Spin-Coated Periodic Mesoporous Organosilica Thin Films with Molecular-Scale Order within the Organosilica Wall

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Periodic mesoporous organosilica (PMO) thin films with long-range molecular order within the organosilica framework have been successfully prepared by spin-coating a solution of 1,4-bis(triethoxysilyl)benzene (BTEB), water, ethanol, HCl, and cetyltrimethylammonium bromide (CTAB) on silicon substrates. Powder XRD patterns of these thin films reveal the presence of a hexagonal phase mesostructure as well as ordered molecular-scale structure. The strong high-angle diffraction peaks indicate the long-range molecular order within the organosilica framework. The degree of organosilica condensation is relatively low, and hydroxyl groups formed in the hydrolysis reaction link the BTEB precursor molecules together in an end-to-end fashion via hydrogen bonding. Infrared spectra of these thin films suggest that the PMO films contain a significant number of hydroxyl groups in a hydrogen bonding environment with a peak at 3200 cm^{-1}. Results from the ^{29}Si magic-angle spinning (MAS) NMR spectroscopy provide additional evidence of the lower degree of organosilica condensation in these PMO thin films. High-resolution transmission electron microscopy (TEM) images reveal both the presence of mesopores and lattice fringes from the ordered packing of the hydrolyzed precursor molecules. The interior wall silanol groups are accessible, and their conversion into Si–O–Si(CH$_3$)$_3$ groups has been demonstrated.

Introduction

Various periodic mesoporous organosilicas (PMO) using bridged silsesquioxane monomers of the type [(EtO)$_3$Si–R–Si(OEt)$_3$] with organic spacers such as ethane, ethene, thiophene, benzene and substituted benzene, biphenylene, ferrocene, and other groups have been synthesized in recent years via surfactant-templated assembly.[1–11] The successful preparation of these organosilica materials enriches the field of mesoporous silica studies. These organosilicas may find use as low-*k* dielectric materials and new optical materials through fluorescent bridging groups and can carry out addition reactions with the bridging ethene groups.[2–5,12] Mesoporous carbon/silica composites can also be made from phenyl-bridged organosilanes.[13] In addition to the above studies on the syntheses of powder materials, PMO thin films with some of the same bridging groups have been prepared.[12,14–17] Among the organosilane monomers that have been used, mesoporous organosilica materials synthesized using benzene and biphenylene-bridged silsesquioxanes are particularly interesting because the resulting materials can display a crystal-like wall structure.[6–9,13a,17] In these studies, the PMO materials were prepared under a strongly basic condition with the addition of a large amount of NaOH relative to the precursor molecules. The products showed pore walls with structural periodicity of 7.6 Å for the benzene-bridged PMO materials, resulting from highly condensed precursor molecules as verified by the ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of the samples. Only a very recent report has described the synthesis of molecularly ordered biphenyl-bridged PMO under acidic conditions.[18] Furthermore, with the exception of one study on the formation of free-standing benzene-bridged PMO films by a hydrothermal approach, all other benzene-bridged PMO materials synthesized have been in the form of powder.[17] Preparation of benzene-bridged PMO thin films by a convenient spin-coating process using an acid-catalyzed precursor sol has not been demonstrated.

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Here, we report the formation of benzene-bridged PMO thin films with molecular-scale periodicity in the organosilica walls by spin-coating substrates. The precursor sol was prepared with the addition of just a tiny amount of HCl as catalyst for the sol–gel reactions, and CTAB surfactant served as the templating agent for the mesophase formation. The PMO thin films show both hexagonal mesophase structure and unusual ordered organosilicate arrangement mediated by hydrogen bonding to give a molecular periodicity with a longer spacing than has been found before for benzene-bridged PMOs. The existence of hydrogen-bonding-mediated framework structure resulting from a lower degree of silsesquioxane condensation in these PMO thin films has been verified using different spectroscopic techniques and electron microscopy.

