Microlamellar Structure?

Additional Proof for the Existence for Microlamellar Structured ZSU-L Templated from Silicone Surfactants

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According to mass conservation, if we use tetraethylorthosilicate (TEOS, 0.02 mol) and silicone surfactant (1 g) to prepare a sample of ZSU-L, 1.9–2.1 g of the product can always be obtained (after being thoroughly washed with water and ethanol and then dried). A maximum of 1.2 g of SiO_2 is obtained when completely converting 0.02 mol of TEOS into SiO_2. It can be shown that almost all of the silicone surfactant molecules enter the SiO_2 matrix. TEOS is stable in neutral aqueous solutions, and no precipitate is obtained. However, in the presence of silicone surfactant, TEOS can hydrolyze to form silica/surfactant composites in neutral water. The formation of such composites in neutral aqueous solution has been shown to proceed by the co-assembly of the TEOS hydrolysis product and neutral silicone surfactants, coupled with inorganic polymerization through hydrogen-bonding interactions. Low-angle X-ray diffraction (XRD) patterns show no peaks for ZSU-L. Therefore, one may wish to discover which structure ZSU-L has adopted. A large number of experiments in our laboratory have demonstrated that ZSU-L has a lamellar structure, as confirmed by some evident proof including TEM images of an ultrathin section of the material.[1–5] Su et al. have commented that the microlamellar structure in ZSU-L is created by ultramicrotoming. Here we present some additional proof that confirms the nature of the microlamellar structure of ZSU-L.

It is well-known from TEM textbooks that the striped patterns, similar to those mentioned by Su et al., can be produced by ultramicrotoming. To rule out the possibility that the lamellar structure of ZSU-L is caused by ultrathin sectioning, a large number of experiments were performed. For example, amorphous SiO_2, TiO_2, and ZrO_2, M41S,[6] SBA-15,[7] MSU-X,[8] and ZSU-L samples were sent to three different laboratories for ultramicrotoming; each sample was ultramicrotomed 10 times. TEM analysis shows that the striped patterns caused by ultramicrotoming can be occasionally observed in amorphous samples of the above-listed materials. However, these striped patterns only take up an extremely small portion on an ultrathin section, and show poorly ordered structure. In our ZSU-L samples, however, highly ordered microlamellar structure was always observed. Moreover, an ultrathin section of ZSU-L consists almost entirely of the highly ordered microlamellar structure. Therefore, we confirm that our ZSU-L samples have true microlamellar structures, as demonstrated in our previously published papers. According to our experience, if the blade of a diamond knife is not sharp or the microtoming process is not optimal, the striped patterns can be often be observed for an ultrathin section of an amorphous sample.

The mixture of ZSU-L (TiO_2) and CMI-1 (SiO_2) with different mass ratios was ultramicrotomed for TEM observation. We found that the number of particles containing microlamellar structure decrease with an increase in the mass ratio of CMI-1 to ZSU-L. Electron dispersive spectroscopy (EDS) analysis performed on lamellar structured particles shows that both Ti and O were detected, as well as a small amount of Si, which comes from the silicone surfactant. But on nonlamellar structured particles, only Si and O were detected (Figure 1). All TiO_2 particles have a lamellar structure, while almost all of the CMI-1 particles do not display the striped pattern. The results supply strong evidence that ZSU-L has microlamellar structure in nature, which is not created by ultramicrotoming. Mixtures of ZSU-L (SiO_2, ZrO_2) and CMI-1 were also ultramicrotomed for TEM analysis, in which we also found that the number of particles having microlamellar structure decreased with an increase in the mass ratio of CMI-1 to ZSU-L (SiO_2, ZrO_2).

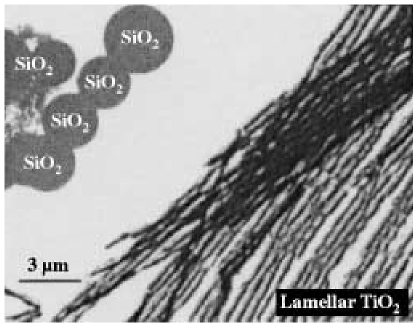

Figure 1. TEM image of an ultrathin section of the mixture of ZSU-L (TiO_2) and CMI-1 (SiO_2). The lamellar structure belongs to ZSU-L (TiO_2), and the black spherical particles are of SiO_2, as determined by EDS analysis.

