17] After drying, the films were calcined in air at 450 °C for 4 h to remove the block copolymers.[15] The XRD pattern (Fig. 2b) of the calcined film shows that the oriented *p6mm* mesostructure is preserved, although the peaks appear at slightly larger 2θ values with a = 95 Å. Three XRD peaks are still observed, demonstrating that the highly ordered and oriented hexagonal mesostructure of the film is thermally stable after post-treatment. SEM images (Fig. 1b) of the calcined film also show that aggregate striations parallel to the coating direction are preserved upon calcination. SEM and optical microscopy images confirm that calcined films with thicknesses up to 1 μm are free of microcracks. Transmission electron microscopy (TEM) images (Fig. 1c,d) of calcined mesoporous silica films prepared using $EO_{20}PO_{70}EO_{20}$ triblock copolymer species show well-ordered 2D hexagonal *p6mm* arrays of mesopore channels.

N_2 adsorption and desorption isotherms (Fig. 3a) of calcined silica film prepared with $EO_{20}PO_{70}EO_{20}$ are type IV with a clear type H_1 hysteresis loop.[18,19] The calcined silica film has a pore size of 90 Å calculated by using the Barrett–Joyner–Halenda (BJH) analysis and a pore volume of 1.13 cm^3/g and Brunauer–Emmett–Teller (BET) surface area of 840 m^2/g. To the best of our knowledge, the highly ordered hexagonal silica film prepared using $EO_{20}PO_{70}EO_{20}$ block copolymer has the largest pore size and largest porosity (75 %) known for ordered mesoporous silica films.

2D hexagonal mesoporous silica films can be grown on substrates over a wide composition range of (molar ratio) 1 TEOS:(6.8–34) $\times 10^{-3}$ $EO_{20}PO_{70}EO_{20}$:4.4–12.2 H_2O:0.002–0.04 HCl:11–65 EtOH at room temperature. Even with substantial changes in the concentration of the triblock copolymer and HCl, the hexagonal (*p6mm*) mesophase is retained, suggesting that the $EO_{20}PO_{70}EO_{20}$ block copolymer favors the formation of the 2D honeycomb *p6mm* mesostructure. Using different block copolymers such as $EO_{17}PO_{85}EO_{17}$ (Pluronic P103), $EO_{20}PO_{30}EO_{20}$ (Pluronic P65), $EO_{26}PO_{39}EO_{26}$ (Pluronic P85), or $EO_{13}PO_{70}EO_{13}$ (Pluronic L64) as the structure-directing agents, 2D hexagonal silica films can also be formed with adjustable pore sizes from 40 to 90 Å and porosities from 51 % to 75 % (Table 1).

Cubic mesoporous silica films can be formed using triblock copolymers with higher EO to PO ratios, such as $EO_{106}PO_{70}EO_{106}$ (Pluronic F127). Figures 4a and b show

