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The preparation of a highly ordered long-range lamellar silica structure with large interlayer spacings†

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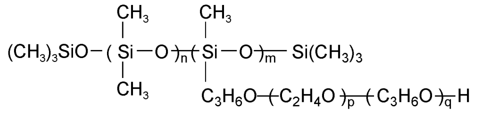
Highly ordered long-range lamellar silicas have been prepared using silicone surfactant as a template; the lamellar silicas have the largest lattice constant to date reported; the results show that silicone surfactants with flexible siloxane chains favor the formation of these unusual lamellar structures.

Surfactant-templated syntheses based on the hydrolysis and cross-linking of inorganic precursors at the surfaces of supramolecular surfactant assemblies have been used to prepare a variety of mesostructured materials[1–6] since the discovery of mesoporous silica.[1] A number of layered materials such as silicates, transition metal oxides and aluminophosphates have been obtained.[1–5] Pinnavaia *et al.* demonstrated that mesoporous silicas with lamellar structures can be obtained through neutral templating routes. They prepared ultrastable silica vesicles with wormlike channels using 1,12-diaminododecane (DADD) and Gemini surfactants.[4] However, these primary amines and quaternary ammonium ion surfactants are expensive and toxic, in contrast to nonionic PEO-based surfactants. Recently, block copolymers have been increasingly used to prepare oxide mesophases, because the architectures of the copolymers can be rationally adjusted to control the interactions between the organic and inorganic species, self-assembly, and the mesophase formation.[6] However, the use of silicone surfactants for preparing silica mesophases has not been reported so far.

Here we report a silicone–polyether copolymer designed to template self-assembly of silica/surfactant lamellar mesophase. The silicone copolymer is composed of a polydimethylsiloxane (PDMS) backbone and a side chain of poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-*b*-PPO)



$$(CH_3)_3SiO{-}(\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}{-}O)_n(\overset{\overset{CH_3}{|}}{\underset{\underset{C_3H_6O-(C_2H_4O)_p-(C_3H_6O)_q-H}{|}}{Si}}{-}O)_m{-}Si(CH_3)_3$$

The essential features of the copolymer were its amphiphilic character, low cost and biodegradability, and high surface activity in comparison with other surfactants such as the Pluronics family and primary amines.[7] The silicone copolymer (n = 36, m = 3, p = q = 12, purity > 95%) was prepared by hydrosilylation addition reaction of PPO-*b*-PEO, allyl end-blocked at the PEO side, to a PDMS polymer containing pendant Si–H groups using a Pt-based catalyst.[7] Gel permeation chromatographic (GPC) analysis of the copolymer gave resolved peaks (M_n = 6850, D = 1.08), consistent with calculations based on the known stoichiometries of the starting materials.

Lamellar silica powders (denoted ZSU-L) were prepared by hydrolysis of tetraethylorthosilicate (TEOS) in the presence of silicone copolymer. In a typical synthesis, 1 g of silicone surfactant was dissolved in 60 ml of water, then 4.5 ml of TEOS was added to this solution. The pH of the solution was adjusted by HCl. The reaction mixture was stirred at room temperature (RT) for 24 h to obtain the ZSU-L. The precipitate was recovered by filtration, washed by water, and air-dried. TEM images were obtained with a JEOL 100CX operated at 100 kV. The samples were embedded in epoxy resin, and ultramicrotomed for TEM measurements. SEM images were obtained with a Hitachi S-520 operated at a beam energy of 20.0 kV.