Experimental Section

1,4-Dibromobenzene (99%) was purchased from Aldrich. Tetraethyl orthosilicate (TEOS, 98%) was obtained from Acros. Tetrahydrofuran (THF) and hexane were acquired from Mallinckrodt. Ethanol (99.8%) and hydrochloric acid were purchased from Riedel-de Haën. Magnesium was obtained from J. T. Baker. 1,4-Bis(triethoxysilyl)benzene (BTEB) was synthesized by the Grignard reaction following a reported procedure with little modification.[19] The final clear colorless oil collected was verified as pure BTEB by ^{1}H nuclear magnetic resonance (NMR) spectra recorded on a Varian Mercury-400 (400 MHz, $CDCl_3$) spectrometer: δ 7.65 (s, 4 H, ArH), 3.85 (q, 12 H, $J = 7.2$ Hz, OCH_2CH_3), 1.22 (t, 18 H, $J = 7.2$ Hz, OCH_2CH_3).

The PMO thin films were synthesized from an acidic organosilicate solution. First, BTEB (0.4 mL), ethanol (2.32 mL), deionized water (0.13 mL), and HCl (0.026 mL, 0.21 N) were added to a plastic vial in the order listed. This solution was stirred for 20 min with the vial cap sealed to prevent loss of ethanol. Next, 3.5 wt % CTAB was added to this solution and stirred for additional 10 min. The molar ratios of the reagents are 1:40:7.4:5.53 × 10^{-3}:0.23 BTEB:ethanol:H_2O:HCl:CTAB. The solution was aged for 15 min without stirring. The stirring and aging time used have been found to be optimal for the retention of the film mesostructure after solvent extraction. Si (100) wafers cut to dimensions of 1 cm × 1 cm were boiled with piranha acid (4:1 H_2SO_4:H_2O_2 volume ratio) for 30 min and then deionized water for 45 min. Acid-treated substrates were cleaned with deionized water and stored in water. A substrate was mounted on a spin-coater. Three drops of the sol solution were added to cover the entire substrate surface. The substrate was spin-coated with the sol to form a thin film using a rotation speed of 1200 rpm for 10 s and then at 3600 rpm for 30 s. One hour after the film formation, the substrates were placed in an oven set at 90 °C for 24 h to complete the condensation reaction. Surfactant was subsequently removed by immersing the oven-dried PMO thin films in a solution of ethanol (2 mL) and 37% HCl (30.4 μL) in a sealed glass vial at 70 °C for 8 h. The extracted thin films were cleaned with ethanol and dried at room temperature.

The presence of mesostructure and molecular scale periodicity of these PMO thin films were determined from their powder X-ray diffraction (XRD) patterns recorded using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were collected on a Perkin-Elmer Spectrum RX I spectrometer. Solid-state ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) and ^{13}C cross-polarization (CP) MAS NMR spectra were obtained from a Bruker DSX-400WB spectrometer. ^{29}Si MAS NMR spectra were recorded at a spin rate of 6.5 kHz and a pulse delay of 5 s. ^{13}C CP MAS NMR experiments were performed at a spin rate of 6.5 kHz, a contact time of 1 ms, and a pulse delay of 2 s. The PMO thin films were scratched off the silicon substrates and combined to an amount sufficient for the NMR characterization. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 transmission electron microscope operating at 200 kV. Cross-sectional film samples for TEM analysis were made by a standard wafer polishing and ion milling procedure. Scanning electron microscopy (SEM) image of the film cross section was acquired using a JEOL JSM-6330F scanning electron microscope. Structural model of the layered arrangement of partially condensed BTEB units was drawn using Chem3D Ultra MM2 calculations with energy minimization.

