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High-quality free-standing and oriented periodic mesoporous organosilica films grown without a solid substrate at the air–water interface†

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In this communication, we report the first synthesis of high-quality free-standing and oriented periodic mesoporous organosilica (PMO) films grown without a solid substrate, by surfactant templating at the air–water interface.

Surfactant-templated binuclear alkoxysilane precursors, $(R'O)_3Si–R–Si(OR')_3$, allow the assembly of periodic mesoporous organosilica (PMO) nanocomposite materials with bridge-bonded organic groups housed inside the channel walls.[1–3] These PMO materials facilitate chemistry of the channels and provide new opportunities for controlling the chemical, physical, mechanical, and dielectric properties of the materials.[4] Recently, mesoporous organosilica films were reported based on the synthesized hydrolytic polycondensation of an alkoxysilane with a bridging organic group ($(R'''O)_3Si–R''–Si(OR''')_3$) ($R''' = –CH_3$ or $–C_2H_5$, R'' = ethane, ethylene, thiophene, and benzene)[5] or a cyclic silsesquioxane precursor ($[(EtO)_2SiCH_2]_3$)[6] using surfactant-templated assembly. These films have low dielectric constants and good mechanical stability. de Theije *et al.*[7a] and Yu *et al.*[7b] synthesized mesoporous low dielectric constant organosilica films containing SiO_3R (R = $–CH_3$, –N=C=O) in a silica and polymer matrix. These mesoporous organosilica films were placed onto silicon or a glass slide substrate using spin- or dip-coating methods. Three groups[8] reported the formation of ordered mesoporous silica films at the air–water interface, but the synthesis of mesoporous organosilica film has not been reported without a solid substrate. To the best of our knowledge, we are the first to report here, a surfactant-templated synthesis of continuous and oriented mesoporous organosilica film at the interface between air and water without a solid substrate.

The synthesis of oriented periodic mesoporous organosilica (PMO) films at the air–water interface is achieved using the following reactant molar ratios and synthesis procedure reported by Park *et al.*[9] (except for the use of BTSE as organosilica source and a polypropylene (PP) bottle): 1.0BTSE : $0.57C_{18}TMABr$: 2.36NaOH : $353H_2O$, where $C_{18}TMABr$ is the cationic surfactant $CH_3(CH_2)_{17}N(CH_3)_3Br$ and BTSE is the organosilica source reagent $(C_2H_5O)_3SiCH_2CH_2Si(OC_2H_5)_3$. Typically, we synthesized the PMO film in a 50 ml PP bottle (diameter, 4.5 cm) with 1/353 scale of the reactant molar ratios. The surfactant solution is mixed with BTSE and stirred at 40 °C for 12 h and heated to 95 °C. The film-forming process works well under static conditions at 95 °C over a reaction time of from 30 min to 24 h. The PMO films, with thickness from 180 nm to 740 nm have been grown at the air–liquid interface (see Fig. S1 of the ESI†). The PMO films were rinsed with distilled water, and dried at 80 °C in air. The PMO films can be transferred from the air–water interface onto a substrate such as glass slide *etc.* by the ‘pull up’ technique. For the yields of the PMO films and the bulk product PMO precipitated on the bottom of the PP bottle, see Table S1 of the ESI†.

A scanning electron microscopy (SEM) image of PMO film that has been transferred onto a copper grid revealed that it is continuous, as shown in Fig. 1(a). The size of the film that is formed at the air–water interface is dependent on the breadth of the reaction bottle. The SEM image in Fig. 1(b) shows a magnified edge part of the PMO film. The film has uniform thickness of ~400 nm.

As-synthesized free-standing PMO films were lifted onto transmission electron microscopy (TEM) grids and viewed directly. The TEM images of the films showed that the films have a highly ordered periodic structure with a hexagonal closed-packed arrangement of channels running parallel to the surface of the film, as shown in Fig. 1(c). This implies growth of the channels in an orientation parallel to the air–water interface. The periodicity with a hexagonal close-packed arrangement of one-dimensional channels viewed orthogonally to the film surface was observed at the bent edge part of the film, as shown in Fig. 1(d). After surfactant-extraction, the pore diameter and surface area of the film obtained from an N_2 sorption isotherm were determined to be 32.8 Å and 811 $m^2\ g^{-1}$ respectively (see Fig. S2 of the ESI†).