The lamellar character of the hybrid silica prepared at pH 2 is clearly shown from the TEM images of an ultrathin section of the as-made ZSU-L (Fig. 1(a)). The spherical silica particles are constructed of lamellar parallel silica plates separated by bilayer copolymer aggregates. The interlayer distance measured from the image is about 170 (±10) nm, which is larger than that of all previously synthesized and natural layered materials.[1–5] The splitting of silica walls is the result of damage caused by untrathin sectioning. TEM observation of the sample under various tilting angles did not show evidence for any framework topology other than lamellae. No peaks at low angle can be observed for the ZSU-L by XRD analysis (Fig. S1, ESI†). Examining many of the TEM images, it is found that lamellar silicas represent 100% of the solid materials. The predominantly well-defined spherical particle morphology of the as-made ZSU-L is confirmed by the corresponding SEM images

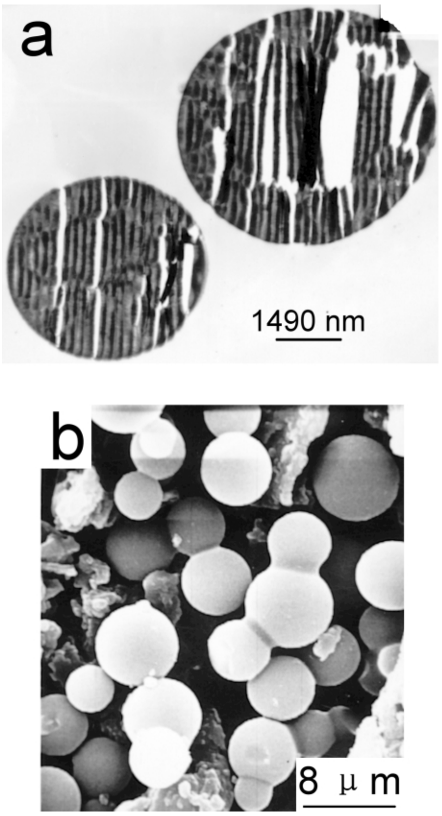


Fig. 1 (a) TEM image of an ultrathin section of the as-made ZSU-L powders formed from silicone surfactant at pH 2. (b) Corresponding SEM image of the as-made ZSU-L silica spherical particles.

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† Electronic supplementary information (ESI) available: Figs. S1–3: XRD, adsorption–desorption isotherms and SEM image. See http://www.rsc.org/suppdata/cc/b2/b204053k/

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shown in Fig. 1(b). The diameter of the particles, ~3–7 μm, determined from the SEM image is in agreement with that observed from TEM. Even with substantial changes in the concentration of silicone surfactant and HCl, the lamellar silica mesophase is retained. Fig. 2 shows a TEM image of an ultrathin section of a silica sample prepared under strong acidic conditions (4 M HCl). It is clearly shown that hybrid silica has highly ordered long-range lamellar structure.

The reported lamellar materials were obtained using very high concentration of surfactant in the reaction mixture, which indicates that the assembly process occurred in the presence of bilayer liquid crystals which acted as templates affording lamellar mesostructures.[1–5] However, in this study the formation of lamellar silicas in dilute aqueous solutions (~1 wt%) has been shown to proceed by the coassembly of the TEOS hydrolysis species and neutral surfactants coupled with inorganic polymerization through H-bonding interactions.[4] The initial dilute surfactant solutions under our reaction conditions are completely clear and devoid of phase segregated planar bilayer structures of the size observed for the mesostructures. No lamellar phase was observed by freeze-fracture electron microscopy analysis in the initial surfactant solution in the absence of TEOS. At these low concentrations, silicone surfactants form isotropic micelles with no long-range order in the solutions. Phase segregation and planar bilayers formation do not occur until the TEOS precursor is added to the solution of the neutral silicone surfactants. We propose that hybrid silica with lamellar structure results from the coassembly of inorganic species and supramolecules rather than the pre-existing bilayers and vesicle templates or liquid crystal phases thought to be responsible for lamellar inorganic/organic adducts.[1–5]

PDMS chains are more flexible than hydrocarbon chains in alkyltrimethylammonium salts (CTA$^+$) or Pluronics family, because the bond angle (Si–O–Si) is significantly wider (~143°) and the bond length (Si–O) (0.165 nm) longer than comparable C–C–C (109°, 0.140 nm) and C–O–C (114°, 0.142 nm) bonds, Thus, the obstacle to rotation is very low (rotation barrier: 0.8 kJ mol^{-1}) and the Si–O bond can freely rotate.[7] That is the reason why even very long PDMS chain surfactants are in liquid state at RT. In contrast, the hydrocarbon surfactants tend to be in the solid state at RT since Krafft temperatures for long and linear hydrocarbon-chain surfactants are high.[7] We suggest that silicone surfactants with more flexible chains than conventional hydrocarbon surfactants or copolymers would be responsible for the formation of lamellar structures.[8]