Results and Discussion

Figure 1 shows the low- and high-angle XRD patterns of the benzene-bridged PMO thin films spin-coated on Si (100) substrates before and after solvent extraction. The XRD patterns are consistent with the presence of a hexagonal mesophase with one-dimensional pore channels in mesoporous sol–gel thin films on a solid substrate.[20] The d-spacing of the (100) diffraction peak decreased from 35.2 Å (unit-cell constant $a = 40.6$ Å, $a = 2d_{(100)}/\sqrt{3}$) to 31.4 Å ($a = 36.3$ Å) after solvent extraction, suggesting a slight shrinkage of the pore diameter. Interestingly, strong diffraction peaks at 8.77, 17.76, 26.67, 35.92, and 45.36° 2θ (or $d = 10.1$, 5.0, 3.3, 2.5, and 2.0 Å) were also recorded, which should correspond to the molecular-scale periodic structure present in the thin films. The observation of these high-angle diffraction peaks after solvent extraction suggests the retention of the ordered molecular arrangement in the films using the reaction conditions described. On the basis of the structural analysis of benzene–silica hybrid material formed by the same BTEB monomer with sharp XRD peaks at $d =$ 7.6, 3.8, 2.5, and 1.9 Å, the PMO thin films formed in this study should also possess a similar crystal-like organosilica framework structure.[6] However, a correct structural model of the regular molecular arrangement between the adjacent benzene–silica layers must account for the additional 2.5 Å spacing observed in these PMO thin films. A possible explanation of this observed effect is the presence of extensive hydrogen bonding as a result of a lower degree of silicate condensation, which should effectively elongate the benzene–silica layers. The molecular packing structure of benzene-bridged bis-silanetriol [$(HO)_3Si–C_6H_4–Si(OH)_3$] has been solved before.[21] Sheets of the bis-silanetriol molecules are stabilized via hydrogen bonding, and the unit–cell parameter a of this solid is equal to 10.056 Å. Thus, the PMO thin films are likely to contain an organosilica framework with largely partially condensed BTEB molecules, and extensive hydrogen bonding elongates the periodic interlayer spacing.

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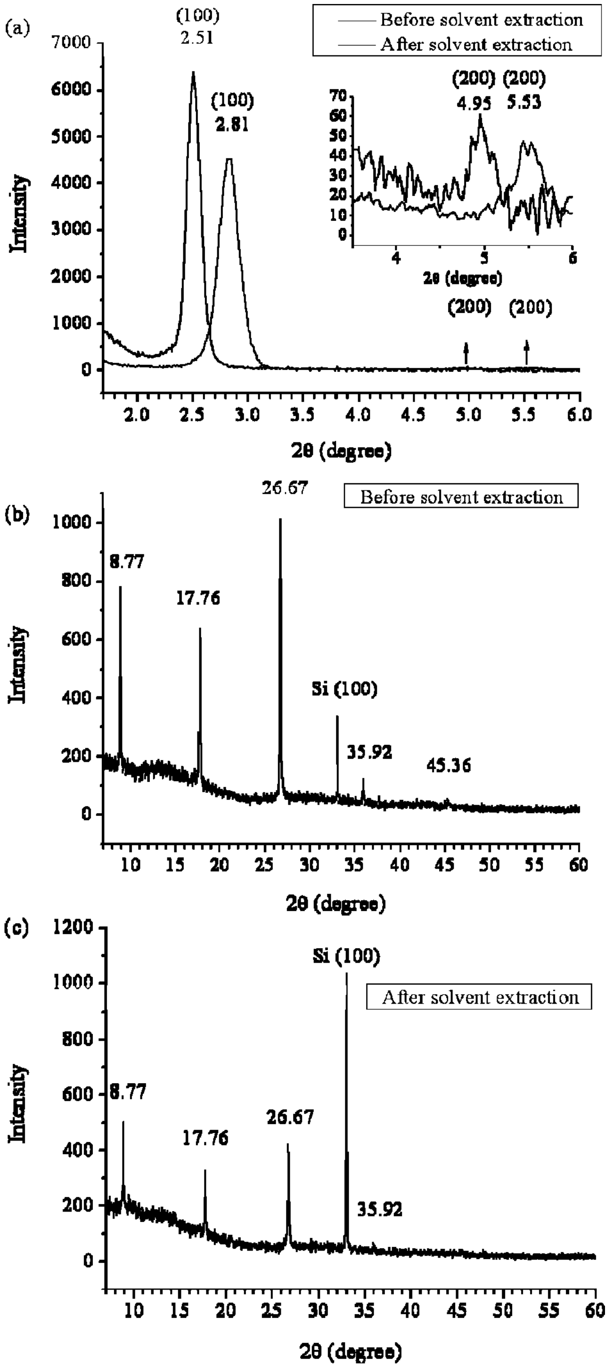

Figure 1. (a–c) Low- and high-angle XRD patterns of the spin-coated PMO thin films before and after solvent extraction.