In general, ultrathin sections are normally ultramicrotomed into a trape-

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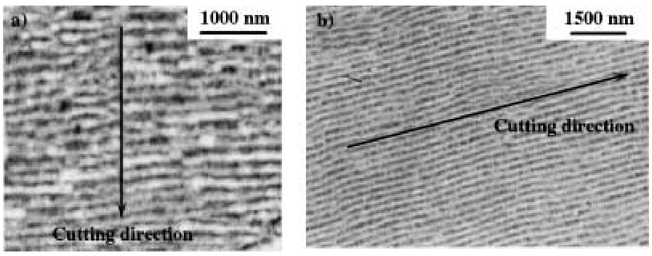

Figure 2. a) TEM image of an ultrathin section of an amorphous silica sample. The striped patterns were created by ultramicrotoming. The cutting direction (arrow) of a diamond knife is perpendicular to the stripes; b) TEM image of an ultrathin section of microlamellar structured ZSU-L. The cutting direction (arrow) of the knife is parallel to the direction of the lamellar structure, which indicates that the lamellar structure was not produced by ultramicrotoming.

zoidal shape; one can always know the cutting direction of a diamond knife on an ultrathin section. Therefore, the stripes produced by ultramicrotoming should be perpendicular to the cutting direction of the knife. Figure 2a shows the striped patterns created by ultramicrotoming. However, in our ZSU-L samples, we found that the direction of the lamellar structure in many slices is not perpendicular to the cutting direction of the knife; some aligned silica wall lines are even parallel to the cutting direction of the knife. Figure 2b shows the cutting direction of the knife and the direction of the lamellar structure of ZSU-L. Moreover, the different directions of lamellar structure in ZSU-L can be always observed. TEM observation was performed under a low electron-energy beam (100 kV) to make sure that the slices did not move.

N_2 sorption analyses show that the as-prepared ZSU-L has a BET surface area of only approximately 2 $m^2 g^{-1}$, but the calcined ZSU-L exhibits a type I isotherm with a hysteresis loop of type H_4 that is typical of lamellar materials (Figure 3),[4,9] and a surface area of 288 $m^2 g^{-1}$. It demonstrates that the co-assembly of a silicone surfactant silicate forms a lamellar structure.

To study the location of the silicone surfactant between the walls (stripes), high-resolution electron energy loss spectroscopy (HREELS) analysis was performed on an ultrathin section of microlamellar-structured TiO_2. HREELS line scans were performed across aligned TiO_2 walls (Figure 4) which indicated that the walls only contain Ti and O; no Si was detected. However, in the area within the walls, Si can be always found, which originates from the silicone surfactant bilayers. These results clearly show that silicone surfactant bilayers were sandwiched by titania walls to form a highly ordered microlamellar structure. The ZSU-L products are constructed of silicone surfactant layers that are sandwiched by thick titania walls that are arranged parallel to each other. It indicates that microlamellar structured TiO_2 was templated from the silicone surfactant. It supplies strong evidence that the lamellar structure in TiO_2 is not produced by ultramicrotoming. Recently, Saravanamuttu et al. has also reported the formation of an ordered microlamellar structure, similar to that of ZSU-L.[10]

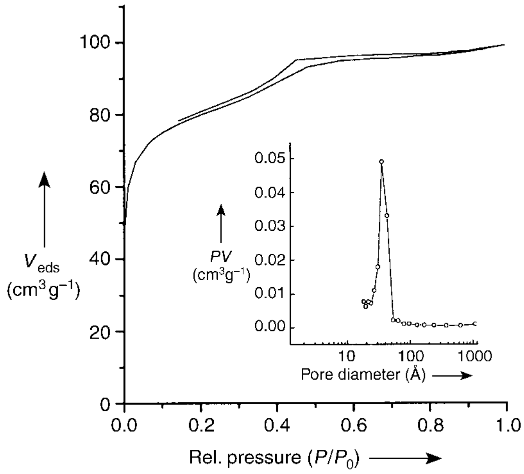

Figure 3. N_2 adsorption–desorption isotherms for the calcined ZSU-L sample (V_{ads} = gas volume adsorbed at standard temperature and pressure). Inset: The corresponding Barret–Joyner–Halenda (BJH) pore-size-distribution curve (*PV* = pore volume).

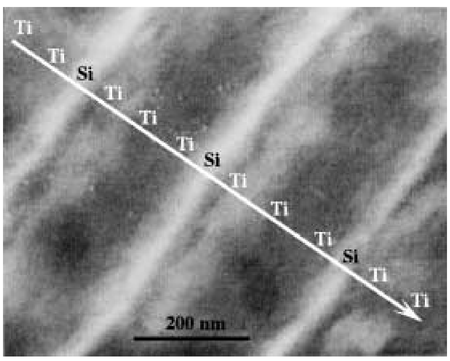

Figure 4. HREELS line scans across the lamellae of microlamellar-structured TiO_2/silicone surfactant composites, which indicate that the silicone surfactant is sandwiched by TiO_2 walls. Si originates from the silicone surfactant, and Ti from TiO_2.

In conclusion, the results presented here further demonstrate that ZSU-L has an inherently microlamellar structure, which is not created by ultramicrotoming. We will report our new results in the near future. Finally, we thank Professor Su and co-workers for their comments, which encouraged us to supply additional evidence that confirms the microlamellar nature of the ZSU-L structure.

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