Fig. 2(a) and Fig. 2(c) show the X-ray powder diffraction (XRD) patterns for the as-synthesized and calcined free-standing films, lifted onto a glass slide substrate. They both reveal (100) and (200) reflections, consistent with the TEM observation that the channels run parallel to the surfactant overlayer at the air–water interface (Fig. 1(c)). The as-synthesized PMO film (Fig. 2(a)) has a *d*-spacing of 46.5 Å obtained from the (100) reflection. Star-signed peaks are due to extra surfactant. These peaks disappeared after calcination at 400 °C for 2 h in N_2 without cracking or loss of mesostructure (Fig. 2(c), see also Fig. S3 of the ESI†). The absence of the (110) reflection for the film sample confirms that the channel axis is oriented parallel to the templating liquid surface. On calcination of the film (Fig. 2(c)), the intensities of the peaks increase and the anticipated contraction (Δd_{100} = 1.2 Å) of the hexagonal *ab*-unit cell is observed, due to the removal of the

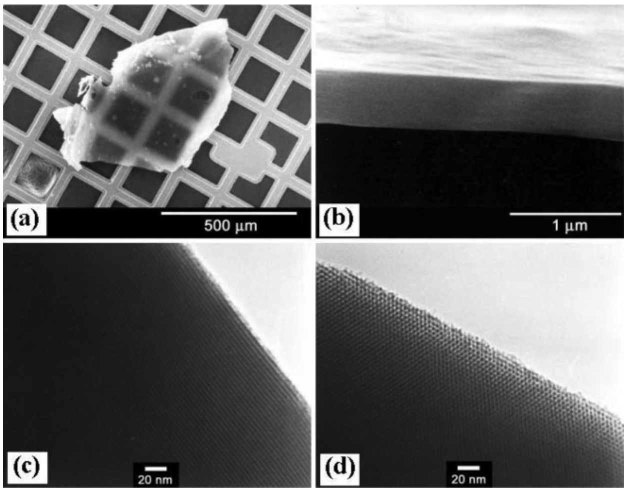

Fig. 1 SEM images of (a) an as-synthesized free-standing PMO film transferred from the air–water interface onto a copper grid (KEVEX Sigma microscope, operated at 20 kV), (b) magnified edge part of the film. TEM images of as-synthesized PMO film (JEOL JEM-2010 microscope, operated at 200 kV), showing (c) a highly ordered periodic structure consistent with a hexagonal close-packed arrangement of channels running parallel to the surface of the film, and (d) hexagonal basal plane with a well-ordered hexagonal array.

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† Electronic supplementary information (ESI) available: magnified SEM images, N_2 adsorption–desorption isotherms, TEM images of the calcined film, ^{29}Si and ^{13}C-NMR spectra of the surfactant-extracted film, yields of the bulk PMO and the PMO films. See http://www.rsc.org/suppdata/cc/b4/b405905k/

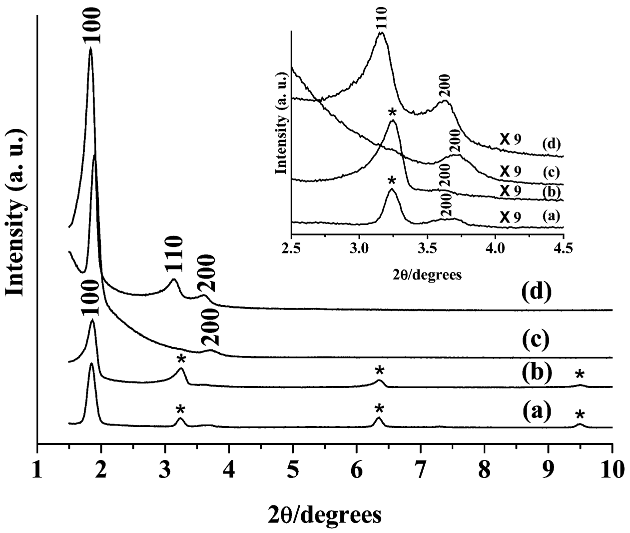

Fig. 2 XRD patterns of (a) as-synthesized free-standing PMO film transferred from the air–water interface onto glass substrate (Rigaku Miniflex, operated at 1.2 kW, using Cu Kα radiation), (b) powdered PMO film, (c) PMO film calcined at 400 °C for 2 h in N_2 with sample (a), and (d) powdered and surfactant-extracted PMO film. Inset shows XRD patterns for 2θ = 2.5–4.5° with an intensity scale expansion of ×9.

surfactant template from the channels and concomitant with the condensation of silanol (SiOH) groups in the channel walls.[5b,8a] Fig. 2(b) shows an XRD pattern of as-synthesized and powdered PMO film. The (100) and (200) peaks are observed with star-signed peaks due to extra surfactant. The (110) reflection could not be observed because of overlap with the peak due to surfactant at 2θ = 3.2°. After surfactant-extraction with the sample in Fig. 1(b) (Fig. 2(d)), the XRD pattern of the powdered PMO film showed the expected (100, 110, 200) reflections in powder PMO materials.[9]