To provide more evidence of the existence of such a framework structure, we took FT-IR spectra of the PMO thin films before and after solvent extraction (see Figure 2). The peaks at 1465, 2850, and 2920 cm^{-1} are assigned to the methylene group vibrations of CTAB.[22] After solvent extraction, these peaks disappeared as the surfactant was removed from the PMO thin films. The broadband centered at 3250 cm^{-1} is attributed to the vibrations of hydrogen-bonded –OH groups.[22] This is a direct evidence of Si–OH groups participating in hydrogen bonding with neighboring hydrolyzed BTEB molecules. After solvent extraction, the band

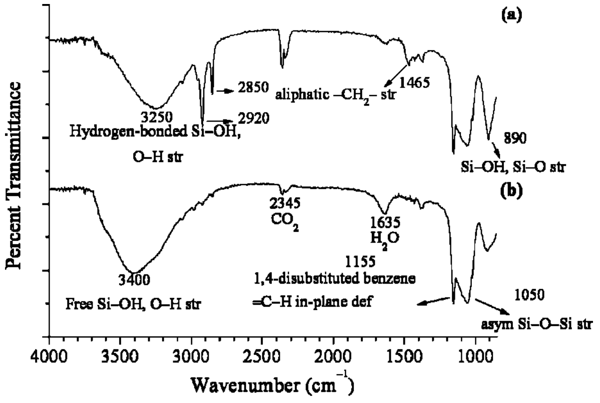

Figure 2. FT-IR spectra of the PMO thin films (a) before and (b) after solvent extraction.

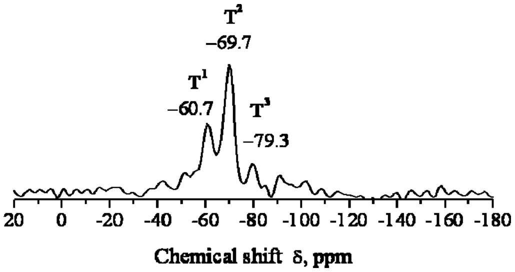

Figure 3. ^{29}Si MAS NMR spectrum of the as-synthesized PMO thin films.

shifted to 3400 cm^{-1}, and a shoulder at around 3600 cm^{-1} was also recorded. This result suggests that a fraction of the hydroxyl groups originally involved in hydrogen bonding has become free –OH groups. This may weaken the overall well-ordered molecular arrangement; the decreased XRD peak intensities of the PMO thin films after solvent extraction are consistent with this observation. The peaks at 890 and 1050 cm^{-1} are from the Si–O stretching vibrations of Si–OH and Si–O–Si groups, respectively. With respect to the intensity of the bridging phenyl C–H vibration band at 1155 cm^{-1}, the spectra also show that the extent of silicate condensation has increased after solvent extraction.

Further characterization of the organosilica framework structure was performed using NMR spectroscopy. ^{13}C CP MAS NMR of the as-synthesized PMO thin films before solvent extraction revealed the expected signals for the $-C_6H_4-$ group and CTAB surfactant (see the Supporting Information). No signals from the $-OCH_2CH_3$ groups were observed, indicating the BTEB molecules have undergone a nearly complete hydrolysis reaction. NMR spectra after solvent extraction were not taken because a sufficient amount of the extracted film sample was hard to obtain. Figure 3 gives a ^{29}Si MAS NMR spectrum of the as-synthesized PMO thin films. Three peaks appeared at −60.7, −69.7, and −79.3 ppm and are attributable to the T^1 ($\mathit{Si}C(OH)_2(OSi)$), T^2 ($\mathit{Si}C(OH)(OSi)_2$), and T^3 ($\mathit{Si}C(OSi)_3$) silicon species. The intensities of the T^1 and T^2 bands are stronger than that of the T^3 band, revealing a lower degree of the organosilicate condensation and a high concentration of hydroxyl groups available for hydrogen bonding. In contrast, benzene-bridged PMO materials prepared under strongly basic conditions showed ^{29}Si NMR peak intensities in the order of $T^3 > T^2 > T^1$.[6,17] Small signals at −91.2 and −101.7 ppm are

