Highly Ordered Lamellar Silica/Surfactant Composites Templated from Nonionic Amphiphilic Copolymer

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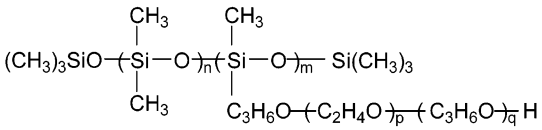
The chemical synthesis of silica-based mesophases requires extremes of pH and temperature. In contrast, biosilicification occurs in water at neutral pH and ambient temperature, producing an amazing diversity of mesostructured frameworks.[1,2] Since the discovery of M41S in 1992,[3] mesostructured materials with different forms have attracted considerable attention.[4−9] A number of layered materials such as silicates, transition-metal oxides, and aluminophosphates have been obtained using surfactants such as primary amines and quaternary ammonium ions.[10−14] However, these surfactants are expensive and toxic in contrast to nonionic poly(ethylene oxide) (PEO)-based surfactants. Recently, block copolymers have been increasingly used to organize mesostructured composites, because the architectures of block copolymers can be rationally adjusted to control the interactions between the organic and inorganic species, self-assembly, and the mesophase formation.[15] However, there has been no report on the preparation of mesostructured silica using silicone-based copolymers as the template so far.

Here we report the synthesis of lamellar silica/surfactant composites using a silicone copolymer as the template. The copolymer is composed of a poly(dimethylsiloxane) (PDMS) backbone and a side chain of PEO-*b*-poly(propylene oxide) (Chart 1). Silicone copolymers were prepared by a hydrosilylation addition reaction, as found elsewhere.[16,17]

Chart 1. Primary Structure of Silicone-Based Copolymers



Lamellar silica powders (denoted ZSU-L) were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of a silicone-based copolymer ($n = 58$, $m = 6$, $p = q = 12$, $M_n = 12\,500$, $D = 1.20$) at neutral pH or acidic conditions and room temperature (RT). In a typical synthesis, 1 g of the copolymer was dissolved in 60 mL of water, and the pH of the solution was adjusted by HCl, if needed. Then 4.16 g of TEOS was added to a templating solution. The reaction mixture was stirred at RT for 24 h to obtain lamellar silica powders. Lamellar silica monoliths and films were prepared by the sol−gel method[18] over a wide composition range of 0.02 mol of TEOS, 0.5−2.5 g of silicone surfactant, 0.08−0.30 mol of H_2O, $(0.3−8) \times 10^{-4}$ mol of HCl, and 0.24−1.5 mol of EtOH. In a typical synthesis, 1.2 g of a silicone surfactant was dissolved in 18 mL of ethanol, and the solution was acidified to pH 2 using hydrochloric acid. The added water content is equal to, or higher than, that required for the stoichiometric hydrolysis of the silica presursor. Then 4.16 g of TEOS was added to a templating solution. Silica films were prepared by a dip-coating process using the sol solution. Transmission electron microscopy (TEM) images were obtained with a JEOL 100CX operated at 100 kV. The samples were embedded in epoxy resin and ultramicrotomed for TEM measurements. The samples for scanning electron microscopy (SEM) measurements were sputter-coated with gold and examined with a Hitachi S-520 operated at a beam energy of 20.0 kV.

The lamellar structure of ZSU-L is clearly shown from the TEM images of an ultrathin section of the as-made sample templated from a silicone surfactant at neutral pH (Figure 1a). The spherical particles are constructed of a surfactant bilayer being sandwiched by thick silica walls that are arranged parallel to each other. The interlayer distance measured from the image is about 240 (±20) nm (matching the wavelength of light), which is shown to be larger than that of all previously synthesized and natural layered materials.[10−14] 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. The predominantly well-defined spherical particle morphology of the as-made ZSU-L powders is confirmed by the corresponding SEM image shown in Figure 1b. The size

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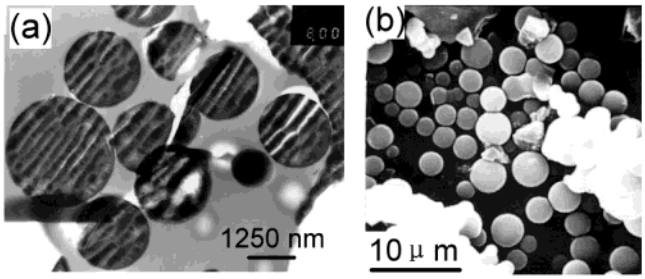

Figure 1. (a) TEM image of an ultrathin section of the as-made lamellar silica powders prepared at neutral pH. (b) Corresponding SEM image of the as-made silica spherical particles.

