Synthesis of Mesostructured Silica Using Nonionic Copolymers as the Templates

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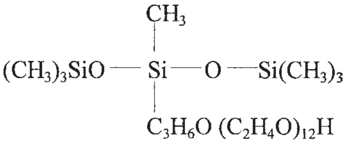
Hierarchically ordered mesostructured silica was prepared using the mixture of silicone surfactant and P123 as the template. Hexagonal nanopores were built in layered silica walls to form complex mesostructures. The lamellar mesophase and hexagonal nanopores in the walls were independently templated from silicone surfactant and P123.

Since the discovery of M41S periodic mesoporous silica,[1] surfactant-templated synthetic processes based on the hydrolysis and cross-linking of inorganic precursors on the surfaces of supramolecular surfactant assemblies have been used to synthesize new families of hexagonal, cubic or lamellar mesostructures.[2–5] Self-assembly of molecules into an exciting diversity of mesostructured frameworks has attracted much attention from a wide range of scientific interests and applications.[2–5] However, the preparation of hierarchically ordered structures in a single body, such as seen in diatoms in nature, has remained an experimental challenge.[6] Recently, block copolymers have been increasingly used to organize mesostructured composites, 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 selection.[7] However, the use of silicone-based surfactant for the assembly of silica mesophases has not been reported to date.

Here we report the synthesis of lamellar silica (denoted ZSU-L) using silicone surfactant as a template. Complex mesostructured silica (denoted ZSU-4) was prepared using the mixture of silicone surfactant and $EO_{20}PO_{70}EO_{20}$ (P123) as a template. Primary structure of the silicone surfactant is shown below. Silicone surfactants were prepared by hydrosilylation addition reaction, as described elsewhere.[8]



$$\begin{array}{c} CH_3 \\ | \\ (CH_3)_3SiO - Si - O - Si(CH_3)_3 \\ | \\ C_3H_6O\ (C_2H_4O)_{12}H \end{array}$$

In a typical synthesis of ZSU-L, 1 g of pure silicone surfactant was dissolved in 60 g of 2 M HCl, then 4.16 g of TEOS was added to a templating solution. The reaction mixture was stirred at 35 °C for 24 h and subsequently heated for 24 h at 90 °C to obtain the templated lamellar product. The precipitate was recovered by filtration, washed by water, and air-dried. ZSU-4 was prepared by the same method just using the mixture of silicone surfactant (0.6 g) and P123 (1 g) instead of pure silicone surfactant. TEM images were obtained with a JEOL 100CX operated at 100 kV. The samples were embedded in epoxy resin, and ultramicrotomed for TEM measurements. Powders X-ray diffraction (XRD) analysis was performed on a Rigaku Rotaflex diffractometer equipped with a rotating anode and Cu Kα radiation. N_2 adsorption measurements were performed at 77 K using a Micromeritics ASAP 2010 system utilizing Barrett-Emmett-Teller (BET) calculations for surface area and BJH calculations for pore size distribution for the adsorption branch of the isotherm.

The lamellar structure of the ZSU-L product is clearly shown from the TEM image of an ultrathin section of the as-made sample (Figure 1a). The hybrid silica particles are composed of surfactant bilayer being sandwiched by silica walls that are arranged parallel to each other. The interlayer distance measured from the image is about 200 (±10) nm, which is shown to be larger than those of all previously synthesized and natural layered materials.[2–5] To the best of our knowledge, this is the largest periodic interlayer spacing mesostructures created at the molecular level so far. The lamellar structures extend to the length of micrometer scale through layer propagation without curvature, as observed in Figure 1a. The splitting of silica walls is the result of damage caused by ultramicrotoming. TEM observation of the sample under various tilting angles did not show evidence for any framework topology other than lamellae.

Siloxane 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

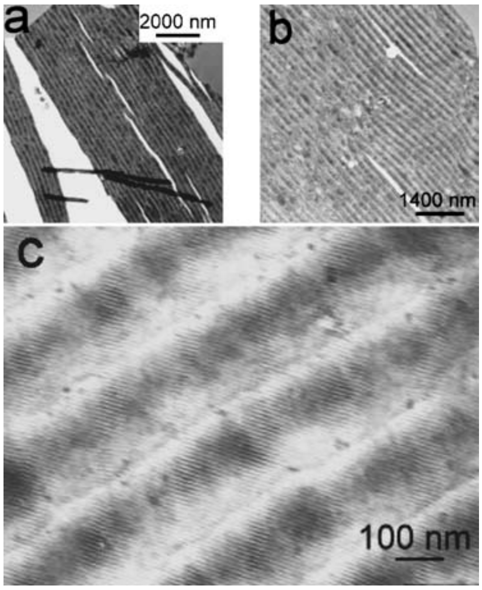


Figure 1. TEM image of an ultrathin section of the as-made ZSU-L sample (a). Low-magnification TEM image (b) and higher-magnification TEM image (c) of an ultrathin section of the as-made ZSU-4 sample.

