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## LETTERS

### Novel Surfactants for the Synthesis of Unusual Highly Ordered Lamellar Oxides

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Highly ordered long-range lamellar oxides were fabricated using a silicone-based graft copolymer as the template. Lamellar oxides have the largest lattice constant known for layered materials reported to date. The results show that silicone surfactants with a highly flexible siloxane chain would lead to the formation of an unusual lamellar mesostructure.

Different surfactants have been used to organized oxides into a variety of mesostructured materials, through the mediation of electrostatic, hydrogen-bonding, dative bonding, and van der Waals interactions.<sup>1-5</sup> Self-assembly of molecules into an exciting diversity of mesostructured frameworks has attracted much attention from a wide range of scientific interests and applications. A number of layered materials such as silicas, transition metal oxides, and aluminophosphates have been obtained using surfactants such as primary amines and quaternary ammonium ions.6-10 However, lamellar oxide structures with large interlayer spacings even matching the wavelength of light have never been reported to date. Recently, block copolymers have been increasingly used to organize mesostructured oxides, because the architecture and compositions 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.<sup>11</sup> However, the use of silicone-based copolymer for preparation of oxide mesostructures has not been reported so far.

Herein we report a novel silicone-polyether copolymer designed to template self-assembly of silica/surfactant lamellar mesophases. The silicone copolymer is composed of a poly-(dimethylsiloxane) (PDMS) backbone and a side chain of poly-(ethylene oxide) (Scheme 1)

The essential properties of silicone-based copolymer were its amphiphilic character, low cost and biodegradability, and

# SCHEME 1: Primary Structure of Silicone-Based Copolymers

$$(CH_3)_3SiO \xrightarrow{CH_3} (CH_3)_3SiO \xrightarrow{(Si-O)_x} (Si-O)_y Si(CH_3)_3 (CH_3)_2 (CH_3)_3 (CH_3)_3$$

high surface activity due to the weak cohesive energy ( $\sim 25$  mN/m) of introduced PDMS chains in comparison with other surfactants such as PEO-*b*-PPO-*b*-PEO and primary amines.<sup>12</sup> It is anticipated that the aforementioned unique properties would endow silicone—polyether surfactants with substantially different behavior from conventional surfactants or block copolymers. Silicone copolymer was prepared by hydrosilylation addition reaction of PEO allyl end-blocked at PEO side to a PDMS polymer containing pendant Si–H groups using Pt-based catalyst, as described elsewhere.<sup>12</sup>

Lamellar silica powders (designated ZSU-L) were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of nonionic amphiphilic silicone surfactant in acidic aqueous media (x = 26, y = 3, z = 12;  $M_n = 4000$ , D = 1.10, purity > 95%). In a typical synthesis, 1 g of silicone copolymer was dissolved in 60 mL of 1 M HCl, and then 4.5 mL of TEOS was added to a templating solution. The reaction mixture was stirred at room temperature for 18 h to obtain the templated lamellar silica. TEM images were obtained with a JEOL 100CX

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**Figure 1.** TEM image of an ultrathin section of the as-made lamellar silica powders (ZSU-L) templated from silicone surfactant in strong acidic media (1 M HCl).

operated at 100 kV. The samples were embedded in epoxy resin, and ultramicrotomed for TEM measurements.

The lamellar structure of ZSU-L is clearly seen from the TEM images of an ultrathin section of the as-synthesized sample (Figure 1). The hybrid silicas are constructed of bilayer aggregates of the surfactant being sandwiched by thick silica walls that are arranged parallel to each other. The interlayer distance measured from the micrograph is about 190 ( $\pm$ 10) nm, which shows to be much larger than those of all previously synthesized and natural layered materials.<sup>6-10</sup> To the best of our knowledge, highly ordered long-range lamellar silica templated from silicone surfactant has the largest periodic interlayer spacing known for lamellar materials. The lamellar structures extend to the length of micrometer scale through layer propagation without curvature, as shown in Figure 1. The splitting of silica walls is the result of damage caused by untramicrotoming. TEM observation of the sample under various tilting angles did not show evidence for any mesostructured framework other than lamellae.