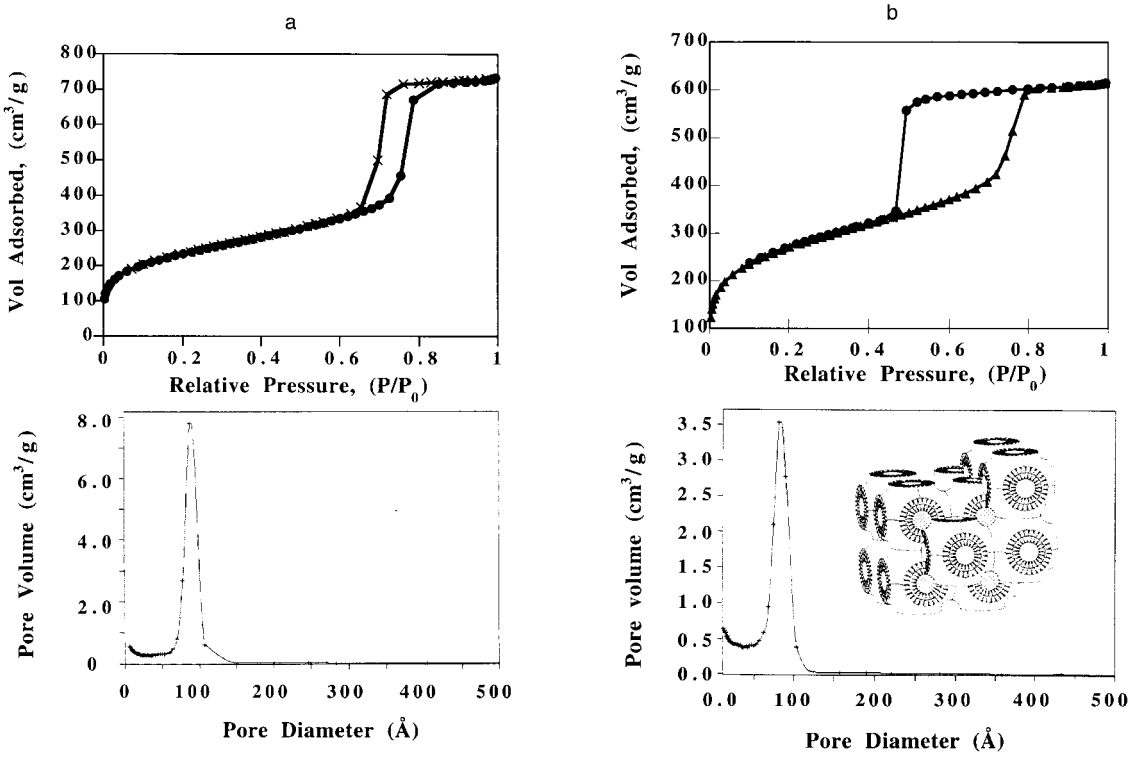

Fig. 3. Nitrogen adsorption(●)–desorption(×) isotherms and pore size distribution plots obtained using a calculated BJH model for the adsorption branch isotherm for a) a calcined hexagonal (*p6mm*) mesoporous silica film prepared with the triblock copolymer $EO_{20}PO_{70}EO_{20}$ and b) a calcined cubic ($Im\bar{3}m$) mesoporous silica film prepared using the triblock copolymer $EO_{106}PO_{70}EO_{106}$. Shown as an inset in b) is a model of the cubic $Im\bar{3}m$ cage-structure based on simulation [20] of surfactant/water system. The isotherms were measured using a Micromeritics ASAP 2000 system. The pore volume was determined from the adsorption branch of the N_2 isotherm curve at P/P_0 = 0.983 single point. The samples were obtained by detaching the calcined supported films from the substrates, followed by outgassing overnight at 180 °C before analysis.

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Table 1. Physicochemical properties of mesoporous silica films.

Surfactant	Phase	Unit cell parameter [Å]	Pore size [Å]	BET surface area [m^2/g]	Pore volume [cm^3/g]	Crack-free threshold thickness
$EO_{20}PO_{70}EO_{20}$	hexagonal (*p6mm*)	*a*=105	90	840	1.13	>1 μm
$EO_{106}PO_{70}EO_{106}$	cubic ($Im\bar{3}m$)	*a* = 184	85	970	0.95	>1 μm
$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	cubic ($Pm\bar{3}m$)	*a* = 121	34	930	0.93	>1 μm
$C_{18}H_{37}(OCH_2CH_2)_{10}OH$	3D hexagonal ($P6_3/mmc$)	*a* = 77.3	35	880	0.81	>1 μm
		c = 129				
$EO_{106}PO_{70}EO_{106}$	3D hexagonal ($P6_3/mmc$)	*a* = 132	65	580	0.45	>1 μm
		c = 211				
$EO_{17}PO_{85}EO_{17}$	hexagonal (*p6mm*)	*a*=101	64	770	0.72	>1 μm
$EO_{20}PO_{30}EO_{20}$	hexagonal (*p6mm*)	*a*=77.5	40	840	0.75	>1 μm
$EO_{26}PO_{39}EO_{26}$	hexagonal (*p6mm*)	*a*=98.7	58	920	0.98	>1 μm
$EO_{13}PO_{70}EO_{13}$	hexagonal (*p6mm*)	*a*=79.2	46	890	0.93	>1 μm