(rotation barrier: 0.8 kJ/mol) and the Si–O bond can freely rotate.[8] That is the reason why even very long PDMS chain surfactants are in liquid state at room temperature (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.[8] 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.[9] Even with substantial changes in the concentration of silicone surfactant and HCl, lamellar silica mesophase is also retained, suggesting that silicone surfactant favors the formation of lamellar structure.

TEM images of an ultrathin section of the as-made ZSU-4 product were shown in Figure 1b and c. Figure 1b shows that lamellar silica mesophase similar to that observed in the ZSU-L product is also retained in the ZSU-4 product templated from the mixture of silicone surfactant and P123. Previously, in systems with Pluronics family, C_nEO_m, CTA^+ or their mixtures serving as templates, a single mesophase such as hexagonal mesoporous silica has been prepared.[1,7,10] Interestingly, we find here that hexagonal pore channels were formed in the thick silica walls for ZSU-4 (Figure 1c). Both the lamellae and hexagonal mesophase are assembled in a single body, representing complex mesostructures (structure within structure). No peaks are observed in XRD patterns for the ZSU-L product, as observed in Figure 2a (ZSU-L lamellar phase was not detected by XRD analysis because of its extremely large lattice constant). However, a high degree of hexagonal mesoscopic order is observed for the calcined ZSU-4 samples (Figure 2b). It appears that the lamellar mesophase and hexagonal mesochannels in the walls were separately templated from silicone surfactant and P123 in the mixed surfactant templating systems, and thus hierarchically ordered silica formed.

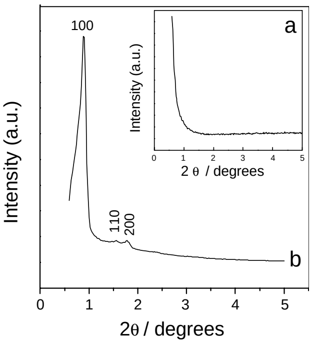


Figure 2. XRD patterns of the as-made ZSU-L (a) and the calcined ZSU-4 at 500 °C (b).

N_2 sorption isotherm and the corresponding BJH (Barret-Joyner-Halenda) pore size distribution curve of the calcined ZSU-4 product (500 °C) is shown in Figure 3 and inset. The N_2 isotherm of the calcined ZSU-4 is a type IV isotherm with a large type H_1 hysteresis loop,[11] similar to that of SBA-15.[7] The calcined ZSU-4 product prepared using the mixture of silicone surfactant and P123 as the template has a BET surface area of 788 $m^2\,g^{-1}$. The BJH analyses show that calcined ZSU-4 exhibits pore sizes of 6.3 nm.

In conclusion, a novel silicone surfactant was first used to synthesize lamellar silica mesophase. Silica materials with complex ordered mesostructures templated from the copolymer blends are of interest from the viewpoint of biominerization, and may find wide applications in catalysis, adsorption and separation. We believe that these findings have provided new insights into the mechanistic issues involved in the formation of this new interesting class of complex mesostructured materials. Further investigation, however, will be required in order to adequately explain the actual formation mechanisms of complex mesophases formed in the mixed surfactant-templating systems. The possibility of producing other oxide materials with this unusual mesostructure using this novel method is also intriguing.

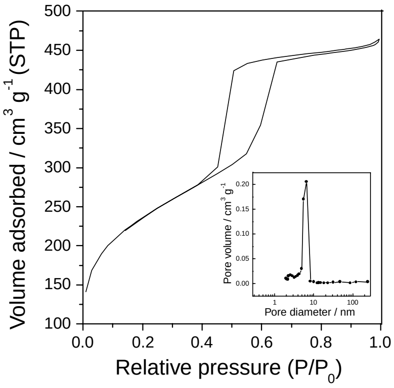


Figure 3. N_2 adsorption-desorption isotherms and corresponding BJH pore size distribution curve (Inset) for the calcined ZSU-4 at 500 °C for 6 h.

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