

# Neutral Templating Route to Unusual Mesostructured Silicas

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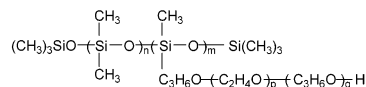
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Highly ordered long-range lamellar silica was prepared using pure silicone surfactant as a structure-directing agent at neutral pH. Moreover, novel hierarchically mesostructured silica (designated ZSU-5) was templated from the mixture of silicone surfactant and TX-100 ( $C_8Ph(EO)_{10}$ , Ph = phenyl) under neutral pH conditions. The results have demonstrated that the lamellar mesophase and the wormlike mesoporosity in the walls were separately templated from silicone surfactant and TX-100 in the mixed two different surfactant systems, and thus, hierarchically mesostructured silica was formed. We suggest that chain configuration of the surfactants is responsible for the formation of silica mesophase with different structures.

## 1. Introduction

The chemical synthesis of silica-based mesophases requires extremes of pH, temperature, or pressure. In contrast, biosilicification occurs in water at neutral pH and ambient temperature, producing an amazing diversity of mesostructured frameworks.<sup>1,2</sup> Different surfactants have been used to organize silica into a variety of mesostructured materials, through a cooperative supramolecular assembly mechanism that incorporates electrostatic interactions,<sup>3</sup> hydrogen bonding,<sup>4</sup> or dative bonding<sup>5</sup> between the headgroups of lyotropic organic micelles and silicate precursors in solution.<sup>6–8</sup> Self-assembly of molecules into an amazing diversity of hierarchically ordered oxides has attracted increasing attention from a wide range of scientific interests and applications. Different mesoporous silicas such as M41S,<sup>3</sup> HMS,<sup>4</sup> MSU-X,<sup>9</sup> and SBA<sup>10</sup> have been prepared via various synthetic routes using a variety of surfactants. Pinnavaia and co-workers demonstrated that mesoporous materials can be obtained through the neutral routes  $S^{0}I^0$  or  $N^0I^0$ , by virtue of hydrogen bonding interactions between primary amine ( $S^0$ ) or poly(ethylene oxide)-type (PEO) surfactants ( $N^0$ ) and neutral inorganic species ( $I^0$ ).<sup>4,9</sup> The synthesis of mesostructured oxides that is difficult or impossible by electrostatic assembly can be afforded through this  $N^0I^0$  process.<sup>11</sup> The advantages of PEO-based nonionic surfactants over neutral long-chain amines and alkyltrimethylammonium salts ( $CTA^+$ ) are their low cost, low toxicity, and biodegradability. HMS and MSU materials possess wormlike disordered mesostructures with uniform pore diameters of 2 to 5.8 nm.<sup>4,9</sup> Mesoporous materials with wormhole framework structures are generally more active heterogeneous catalysts in comparison to their ordered hexagonal analogues. The enhanced reactivity has been attributed, in part, to a mesopore network that is connected in three dimensions (3D), allowing the guest molecules to more readily access reactive centers that have been designed into the framework surfaces.<sup>12,13</sup> 1D hexagonal pore channels such as SBA-15 and MCM-41 have the disadvantage in the diffusion and transport of molecules, which limits their extensive applications in catalysis and separation.<sup>13</sup> Recently, block copolymers have been increasingly used to organize oxide mesophases, because the composition and architecture of the amphiphilic block copolymers can be

## SCHEME 1: Primary Structure of Polyether Modified Polysiloxane



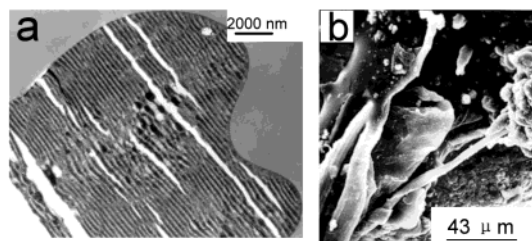
rationally adjusted to control the interactions between the organic and inorganic species, the self-assembly, and the mesophase selection.<sup>10</sup> Some reports have been made on the synthesis of mesoporous silica using  $C_nEO_m$  as the template at neutral pH or acidic conditions.<sup>14–16</sup> However, the use of silicone-polyether graft copolymers and the mixed silicone copolymer/ $C_nEO_m$  for the assembly of silica mesophases at neutral pH has not been reported to date.