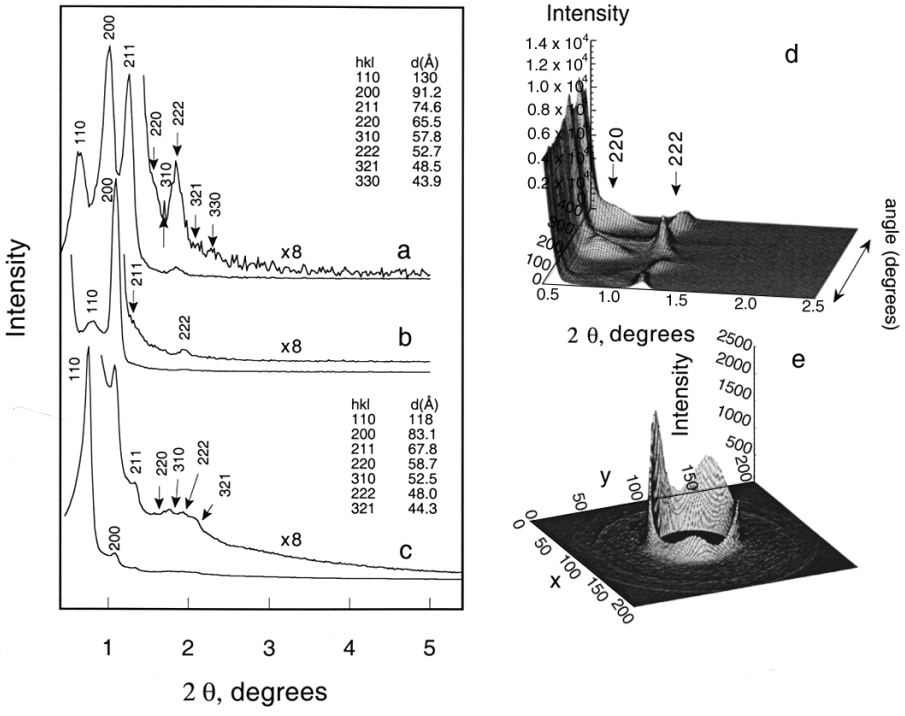

Fig. 4. XRD patterns of a) as-deposited and b) calcined $Im\bar{3}m$ cubic mesoporous silica films prepared using amphiphilic $EO_{106}PO_{70}EO_{106}$ triblock copolymer species as structure-directing agents. c) XRD pattern of a bulk sample of SBA-16 prepared using the same block copolymer at room temperature as described in [14]. d,e) 2D XRD patterns of as-deposited cubic silica film recorded d) by rotation of the film plane starting from coating direction and e) for different directions of the X-ray beam with respect to the film coordinate frame.

XRD patterns of as-deposited and calcined silica films prepared by using $EO_{106}PO_{70}EO_{106}$ triblock copolymer. The XRD pattern (Fig. 4a) of the as-deposited film shows three strong reflections in the 2θ range of 0.4°–1.2°. Five additional weak peaks are observed in the 2θ range of 1.2°–2.5°. These have *d*-spacing ratios of $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{5}{:}\sqrt{6}{:}\sqrt{7}{:}\sqrt{9}$, and can be indexed as the (110), (200), (211), (220), (310), (222), (321), and (330) reflections, respectively, in the cubic space group ($Im\bar{3}m$).[20,21] When compared with the XRD pattern (Fig. 4c) of a bulk sample synthesized using the same block copolymer under strong acidic conditions,[14] both samples show similar Bragg reflections in their XRD patterns, but with different relative intensities. These results suggest that the cubic silica film has an orientationally ordered 3D structure (a = 184 Å).[12] After calcination at 450 °C, the reflections in the XRD pattern (Fig. 4b) appear at higher angles, consistent with contraction of the framework; some of the weak XRD peaks are no longer resolved. Four peaks are observed that can be indexed as (110), (200), (211), and (222) reflections with a = 160 Å, showing that the 3D cubic mesoporous film is thermally stable. TEM images of the calcined films show well-ordered cubic mesostructures along the [110] and [100] zone axes (Fig. 1e,f) and further confirm that the silica film

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formed with $EO_{106}PO_{70}EO_{106}$ has a highly ordered 3D cubic mesostructure. SEM images of the as-deposited and calcined 3D cubic mesoporous films made with $EO_{106}PO_{70}EO_{106}$ show smooth, crack-free, and continuous surfaces.