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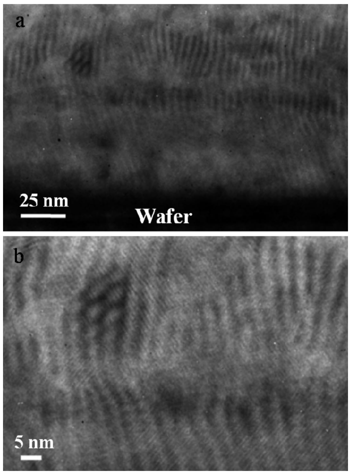

Figure 4. (a) Cross-sectional TEM image of a PMO thin film with solvent extraction. (b) TEM image of the upper left corner in panel a. Two sets of lattice fringes with different directions can be discerned.

assigned to the Q^2 and Q^3 bands of tetraethyl orthosilicate (TEOS). A tiny amount of TEOS may be inadvertently distilled into the BTEB solution during its synthesis in a few cases, but should not affect the overall film structure. Most film samples were made using pure BTEB solution.

Figure 4 presents the cross-sectional TEM images of a PMO thin film. Despite the fact that the film thickness was found to be ~650 nm, as measured from the cross-sectional SEM image of a PMO thin film (see the Supporting Information), only a portion of the well-ordered pore channels was clearly visible in this TEM image. Unfortunately, efforts to prepare more cross-sectional samples were not quite successful. For this solvent-extracted film sample, surfactant removal was not complete as verified by its FT-IR spectrum, and its XRD pattern showed a weak (100) peak at approximately the same position as that of a PMO thin film without solvent extraction. The black stripes are believed to be the organosilica and the white stripes are the pore channels. The spacing between adjacent channels is about 4 nm, which is consistent with the unit-cell parameter *a* found in the XRD pattern given in Figure 1. Interestingly, many lattice fringes with a spacing of ~10 Å are also observed, which matches with the spacing of molecular-scale periodicity found in the XRD pattern. The lattice fringes make an angel of roughly 45–60° with respect to the direction of the pore channels, in sharp contrast to the more typical perpendicular arrangement reported in the literature.[6,9,17] The TEM image also shows the vertical alignment of the channels to the substrate surface. This channel orientation is unusual and rarely observed, as parallel channel alignment is more often obtained for mesoporous silica thin films. However, strong (100) peak intensity in the XRD pattern of the PMO thin films suggests preferential parallel channel alignment to the substrate surface. These results seem to say that although the film mesostructure is predominantly oriented parallel to the silicon wafer, at least a portion of the mesopores are aligned vertically. Optical and SEM images of the spin-coated PMO thin films display a flaky film texture with some cracks (see Figure 5 and the Supporting Information). This film structure may give rise to domains with different mesostructure orientations.

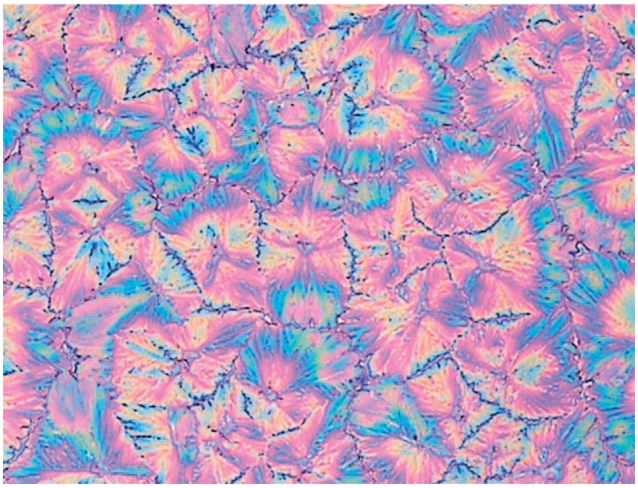

Figure 5. Bright-field optical image of an as-synthesized PMO thin film showing its flaky texture (×200). The film is not smooth and continuous, but contains cracks.

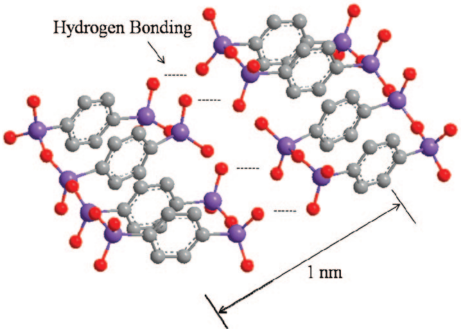

Figure 6. Structural model of the layered arrangement of the partially condensed BTEB units in the walls. Silicon, purple; oxygen, red; carbon, gray; hydrogen, omitted in this model.