Here, we report the synthesis of highly ordered long-range lamellar silica (denoted ZSU-L) using pure silicone surfactant as a structure-directing agent at neutral pH. Moreover, novel complex mesostructured silica (designated ZSU-5) was templated from the mixture of silicone surfactant and TX-100 ( $C_8Ph(EO)_{10}$ , Ph = phenyl) under neutral conditions. The silicone surfactant is composed of a poly(dimethylsiloxane) (PDMS) backbone and a side chain of poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-PPO) (Scheme 1). Silicone-based surfactants were prepared by hydrosilylation addition reaction, which was found elsewhere.<sup>17,18</sup> The essential features of silicone surfactants are amphiphilic, low glass transition temperature, low cost, nontoxic and biodegradability, higher surface activity than that of conventional hydrocarbon surfactants, and wide applications in industries.<sup>17,18</sup>

## 2. Experimental Section

Mesolamellar silica/surfactant composites (ZSU-L) were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of pure silicone-based surfactant ( $n = 110$ ,  $m = 15$ ,  $p = q = 12$ ,  $M_n = 28400$ ,  $D = 1.40$ , purity > 95%) at neutral pH with the composition TEOS/silicone surfactant/ $H_2O = 1/1.8 \times 10^{-3}/167$  (molar ratios). In a typical synthesis, 1 g of pure silicone surfactant was dissolved in 60 mL of deionized water, and then 4.16 g of TEOS was added into that solution under stirring. The reaction mixture was stirred at room temperature (RT) for 24 h to obtain the templated ZSU-L product in almost-quantitative yield. The precipitate was

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**Figure 1.** TEM image of an ultrathin section of the as-synthesized ZSU-L silica composites with lamellar structures (a) and corresponding SEM image (b). The ZSU-L material was prepared by using silicone surfactant as the template at neutral pH.

recovered by filtration, washed by water, and air-dried. Complex silica mesostructures (denoted ZSU-5) were prepared by the same method just using the mixture of silicone surfactant (1 g) and TX-100 (1 g) instead of pure silicone surfactant in the above experiment with the composition TEOS/silicone surfactant/TX-100/H<sub>2</sub>O =  $1/1.8 \times 10^{-3}/7.7 \times 10^{-2}/167$  (molar ratios). The template was removed by calcination at 560 °C for 6 h in air (heating rate, 1 °C min<sup>-1</sup>).

TEM photographs 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. Powder X-ray diffraction (XRD) analysis was performed on a Rigaku Rotaflex diffractometer equipped with a rotating anode and Cu K $\alpha$  radiation. N<sub>2</sub> 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.

### 3. Results and Discussion

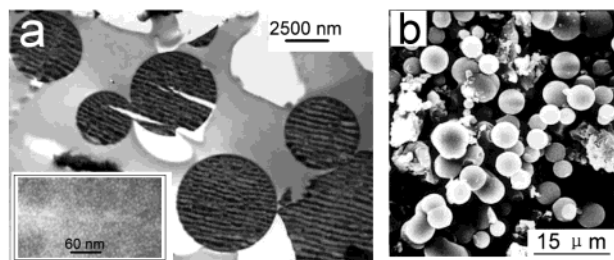
The multilamellar silica mesostructure with long-range order is clearly shown from the TEM images of an ultrathin section of the as-synthesized ZSU-L sample (Figure 1a). The hybrid silica particles are constructed of the surfactant aggregates being sandwiched by thick silica walls that are arranged parallel to each other. The interlayer distance measured from the image is about 240 ( $\pm 20$ ) nm, which is shown to be larger than those of all previously synthesized and natural layered materials.<sup>19–26</sup> To the best of our knowledge, ZSU-L silicas have the largest lattice constant known for layered materials. The silica walls do not bend to form curved silica frameworks such as closed bilayer structures, i.e., vesicles populated with concentric parallel silica layers,<sup>19–26</sup> which was never observed in our samples. 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 ultrathin sectioning. TEM observation of the sample under various tilting angles did not show evidence for any framework topology other than lamellae. SEM image of the as-synthesized ZSU-L product is shown in Figure 1b. It can be seen that the hybrid lamellar silica particles have irregularly shaped morphology with large particle size.

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.<sup>3, 19–21</sup> However, in this study the formation of silica-surfactant lamellar composites in dilute aqueous solutions ( $\sim 1$  wt %) has been shown to proceed by the coassembly of the TEOS hydrolysis species and neutral