To test silicone surfactants for favoring the formation of lamellae, we prepared silica monoliths and films by the sol–gel method[9] using a silicone surfactant as the template. Lamellar silica monoliths and films were prepared over a wide composition range of 0.02 mol TEOS : 0.5–2.5 g silicone surfactant : 0.08–0.25 mol H_2O : (0.4–8) × 10^{-4} mol HCl : 0.25–1 mol EtOH. The optically transparent monolithic gel adopts the shape of the reaction vessel. The sol solution can be used to prepare thin films by a dip-coating process. The lamellar structure of silica is clearly shown in Fig. 3. The lattice constant of lamellar silica measured from Fig. 3 is ~150 (±10) nm. The results further supply strong evidence that silicone surfactants favor the formation of lamellar structures.

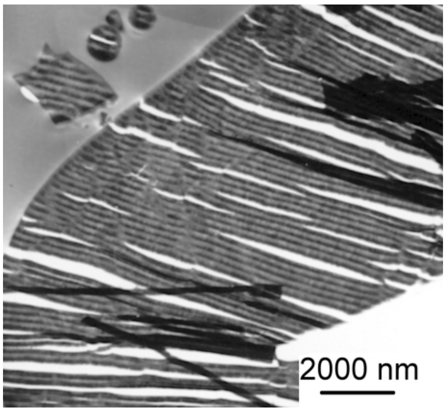

Fig. 2 TEM image of an ultrathin section of the as-made lamellar silica powders templated from silicone surfactant in strong acidic media (4 M HCl).

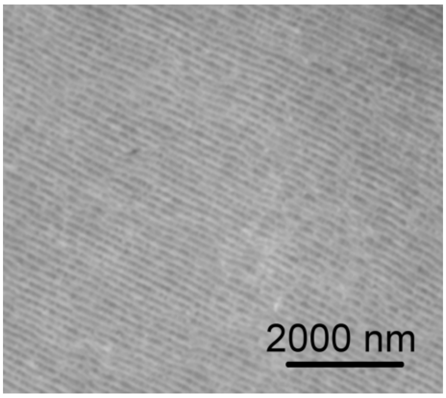

Fig. 3 TEM image of an ultrathin section of the as-synthesized silica monoliths and films using silicone surfactant as the template.

N_2 sorption analyses show that the calcined ZSU-L (600 °C) exhibits a type I isotherm with hysteresis loop of type H_4 that is typical of lamellar materials.[4,10] The type H_4 loop is associated with narrow slit-like pores.[10] BJH analysis shows that the calcined ZSU-L exhibits a pore size of 3.6 nm (Fig. S2, ESI†). The calcined ZSU-L has a BET surface area of 276 $m^2\ g^{-1}$. Since the as-made sample has a BET surface area of only ~2 $m^2\ g^{-1}$, it can be concluded that the removal of surfactant led to slit-like mesopores in the calcined product. When calcined at 800 °C, the spheres in ZSU-L powders remained intact without a decrease in the size, and the surface of the particles remained smooth with little evidence of fracture or breakage (Fig. S3, ESI†). Little change was observed in BET surface area and pore size of the ZSU-L powders calcined at 800 °C. The results indicate that the ZSU-L has exceptional thermal stability.

In summary, we demonstrate for the first time that novel graft silicone–polyether copolymer can successfully template the assembly of lamellar silica with unprecedented large lattice constants. Such organic/inorganic composites with long-range highly ordered lamellar structure are of interest from the viewpoint of biominerization, and may find potential applicaitons. The possibility of producing other oxide materials with unusual lamellar mesostructures using this novel method is also intriguing.

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