

Organosilicate–surfactant lamellar mesophase with molecular-scale periodicity in the silicate layers

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The synthesis of lamellar mesophases of organosilicate–surfactant composites with periodicity within the silicate layers due to periodic arrangement of phenylene- and biphenylene–silica moieties is reported.

Since the discovery of organic–inorganic hybrid mesoporous materials,¹ rapid advancement in the field has encouraged the researchers to synthesize materials with versatile applications in diverse areas.^{2–4} Previously reported phenylene⁵ and biphenylene–silica⁶ hybrid mesoporous solids with 2D-hexagonal symmetry (lattice constants of 52.5 and 48.3 Å, respectively) and molecular-scale periodicity within the pore walls (*d*-spacings of 7.6 and 11.6 Å, respectively) could be the smart materials in number of advance applications such as sensing, membranes and optoelectronic devices. The formation of the crystal-like pore wall is based on periodic arrangements of phenylene- or biphenylene-bridged organosilane precursor molecules [(EtO)₃Si–R–Si(OEt)₃, R=C₆H₄, C₆H₄C₆H₄] due to their hydrophobic–hydrophilic interaction and precisely due to the π – π stacking interaction of the bridging functional groups.

Herein, we report new lamellar mesophases of phenylene- and biphenylene-bridged organosilica/surfactant nanocomposites. Interestingly, the phenylene–silica layers of the lamellar mesophase include 4.2 Å periodicity, that is different from the 7.6 Å periodicity observed in the pore walls of crystal-like mesoporous phenylene–silica. The lamellar hybrid mesophases are very important and can find applications in intercalation chemistry, as additives for polymer nanocomposites, host–guest materials for optical functionality, and sorbents. This should lead to the expansion of the synthetic techniques of the hybrid mesophase materials and support their advantage in variety of direct applications. The results described in this study demonstrate the formation of lamellar mesophases with periodicity within the layers using phenylene- and biphenylene-bridged organosilane precursors, 1,4-bis(triethoxysilyl)benzene (BTEB) and 4,4'-bis(triethoxysilyl)biphenyl (BTEBP), respectively, in presence of octadecyltrimethylammonium chloride (C₁₈TMA) surfactant.

The initial molar composition of starting materials for mesoporous phenylene–silica was 1.0 BTEB : 0.96 C₁₈TMA : 4.03 NaOH : 560 H₂O. The modified synthetic conditions were used from earlier reported phenylene–silica hybrid materials.⁵ The lamellar mesophases could be simply obtained by stirring the initial mixture at rt, 55 and 75 °C for 24 h. 2D-hexagonal mesophase was obtained by stirring the initial mixture at rt for 24 h and further

stirring at 98 °C for 24 h. While, in case of biphenylene-bridged materials, the optimized molar composition and synthetic conditions were different to those described earlier.⁶ For the lamellar mesophase, the composition used was 1.0 BTEBP : 3.1 C₁₈TMA : 0.12 NaOH : 664 H₂O. The reaction was performed by stirring the resultant mixture at 4 °C for 24 h. The mesostructural products were recovered by filtering, washing and subsequent drying.

All materials were analyzed by X-ray diffraction. The sharp lower reflection peaks at *d*-spacings of 37.2 and 18.6 Å, which can be indexed to a lamellar lattice and evidently confirmed the lamellar mesophase formation (Fig. 1a). In addition, the XRD pattern displays a sharp reflection at *d*-spacing of 4.2 Å. This diffraction peak can be assigned to the periodic structure formed within the organosilica layers of the lamellar mesophase. The lamellar mesophases with periodicity within the layers could also be obtained even upon refluxing the initial mixture at 55 and 75 °C, respectively (Figs. 1b and 1c), indicating that stable lamellar mesophases are likely to be formed under a wide range of condensation temperatures. However, the further increase in condensation temperature resulted in the transformation of lamellar to 2D-hexagonal mesophase with 7.6 Å periodicity and its higher order.⁵ (Fig. 1d)