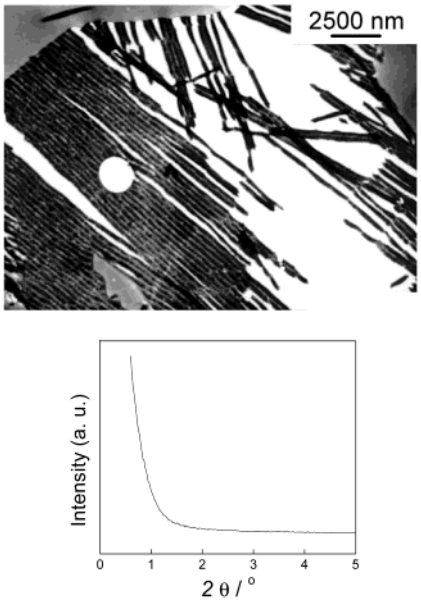

Figure 2. TEM image of an ultrathin section and XRD pattern for the as-made lamellar silica powders prepared in strong acidic media (2 M HCl).

of the particles in diameter of ∼1−5 μm determined from the SEM images is in agreement with that observed from TEM. Even with substantial changes in the concentration of the silicone surfactant and HCl, the lamellar silica mesophase is still preserved. Figure 2 shows a TEM image of an ultrathin section of silica powders prepared under strong acidic conditions (2 M HCl). It is clearly shown that hybrid silica has a highly ordered long-range lamellar structure with the same lattice constant. The ^{29}Si magic-angle-spinning NMR analysis of as-made ZSU-L shows that the Q^4/Q^3 ratio is ∼0.96, indicating that ZSU-L has a low degree of condensation compared to SBA-15.[15] Zhao et al. recently prepared a variety of mesoporous silica (SBA-15) using the Pluronics family such as $EO_{20}PO_{70}EO_{20}$ (P123) as the template under acidic conditions.[15] However, in this study, no mesophase other than the lamellar structure can be detected, as observed in Figure 2. No peaks at low angle can be found in powder X-ray diffraction (XRD) patterns for ZSU-L prepared under acidic conditions (the ZSU-L lamellar phase was not detected by XRD analysis because of its extremely large lattice constant).

The previously reported lamellar materials were obtained using a 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.[10−14] However, in this study the formation of silica/surfactant lamellar composites 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.[9] 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 bilayer formation do not occur until the TEOS precursor is added to the solution of the neutral silicone surfactants. We propose that hybrid silica powders with lamellar structure results 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.[10−14]

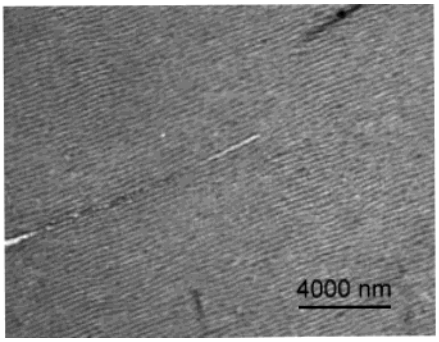

Figure 3. TEM image of an ultrathin section of multilamellar silica/surfactant films.

PDMS chains are more flexible than hydrocarbon chains in alkyltrimethylammonium salts (CTA^+) or the Pluronics family (PEO−PPO−PEO), because the bond angle (Si−O−Si) is significantly wider (∼143°) and the bond length (Si−O; 0.165 nm) longer than those of comparable C−C−C (109° and 0.140 nm) and C−O−C (114° and 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.[16,17] That is the reason even very long PDMS chain surfactants are in the liquid state at RT. In contrast, the hydrocarbon surfactants tend to be in a solid state at RT because Krafft temperatures for long and linear hydrocarbon chain surfactants are high.[16,17] We suggest that silicone surfactants with more flexible chains than conventional hydrocarbon surfactants or copolymer would be responsible for the formation of these lamellar silica mesophases with large lattice constants.[4]

To test the silicone surfactant for favoring the formation of lamellae, we prepared silica films by the sol−gel method using a silicone surfactant as the template. Zhao et al. recently prepared hexagonal mesoporous silica films using P123 as the template by the same method.[18] However, in this study only lamellar silica films can be obtained. The lamellar structure of silica films is clearly shown in Figure 3. The interlayer

distance of the lamellar silica measured from Figure 3 is ~180 (±10) nm. The presented results further supply strong evidence that silicone surfactants favor the formation of a lamellar structure. Other oxides such as TiO_2 and ZrO_2 films with lamellar structure can also be obtained using a silicone surfactant as the template and corresponding metal alkoxides as precursors by the sol−gel method (Figure 1 in the Supporting Information).

In conclusion, a novel silicone surfactant was first used as the template for the synthesis of lamellar silica powders and films with unprecedented large interlayer distances. We found that the silicone surfactant favors the formation of a lamellar structure. Such organic/inorganic composites with highly ordered long-range lamellar structure are of interest from the viewpoint of biominerization and may find potential applications. The possibility of producing other oxide materials with unusual lamellar mesostructures using this novel method is also intriguing.

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Supporting Information Available: TEM images of an ultrathin section of the as-synthesized lamellar TiO_2 and ZrO_2 films. This material is available free of charge via the Internet at http://pubs.acs.org.

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