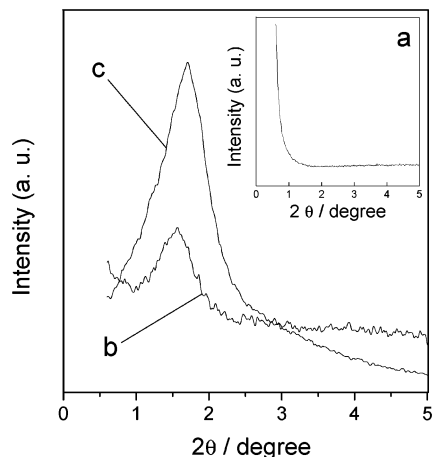
surfactants coupled with inorganic polymerization through H-bonding interactions.<sup>4,9,24–26</sup> No TEOS hydrolysis was observed in the absence of silicone surfactant, because TEOS is stable when mixed with water at neutral pH and a successful biomimetic silica synthesis from this precursor requires an agent that displays hydrolysis activity simultaneously with structure directing properties. It has been proposed that the assembly of mesostructures using nonionic PEO-based surfactants under neutral pH conditions proceeds by the prehydrolysis of the TEOS, plausibly catalyzed by the increased nucleophilicity of water molecules bound to the oxygen atoms along the PEO chains of the surfactants (i.e., the surfactant corona).<sup>27</sup> 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 ZSU-L products with highly ordered long-range lamellar structures here result from the coassembly of inorganic species and supramolecules rather than the preexisting bilayers and vesicle templates or liquid crystal phases thought to be responsible for lamellar inorganic/organic adducts.<sup>19–23</sup>

Even with substantial changes in the concentration of silicone surfactant, lamellar oxide mesophase is retained, suggesting that silicone surfactant favors the formation of lamellar mesostructure. PDMS chains are more flexible than hydrocarbon chains in alkyltrimethylammonium salts (CTA<sup>+</sup>) or Pluronics family (PEO–PPO–PEO), because the bond angle (Si–O–Si) is significantly wider ( $\sim 143^\circ$ ) 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 and tilt.<sup>17,18</sup> This illustrates the important role of the flexibility of the Si–O chain in the behavior of silicone surfactants: the siloxane group tends to adopt a configuration that allows it to accommodate the preferred cross-sectional area of the polar group, in this case the coil of the hydrated PEO chain.<sup>17</sup> This indicates that free chain configuration can allow the system to increase interfacial area through rotating or tilting the Si–O chains, while maintaining a planar structure. In this case, the wall thickness simultaneously increases to keep the volume ratio silicone–surfactant/SiO<sub>2</sub> constant. Polymerization normal to the interface substantially thickens the walls at neutral conditions. Thus, the unrestricted supramolecule chain configuration always leads to the formation of the lamellar mesostructure, and the lamellar-to-hexagonal mesophase transformation was never observed in the product templated from silicone surfactant. We suggest that silica polymerization leads to an increase in interfacial area that is achieved through tilting siloxane chains. The previously reported lamellar-to-hexagonal mesophase transformation occurred through corrugation of the lamellar surfactant–silicate sheets,<sup>28</sup> because tilting hydrocarbon chains is entropically disfavored by the restrictive hydrocarbon chain configuration, thus, the hexagonal mesophase formed in the end.<sup>28</sup> Our previous studies also demonstrated that the oxide mesophase is governed by a supramolecular chain configuration.<sup>29</sup>

Complex mesostructured silica (ZSU-5) was prepared using the mixture of silicone-based surfactant and TX-100 as a

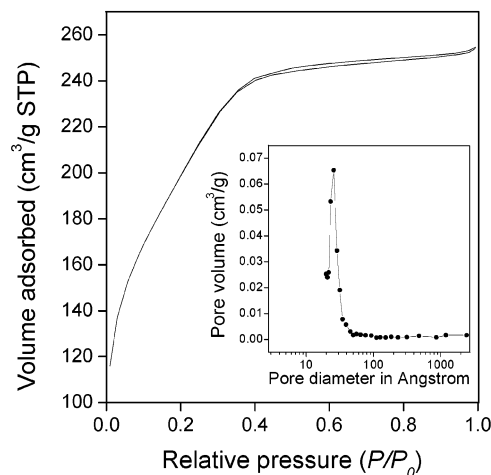


**Figure 2.** (a) TEM image of an untrathin section of the as-made ZSU-5 product. Inset in Figure 2a is a higher-magnification TEM image of the as-made ZSU-5 showing wormlike mesopores. (b) SEM image of the as-made ZSU-5 sample. The ZSU-5 sample was obtained by using the mixture of silicone surfactant and TX-100 as a structure-directing agent at neutral pH.