²⁹Si MAS NMR spectrum (Fig. 2a) of the lamellar material showed the dominant resonance at –72.7 ppm and a lower intensity resonance at –81.2 ppm, corresponding to T²[SiC(OH)(OSi)₂] and T³[SiC(OSi)₃] resonance, respectively. This suggests that compared to the 2D-hexagonal mesophase of phenylene–silica (Fig. 2b) the lamellar mesophases of phenylene–silica exhibit relatively lower degree of condensation (Si–O–Si

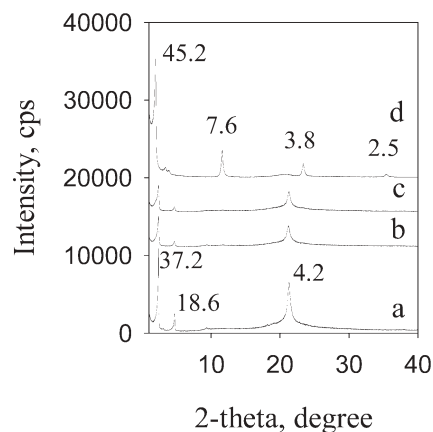


Fig. 1 X-ray diffraction patterns of mesophases of phenylene–silica hybrids synthesized at different temperatures. (a) rt, (b) 55 °C, (c) 75 °C and (d) rt followed by heating at 98 °C.

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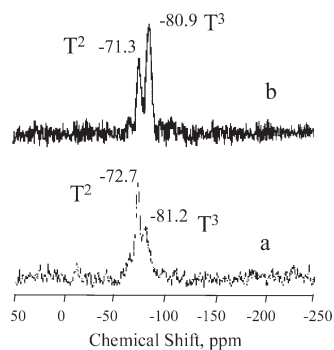


Fig. 2 ^{29}Si MAS NMR spectra of (a) lamellar and (b) 2D-hexagonal mesophases of phenylene-silica hybrid solids.

network) during simultaneous hydrolysis and polymerization reaction. The absence of signals due to Q^i species between -90 and -110 ppm, confirmed that Si-C bonds were preserved in the lamellar phenylene-silica hybrids.

Based on the XRD and ^{29}Si MAS NMR results, a model structure of the lamellar mesophase of phenylene-silica is presented in Fig. 3. The material has a layered structure composed of organosilicate layers and bilayer arrangement of surfactant molecules. There are ionic interactions between the organosilicate anions and the surfactant cations. The interlayer distance of 37.2 \AA is very reasonable for the a bilayer structure with tilted orientation of alkyl chain of the surfactant.

The organosilica layers have molecular-scale periodicity of 4.2 \AA , which is very close to the phenylene-phenylene distance (4.4 \AA) observed in the simulated model of the 2D-hexagonal mesophase of phenylene silicas (Fig. 4).⁵ However, the periodicity of 7.6 \AA , which is due to the periodicity of phenylene-silica moieties (Fig. 4), was not observed in the lamellar mesophase. The result suggests that the organosilica layers have only the parallel stacking of phenylene-silica moieties due to π - π interactions. The studies on precise arrangement of organic moieties in the silicate layered structures are currently underway.

The transformation from lamellar to hexagonal phases was possible because the condensation degree of the lamellar phase was

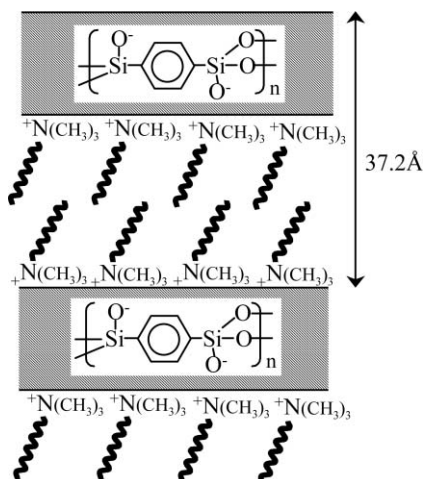


Fig. 3 Representative structural model of the lamellar mesophase phenylene-silica hybrid material.