The Si–C bonding in the framework was confirmed by ^{29}Si and ^{13}C CP MAS NMR experiments, as shown in Fig. 3. The ^{29}Si MAS NMR spectrum of the as-synthesized PMO film (Fig. 3(a)) shows two peaks at −61.2 and −69.3 ppm, which can be assigned to T^2 $C(OH)Si(OSi)_2$ and T^3 $CSi(OSi)_3$.[1a,b] The ^{13}C CP MAS NMR spectroscopy of the as-synthesized PMO film exhibits a peak at 6.3 ppm, which is attributed to carbon covalently linked to Si ($Si–CH_2–CH_2–Si$) (Fig. 3(c)).[1a,b] Peaks due to surfactant carbon atoms were observed at 14.1, 23.2, 26.7, 30.5, 32.6, 53.7, and 67.0 ppm.[2] After surfactant-extraction, no carbon peaks due to surfactant were observed (see Fig. S4 of the ESI†). It was confirmed by NMR experiments that the organic–inorganic moiety ($–Si–CH_2–CH_2–Si–$) is the basic structural unit in the film. The PMO film was calcined at 400 °C in N_2 and investigated by ^{29}Si MAS NMR spectroscopy (Fig. 3(b)). The spectrum shows two peaks (T^2 and T^3), proving that the Si–C bonds remained intact. The fraction of T^3 obtained from fitted curves for calcined PMO film (33.8 % and 66.2 % for T^2 and T^3, respectively) is higher than that of as-synthesized PMO film (35.9 % and 64.1 for T^2 and T^3, respectively), which is consistent with the XRD result for the film (*i.e.* the decreasing *d*-spacing after calcination.)

Yang *et al.*[8a] reported that the formation of a mesoporous silica film involves collective interactions between silicate building-blocks, micellar solution species and a surfactant 'hemi-micellar' overstructure localized at the air–water interface. The PMO film growth is probably regulated by matching charge and geometry between micellar aggregates and organosilica precursors at a surfactant structured air–water interface, as suggested in the case of silica film.

The PMO films have potential use in applications such as catalysis, sensing, and separation. The quality of the films produced with change in the initial compositions is now under investigation.

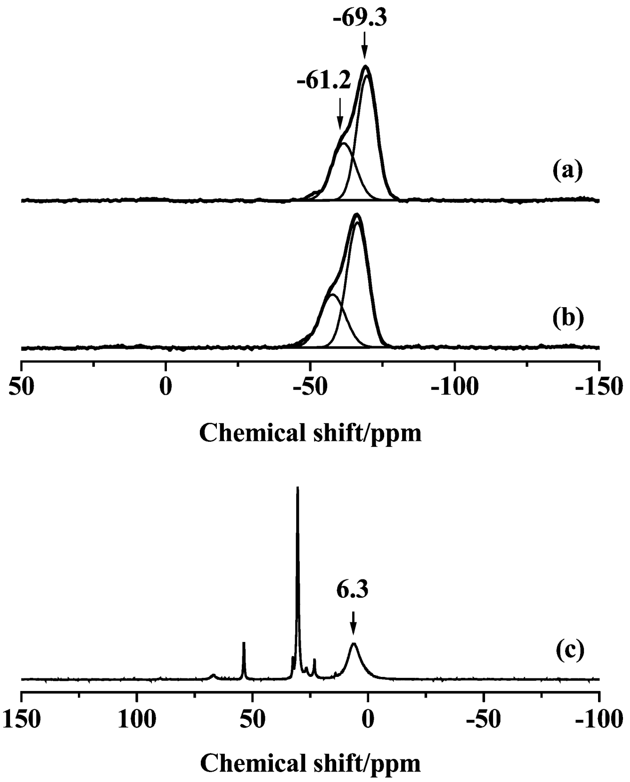

Fig. 3 ^{29}Si MAS NMR spectra of (a) as-synthesized PMO film, (b) PMO film calcined at 400 °C for 2 h in N_2, and (c) ^{13}C cross-polarization (CP) MAS NMR spectrum of as-synthesized PMO film. The spectra were obtained on a Bruker DSX400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 MHz and 100.6 MHz for ^{29}Si and ^{13}C CP MAS NMR, respectively; 90° pulse width of 5 μs, contact time 2 ms, recycle delay 3 s for both ^{29}Si and ^{13}C CP MAS NMR).

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