2D XRD patterns of the as-synthesized cubic film prepared using $EO_{106}PO_{70}EO_{106}$ triblock copolymer surfactant species are shown in Figures 4d and e. The scattering intensities from the (220) and (222) reflections for the as-deposited film vary with the angle between the X-ray beam and the coating direction (Fig. 4d). In the *x–y* frame a scattering pattern with four peaks is observed (Fig. 4e). This is a typical 2D XRD pattern for a film with a 3D cubic mesostructure,[12] whose (100) plane is aligned parallel to the substrate.

N_2 adsorption/desorption isotherms (Fig. 3b) obtained for the calcined 3D cubic mesoporous silica film (prepared with $EO_{106}PO_{70}EO_{106}$) show type IV adsorption isotherm behavior with a large type H_2 hysteresis loop.[18,19] This is consistent with the film's large cage structure (Fig. 3b),[20,22] which to our knowledge is the first demonstration of such 3D cubic features. The calcined films exhibit a large pore size of 85 Å, a high BET surface area of 970 m^2/g, and a porosity of 67 %.

Mesoporous silica films with 3D cubic structures can be grown at room temperature on substrates over a relatively wide range of reaction compositions, for example, 1 TEOS:(2.4–12) $\times$ 10^{-3} $EO_{106}PO_{70}EO_{106}$:4.4–14 H_2O:0.002–0.04 HCl:15–65 EtOH in molar ratio. Interestingly, when much higher concentrations of the triblock copolymer species $EO_{106}PO_{70}EO_{106}$ in ethanol are used (e.g., 1 TEOS:(6–11) $\times$ 10^{-3} $EO_{106}PO_{70}EO_{106}$:1–2 H_2O:0.005–0.015 HCl:3–4 EtOH), a hexagonal ($P6_3/mmc$) mesostructured silica film (a = 132 Å, c = 211 Å, c/a = 1.60) is formed, based on XRD and TEM results. This hexagonal mesostructured silica film exhibits a large pore size of 65 Å, a BET surface area of 580 m^2/g, and a porosity of 51 % (Table 1).

Other $P6_3/mmc$ hexagonal mesostructured silica films with smaller pore sizes can be formed at room temperature using lower molecular weight alkyl(ethylene oxide) nonionic surfactants, such as $C_{18}H_{37}(OCH_2CH_2)_{10}OH$ ($C_{18}EO_{10}$), over a wide composition range, for example 1 TEOS:0.07–0.28 $C_{18}EO_{10}$:3.4–12.2 H_2O:0.002–0.06 HCl:11–65 EtOH. As shown in Figure 5a, the XRD pattern of the as-deposited film prepared with $C_{18}EO_{10}$ is well-resolved. Eight peaks are observed over the 2θ range of 1°–7°, which can be indexed as the (100), (002), (101), (110), (112), (211), (300), and (310) reflections of a hexagonal (space group $P6_3/mmc$) mesostructure (unit cell parameter a = 72.8 Å, c = 118 Å, c/a = 1.62).[22] From N_2 adsorption/desorption measurements, the calcined films exhibit a narrow pore size distribution (full width at half maximum (FWHM) = 6 Å) centered at a mean value of 35 Å. These pore dimensions are larger than those (18–25 Å) measured for silica films prepared using cationic surfactants, such as