Even with substantial changes in the concentration of silicone surfactant and HCl, lamellar silica is also retained, suggesting that silicone surfactants favor the formation of lamellar materials. It is unprecedented that lamellar silica has an extremely large interlayer distance. There would exist a different templating mechanism between ZSU-L and SBA-15 or MCM-41. It is very likely that special properties of silicone copolymer would be responsible for the formation of lamellar structure with a large lattice constant. Both silicone surfactant and the Pluronics family (such as PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>, P123) are amphiphilic supramolecules with the same hydrophilic headgroup PEO. The only difference is that silicone surfactant contains a hydrophobic PDMS chain but P123 has a hydrophobic PPO tail. The PDMS chain is more flexible than the PPO chain in the Pluronics family or the hydrocarbon chain in alkyltrimethylammonium salts  $(CTA^+)$ , 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-O-C (114°, 0.142 nm) bonds or C-C-C (109°, 0.140 nm). Thus, the obstacle to rotation is very low (rotation barrier: 0.8 kJ/mol) and the Si-O bond can freely rotate and tilt.12 That is the reason even very long PDMS chain surfactants are in the liquid state at room temperature. In contrast, the hydrocarbon surfactants tend to be in a solid state at room temperature because Krafft temperatures for long and linear hydrocarbon-chain surfactants are high.<sup>12</sup> We suggest that silicone surfactants with more flexible chains (unrestricted supramolecular chain configuration) than conventional hydrocarbon surfactants or copolymer (restrictive supramolecular chain configuration) would be responsible for the formation of this unusual lamellar silica mesophase.

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Figure 2. TEM image of an ultrathin section of the as-synthesized lamellar silica monoliths and films using silicone surfactant as the template.



Figure 3. TEM images of an ultrathin section of the as-synthesized lamellar  $TiO_2$  and  $ZrO_2$  templated from silicone surfactant in non-aqueous solutions.

To demonstrate silicone surfactant for favoring the formation of lamellae, we fabricated transparent silica monoliths and films by the sol-gel method13 using silicone surfactant as the template. Lamellar silica monoliths and films were prepared over a wide composition range of 0.02 mol of TEOS:0.4-2.5 g of silicone surfactant:0.08-0.30 mol of H<sub>2</sub>O: $(0.4-12) \times 10^{-4}$ mol of HCl:0.25-1.5 mol EtOH. In a typical synthesis, 1 g of silicone surfactant was dissolved in 15 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. The reaction mixture solution was transferred to a vessel for reaction in air at room temperature for 24 h to obtain the templated lamellar product. Transparent and continuous silica films were prepared by the dip-coating process using the sol solution. The lamellar feature of silica is clearly shown in Figure 2. The lattice constant of lamellar silica measured from Figure 2 is about 170  $(\pm 10)$ nm. The results further supply strong evidence that silicone surfactants favor the formation of unusual lamellar mesostructure. Other lamellar oxide monoliths and films such as TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> can be obtained using silicone surfactant as the template and corresponding metal alkoxides as precursors.

Yang et al.<sup>14</sup> prepared a series of hexagonal metal oxide mesophases using the Pluronics family such as P123 as the template in nonaqueous solutions. However, in this study, only lamellar metal oxides such as TiO<sub>2</sub> and ZrO<sub>2</sub> were obtained by using the silicone surfactant as the template in nonaqueous solutions by the same method described by Yang et al.<sup>14</sup> The lamellar structure of TiO<sub>2</sub> and ZrO<sub>2</sub> is clearly shown in Figure 3A and B, respectively. The interlayer distance of lamellar TiO<sub>2</sub> and ZrO<sub>2</sub> measured from Figure 3A,B is about 230 (±10) and 170 (±10) nm, respectively. The present results support the proposal that oxide mesophases are governed by supramolecular chain configuration; i.e., unrestricted chain configuration (such as silicone surfactants) is responsible for the formation of the zero-curvature (planar) lamellar silica mesophase, and restrictive chain configuration (such as Pluronics family,  $C_{16}TA^+$ ) is responsible for high curvature hexagonal mesophase.<sup>15</sup> Other metal oxides such as SnO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with similar lamellar structure can also be obtained using silicone surfacant as the template and corresponding anhydrous metal chlorides as precursors in nonaqueous solutions.

In conclusion, we have demonstrated that novel silicone-based copolymer can successfully template the assembly of the hybrid layered oxide mesophase with the largest interlayer spacings for the first time. The synthesis of unusual lamellar oxide materials with silicone surfactants as the template illustrates the novelty of this synthetic strategy. We suggest that the unrestricted supramolecule chain configuration of siloxane may be responsible for the formation of these unusual lamellar oxide materials. Such hybrid oxides with long-range ordered lamellar structure are of interest from the viewpoint of biomineralization and may find potential applications. The possibility of producing other oxide materials with unusual mesostructures using this novel method is also intriguing. It will enrich our ability to create highly ordered inorganic/organic mesostructure with larger periodic spacing using the bottom-up approach.

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