Synthesis of Highly Ordered Long-range Lamellar Silica Composites

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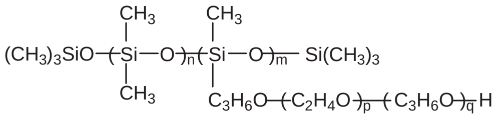
Highly ordered long-range lamellar silica was prepared using silicone surfactant as the template. Lamellar silica has the largest lattice constant known for layered materials reported to date. The results show that silicone surfactants with flexible siloxane chain favor the formation of these unusual lamellar structures.

Different surfactants have been used to prepare a variety of mesostructured materials[1–6] since the discovery of mesoporous silica.[1] Self-assembly of molecules into an amazing diversity of mesostructured frameworks has attracted increasing attention from a wide range of scientific interests and applications. A number of layered materials such as silicates, transition metal oxides and aluminophosphates have been obtained.[1–5] Pinnavaia demonstrated that mesoporous silicas with lamellar structures can be obtained through the 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 organize oxide mesostructures, because the composition and architecture of the amphiphilic block 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 never been reported so far.

Here we report the synthesis of silica/surfactant lamellar mesophase using silicone surfactant as the template. 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)



$$\mathrm{(CH_3)_3SiO\left(\overset{CH_3}{\underset{CH_3}{Si}}{-}O\right)_n\left(\overset{CH_3}{\underset{C_3H_6O(C_2H_4O)_p(C_3H_6O)_qH}{Si}}{-}O\right)_m Si(CH_3)_3}$$

The essential features of silicone copolymer were its amphiphilic character, low cost and biodegradability, and high surface activity in comparison with conventional surfactants such as PEO-*b*-PPO-*b*-PEO and primary amines.[7] Silicone copolymer was prepared by hydrosilylation addition reaction, as described elsewhere.[7]

Lamellar silica powders (denoted ZSU-L) were prepared by hydrolysis of tetraethylorthosilicate (TEOS) in the presence of nonionic silicone copolymer. In a typical synthesis, 1 g of silicone surfactant ($n = 48, m = 4, p = q = 12$) was dissolved in 60 ml of deionized water, then 4.5 ml of TEOS was added to a templating solution. pH of the solution was adjusted by HCl. The reaction mixture was stirred at room temperature (RT) for 24 h to obtain the templated lamellar product. 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 hybrid silica prepared at pH 2 is clearly shown from the TEM images of an ultrathin section of the as-synthesized ZSU-L sample (Figure 1A–C). The spherical silica particles are constructed of lamellar parallel silica plates separated by surfactant aggregates. The interlayer distance measured from the images is ca. 160 (±10) nm, which is shown to be larger than those of all previously synthesized and natural layered materials.[1–5] The splitting of silica walls is the result of damage caused by ultrathin sectioning. TEM observation of the sample under various tilting angles did not show evidence for any framework topology other than lamellae. Examining many of the TEM micrographs, it is found that mesostructured lamellar silicas represent 100% of the solid materials. The predominantly well-defined spherical particle morphology of the as-made ZSU-L powders is confirmed by the corresponding SEM images shown in Figure 1D. The size of the particles in diameter of ca. 2–8 μm determined from the SEM images is in agreement with that observed from TEM. Even with substantial changes in the concentration of silicone surfactant and HCl, lamellar silica mesophase is also retained, indicating silicone surfactants favor for the formation of this unusual lamellar structure.

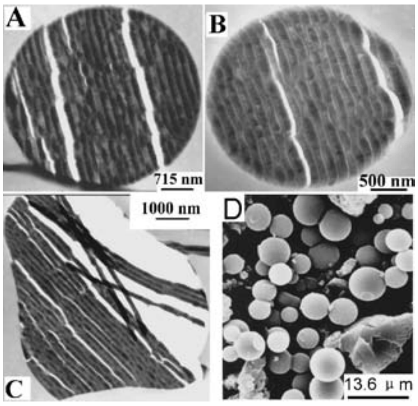


Figure 1. TEM images of an ultrathin section (A–C) and SEM image (D) of the as-synthesized ZSU-L sample.

The previously reported mesolamellar materials were obtained using very high concentration of surfactant in the reaction mixture, which indicates 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 silica/surfactant lamellar composites in dilute aqueous solutions (ca. 1 wt%) has been shown to proceed by the coassembly of the TEOS hydrolysis species and neutral surfactants coupled with inorganic polymerization through Hbonding 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 the hybrid silica product 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 (PEO-PPO-PEO), because the bond angle (Si–O–Si) is significantly wider (ca. 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) 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 a 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 copolymer would be responsible for the formation of this unusual lamellar silica mesophase.[8]

To test silicone surfactant for favoring the formation of lamellae, we prepared silica monoliths and films by the sol-gel method[9] using 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 g silicone surfactant: 0.08–0.25 mol H_2O: $(0.4\text{–}9) \times 10^{-4}$ mol HCl: 0.25–1 mol EtOH. The optically transparent monolithic gel takes the shape of the reaction vessel. The sol solution can be used to prepare thin film by dip-coating process. The lamellar structure of silica monoliths and films is clearly shown in Figure 2. The lattice constant of lamellar structure measured from TEM image is ca. 150 (±10) nm. The results further supply strong evidence that silicone surfactants favor the formation of lamellar mesostructures.

In conclusion, lamellar silicas with unprecedented large lattice constants (close to the wavelength of light) were first prepared using silicone surfactant as the template. Such organic/inorganic composites with highly ordered long-range lamellar structure are of interests 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. The results demonstrate that this study will enrich our ability to create highly ordered inorganic/organic mesostructures using the bottom-up approach.

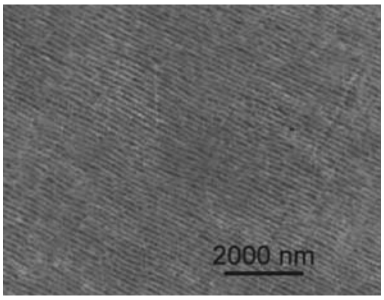


Figure 2. TEM image of an ultrathin section of as-made lamellar silica monoliths templated from silicone surfactant.

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References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuwli, and J. S. Beck, *Nature*, **359**, 710 (1992).

2 S. Oliver, A. Kuperman, N. Coombs, A. Lough, and G. Ozin, *Nature*, **378**, 47 (1995).

3 M. Ogawa, *J. Am. Chem. Soc.*, **116**, 1941 (1994).

4 a) P. T. Tanev and T. J. Pinnavaia, *Science*, **271**, 1267 (1996). b) P. T. Tanev, Y. Liang, and T. J. Pinnavaia, *J. Am. Chem. Soc.*, **119**, 8616 (1997). c) S. S. Kim, W. Zhang, and T. J. Pinnavaia, *Science*, **282**, 1302 (1998).

5 a) A. Sayari, V. R. Karra, J. S. Reddy, and I. L. Moudrakovski, *J. Chem. Soc., Chem. Commun.*, **1996**, 411. b) A. Chenite, Y. Le Page, V. R. Karra, and A. Sayari, *J. Chem. Soc., Chem. Commun.*, **1996**, 413.

6 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*, **279**, 548 (1998).

7 M. H. Randal, ''Silicone surfactants,'' Marcel Dekker, New York (1998).

8 A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, and B. F. Chmelka, *Science*, **261**, 1299 (1993).

9 D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, and G. D. Stucky, *Adv. Mater.*, **10**, 1380 (1998).