**Figure 3.** Powder X-ray diffraction patterns of the as-synthesized ZSU-L material (a, inset), the as-made ZSU-5 product (b), and the calcined ZSU-5 at 560 °C in air for 6 h (c).

structure-directing agent at neutral pH. Figure 2a shows that the lamellar silica mesophase similar to that observed in the ZSU-L product is also retained in the ZSU-5 product templated from the mixed silicone surfactant/TX-100 templating systems. Examining many of the TEM micrographs, it was found that mesostructured lamellar silicas represent 100% of the solid materials. No peaks are observed in XRD patterns for the ZSU-L product, as observed in Figure 3a (ZSU-L lamellar phase was not detected by XRD analysis because of its extremely large lattice constant). However, one peak in XRD patterns for ZSU-5 can be observed. XRD patterns of the as-made and calcined ZSU-5 samples are shown in Figure 3, parts b and c. The low angle XRD pattern for the as-made ZSU-5 sample contains a broad diffraction peak centered at 5.6 nm (Figure 3b), indicating ZSU-5 has wormlike mesoporous structure.<sup>4,9</sup> Upon removal of the template by calcination, the basal spacing decreases to 5.2 nm and the scattering intensity increases substantially (Figure 3c). Similar changes in XRD intensities have been observed for MSU-X and MCM-41 silicas.<sup>3,9</sup> Wormlike mesopores are clearly shown in Figure 2a (inset). Both the lamellae and disordered hexagonal mesophase are assembled in a single body, representing complex mesostructures (structure within structure). It is clearly shown that the lamellar mesophase and the wormlike mesoporosity in the walls were separately templated from silicone surfactant and TX-100 in the mixed two different surfactant systems, and thus, hierarchically ordered silica formed. Previously, in systems with Pluronics family,  $C_nEO_m$ , CTA<sup>+</sup>, or their mixtures serving as templates, a single mesophase such as hexagonal mesoporous silica has been prepared.<sup>3–6,30–32</sup> Interestingly, in this study, we find that two



**Figure 4.** Nitrogen adsorption-desorption isotherms for the ZSU-5 product calcined at 560 °C in air for 5 h. Inset, Corresponding BJH pore size distribution curve from the adsorption branch of the isotherm. The samples were outgassed overnight at 220 °C before the analyses.

different mesophases such as wormlike mesopore and lamellae were formed in a single body in the mixed silicone surfactant/TX-100 systems. The predominantly well-defined spherical particle morphology of the as-made ZSU-5 silica is confirmed by the corresponding SEM images shown in Figure 2b. The size of the particles in diameter of  $\sim 3\text{--}7\ \mu\text{m}$  determined from the SEM images is in agreement with that observed from TEM measurements.

Representative  $N_2$  sorption isotherm and the corresponding BJH (Barret-Joyner-Halenda) pore size distribution curve (inset) of the calcined ZSU-5 product (560 °C) are shown in Figure 4. A small hysteresis loop is observed for the calcined ZSU-5 product. The calcined ZSU-5 product prepared using the mixture of silicone surfactant and TX-100 as a template has a BET surface area of  $717\ \text{m}^2\ \text{g}^{-1}$ . The BJH analyses show that calcined ZSU-5 exhibits pore sizes of 2.6 nm (Figure 4, inset). These data are in agreement with the results of MSU-2 silica obtained from pure TX-100 at neutral pH.<sup>9</sup> Silicone surfactants have extremely low vapor pressures. Calcining the as-made mesostructure almost certainly converts the silicone component to silica. Therefore, about 18% of the total silica in the final calcined products originates from the silicone surfactant decomposition according to the reaction mixture molar ratios.

#### 4. Conclusions

In summary, highly ordered long-range lamellar hybrid silica with large interlayer spacings was obtained using silicone surfactant as the template at neutral pH for the first time. We found that silicone surfactants favor the formation of lamellar mesophases. The addition of TX-100 can create disordered hexagonal mesophases in the layered walls, which supply a novel simple route to synthesize and design new complex mesostructured materials. Coassembly of inorganic and organic species together with the special supramolecule chain configuration of silicone surfactants preferably maintaining the planar structure are responsible for the high regularity of the lamellar silica mesophase. We believe that this novel route is universal and offers significant overall benefits for the controlled design of a wide range of new materials with complex mesostructures. Oxide materials with hierarchically ordered mesostructures are of interest from the viewpoint of biomineralization and may find wide applications in catalysis, adsorption and separation, etc. We believe that these findings have provided new insights into



the mechanistic issues involved in the formation of this interesting class of mesostructured materials. Further investigation, however, will be required in order to adequately elucidate the actual formation mechanisms of complex mesophases formed in the mixed surfactant-templating systems containing silicone surfactant. Moreover, this simple yet general one-pot route has some special advantages in providing a pathway for large-scale convenient synthesis of silica mesophases using silicone-polyether surfactants and PEO-based surfactants as an inexpensive template. The possibility of producing other oxide materials with unusual mesostructures using this facile biomimetic strategy is also intriguing. It will enrich our ability to create hierarchically ordered inorganic/organic mesostructures using the bottom-up approach.

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