On the basis of the above experimental results, a structural model for the layered arrangement of the partially condensed BTEB units in the walls was constructed and is shown in Figure 6. Because of the relative simplicity of the program used, this model is just intended for the visualization of the local molecular structure. Nevertheless, it was constructed taking into account the low degree of BTEB condensation with mainly T^1 and T^2 silicon species and the necessity to form hydrogen bonds between the organosilicate layers. The interlayer spacing was measured to be ~10 Å with this model. In addition to the siloxane covalent linkages, this model shows that the structure is also stabilized by the hydrogen bonding and π–π interactions of the phenyl groups. Notice that long-range-ordered phenyl group stacking is not achieved in this structural model, which may explain the absence of a reflection peak in the XRD pattern of the thin films at 20.2° 2θ (or $d = 4.4$ Å) because of the intermolecular distance of benzene rings.[6]

To investigate the accessibility of interior silanol groups, and further confirm the presence of significant silanol groups within the walls, we treated some solvent-extracted PMO thin films with hexamethyldisilazane ($(CH_3)_3Si–NH–Si(CH_3)_3$, HMDS). The PMO films were immersed in HMDS solution for 24 h, washed with ethanol, and dried at room temperature. XRD patterns of the resulting samples indicate the retention of mesostructure with *d*-spacing of the (100) peak shifted to 2.55° 2θ (or $a = 40.0$ Å) and a loss of molecular-scale periodicity (see the Supporting Information). Silanol groups functionalized to $Si–O–Si(CH_3)_3$ groups caused a slight expansion of the organosilane wall thickness with the $–Si(CH_3)_3$ group insertion and effectively destroyed the molecular-scale periodicity. The FT-IR spectrum of the HMDS-treated PMO thin film shows almost no peaks at 890 and 3400 cm^{-1}, as silanol groups have been modified (see the Supporting Information). The appearance of a new peak at 1257 cm^{-1} assigned to the CH_3 vibrations of the $Si(CH_3)_3$ group further proves that the functionalization is successful.[22] The resulting PMO thin films should also become more hydrophobic.

The stability of the thin films is affected by the degree of hydrolysis and condensation reactions of the BTEB molecules. A precise control of the reaction conditions is critical to forming PMO thin films with both mesoscale and molecular-scale order. Four different HCl concentrations have been tested (that is, 0.07, 0.14, 0.21, and 0.28 N); the hexagonal mesostructure was preserved after solvent extraction only for films prepared with 0.21 N HCl in the sol. Increasing the total stirring and aging time to 60 min or longer resulted in the loss of both mesostructure and molecular-scale order because of highly condensed BTEB molecules. It was found that stirring the final sol for 20 min and aging for 10–20 min yielded stable PMO thin films.

Conclusion

In summary, we have demonstrated a spin-coating procedure for the formation of benzene-bridged PMO thin films with both hexagonal mesostructure and molecular-scale order. The acid-catalyzed procedure leads to a low degree of siloxane linkages, and the hydrolyzed organosilane precursor molecules form extensive hydrogen bonding with neighboring molecules. The film structures have been studied using several techniques. This unusual molecular arrangement within the organosilica framework increases the periodic intermolecular spacing to 10.1 Å, which is 2.5 Å longer than PMO materials made using the same precursor but with a high extent of polycondensation. At least some regions of the PMO thin films contain pore channels with vertical orientation relative to the substrate surface. The interior wall silanol groups are accessible, and their conversion into $Si–O–Si(CH_3)_3$ groups has been demonstrated. By properly selecting the reaction conditions such as the acid concentration and the stirring and aging time, we can maintain the film mesostructure and molecular-scale periodicity after solvent extraction. The procedure described here should be extendable to synthesize PMO thin films using other organosilane monomers.

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Supporting Information Available: ^{13}C CP MAS NMR of the as-synthesized PMO thin films, SEM image of the film, and XRD patterns and FT-IR spectrum of the HMDS-treated film sample (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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