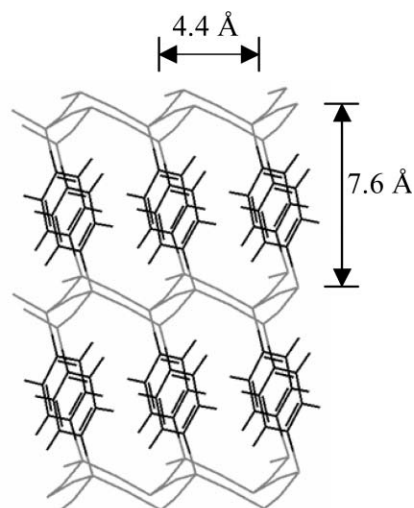


Fig. 4 Simulated model of pore walls of 2D-hexagonal mesoporous phenylene-silica.⁵

quite low (Fig. 2a). During the transformation, the peak at d -spacing 4.2 \AA due to phenylene-phenylene distance of the stacking disappeared, however we also do believe that the periodicity arises from phenylene-phenylene stacking probably also exists in phenylene-silica with a hexagonal array of mesopores in addition to the 7.6 \AA periodicity.⁵

Biphenylene-silica hybrid synthesized at $4 \text{ }^\circ\text{C}$ also shows evidence of a lamellar mesophase as clearly shown by the XRD pattern (Fig. 5). The diffraction peaks at lower angle region appeared at d -spacings of 30.0 and 14.9 \AA , confirming a lamellar lattice in the material (Fig. 5a). The XRD pattern largely differed to the hexagonal mesophase of the biphenylene-bridged hybrid silica (Fig. 5b) synthesized at $98 \text{ }^\circ\text{C}$ using the synthetic procedure described earlier.⁶ In lamellar biphenylene-silica mesophases, the observed 4.2 \AA periodicity was relatively lower compared to the lamellar phenylene-silica mesophases.

Fig. 6 shows the X-ray diffraction patterns of the lamellar mesophase of biphenylene-silica hybrid solids before and after infiltration with toluene into the sample powder. Evidently, the XRD peaks were shifted to higher d -spacings of 46.7 \AA and 23.4 \AA , indicating swelling of the interlayer region of the lamellar hybrid material. However, the remaining intensity peaks at d -spacings of 30.0 \AA and 14.9 \AA are due to heterogeneous infiltration of toluene.

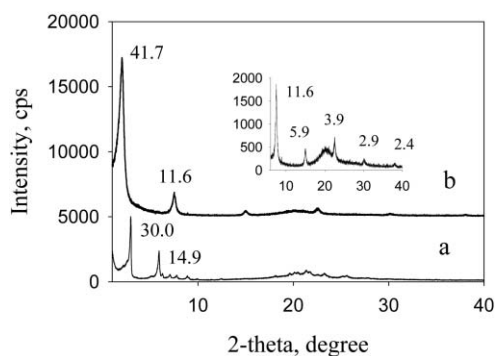


Fig. 5 X-ray diffraction patterns of (a) lamellar, (b) 2D-hexagonal mesophases of biphenylene-silica hybrids [inset: enlarged curve b].

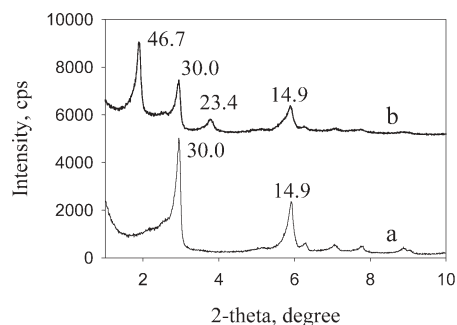


Fig. 6 X-ray diffraction patterns of lamellar mesophase of biphenylene-silica hybrids (a) before and, (b) after treatment with toluene.

This phenomenon clearly indicates that the lamellar mesophase has an expandable layered structure as described in the plausible model shown in Fig. 3.

In summary, the ordered lamellar mesophases of phenylene- and biphenylene-silica with periodic sheets structure have been synthesized. The intercalation of lamellar mesophase of biphenylene-silica with toluene successfully demonstrated the unique flexible features of these expandable inter-layered structured materials. To the best of our knowledge, this is the first report of a true lamellar mesophase organosilica hybrid having a crystal-like sheet structure. Its potential applications are eagerly anticipated.

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