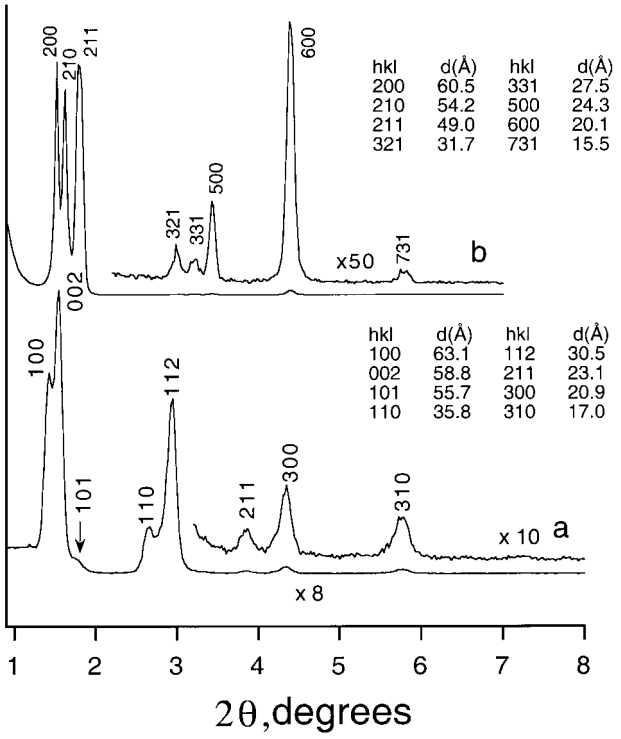

Fig. 5. XRD patterns of a) as-deposited $P6_3/mmc$ hexagonal mesoporous silica film prepared using non-ionic $C_{18}EO_{10}$ surfactant species as structure-directing agents and b) as-deposited 3D cubic ($Pm\bar{3}m$) mesoporous silica film prepared using $C_{16}EO_{10}$.

$C_{16}H_{33}N(CH_3)_3Br$ (CTAB), $C_{16}H_{33}N(CH_2CH_3)_3Br$, or gemini $C_{18\text{-}3\text{-}1}$.

Using non-ionic $C_{16}EO_{10}$ surfactant species as structure-directing agents under acid conditions yields 3D cubic mesoporous silica films. Three strong diffraction peaks are observed in the 2θ range of 1°–2°, and five additional well-resolved peaks are also observed between 2θ values of 2° and 6° (Fig. 5b). These can be indexed as (200), (210), (211), (321), (331), (500), (600), and (731) reflections of a highly ordered 3D cubic ($Pm\bar{3}m$) mesostructure. The 2D XRD pattern (not shown here) displays two strong reflections peaks in every three circle scatters from (200), (211), and (500) diffractions within the *x–y* planes suggesting that the (110) plane of the 3D cubic film is oriented on average parallel to the substrate plane. Lu et al.[9] have prepared a 3D cubic (possibly $Pm\bar{3}m$) mesoporous silica film by calcination-induced transformation from an as-deposited 3D hexagonal film prepared using the cationic surfactant CTAB. They suggested that the formation of the 3D cubic film was derived from 1D shrinkage due to a constrained 1D distortion of the cubic cell along the (110) direction. However, our 3D cubic film made with $C_{16}EO_{10}$ is formed directly by self-assembly and preserved during subsequent calcination treatment. The calcined 3D cubic film prepared with $C_{16}EO_{10}$ exhibits a large mean pore size of 34 Å with a narrow pore size distribution (FWHM = 5 Å), a high BET surface area of 930 m^2/g, and a pore volume of 0.93 cm^3/g.

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Such 3D cubic ($Pm\bar{3}m$) films can be formed over a range of compositions (e.g., 1 TEOS:0.07–0.29 $C_{16}EO_{10}$:3.4–12.2 H_2O:0.002–0.06 HCl:11–65 EtOH).

Dielectric constants (k) were measured on the calcined silica films deposited on heavily n-doped (100) silicon substrates by performing frequency dependent capacitance–voltage measurements on a metal-oxide-semiconductor structure.[23] The k values of these highly ordered mesoporous silica films are 1.45–2.1, and are strongly dependent on the structure and porosity of the film. Larger porosities generally give lower k values for the same structure.

In summary, a series of continuous, crack-free, highly ordered mesoporous silica films with large periodic pore structures, including 2D hexagonal ($p6mm$), 3D cubic ($Im\bar{3}m$, $Pm\bar{3}m$), and 3D hexagonal ($P6_3/mmc$) symmetries, can be formed using non-ionic poly(alkylene oxide) triblock copolymers and low molecular weight alkyl(ethylene oxide) surfactants under acidic medium by employing a dip-coating technique. The continuous films have highly ordered large pore sizes (34–90 Å), porosities of 51 %–75 %, uniform thicknesses of 300 nm to several hundred micrometers, and exhibit preferred orientations with low dielectric constant values (k = 1.45–2.1). The dielectric properties are being investigated in detail and will be described in a separate publication.

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