Macrolamellar Structure?

Do Mesostructured Materials Have an Unusual Macrolamellar Structure?**

*Zhong-Yong Yuan, Marie-France Six-Boulanger, and Bao-Lian Su**

Stichwörter:
lamellar structures · mesophases · oxides · silicon · surfactants

The synthesis of inorganic mesoporous materials by using organic molecules as structure-directing agents or templates is an area of rapid growth with diverse applications that include separation technology and catalysis. Surfactant templating techniques based on electrostatic, hydrogen-bonding, covalent, and van der Waals interactions between amphiphilic and ceramic species have been developed for the synthesis of these materials with a narrow mesopore size distribution and controlled pore structure.[1,2] Despite considerable successes, it remains a challenge for chemists and materials scientists to mimic the natural pathways that would aid the development of simple and efficient routes to advanced functional materials. Recently Xu and co-workers[3–11] have published a series of papers reporting the synthesis of a highly ordered long-range lamellar structure (designated ZSU-L) and hierarchically ordered silica mesostructures (designated ZSU-4, -5, -38). An amphiphilic silicone surfactant was used to direct highly ordered lamellar oxides with large interlayer spacings (160–240 nm).[3–11] The mixture of a silicone surfactant and conventional surfactants (for example, P123, TX-100, C_{16}TAB) was claimed to be able to direct the formation of the unusual hierarchical mesostructures.[3,9–11] The macrolamellar structures reported by Xu and co-workers were investigated by transmission electron microscopy (TEM), and the specimens for TEM observation were prepared by embedding samples in epoxy resin and then ultramicrotoming them. In this communication, we would like to comment on the highly ordered macrolamellar structure presented in the studies of Xu and co-workers, on the basis of our previous work and on work that was carried out after the appearance of Xu's papers.

In our laboratory we have synthesized various mesoporous materials with different pore structures and compositions by using surfactant-templating techniques. CMI-1[12] is a mesoporous silica material with an ordered hexagonal-pore array synthesized by using polyoxyethylene oxide surfactant under weakly acidic conditions. The specimens for TEM observation were prepared by embedding in epoxy resin and ultramicrotoming. Figure 1 presents several TEM images of CMI-1. Clear striped patterns are observed in low-magnification images and the repeat distance of the striped patterns was approximately 160–200 nm (Figure 1 a–c). Both the striped patterns and the "interlayer distance" are quite similar to those in the images in Xu's papers.[3–11] Moreover, these striped patterns have almost the same directionality in all particle slices (Figure 1 b and d). Figure 1 e and f are typical high-magnification TEM images showing an ordered hexagonal array of 4-nm mesopores between the more widely spaced stripes. Under electron-beam irradiation, the particle slices could become split up or constricted (see Figure 1 c). Such wide striped patterns can also be seen in all the ultrathin sections of other mesostructured materials synthesized in our laboratory, whatever their mesostructures or compositions.

Have all mesostructured materials such a macrolamellar structure? For the sake of comparison, we also prepared specimens by dispersing the particles in alcohol by ultrasonic treatment, and dropping them onto a holey carbon film supported on a copper grid. In the analysis of these samples by TEM, we continued to see the ordered mesopore array, but the large stripes were now absent. No macrolamellar structure was seen in any of our mesostructured materials. This is a strong indication that the macrolamellar structure observed by Xu and co-workers is artificial.

In order to further confirm the artificialness of the so-called macrolamellar structure, samples of amorphous silica, titania, and zirconia were prepared by the simple hydrolysis of Si, Ti, and Zr alkoxides in water without the addition of any organic surfactant species, followed by preparation of the TEM specimen by ultrathin sectioning. The same striped patterns are present in low-magnification images of these ultrathin sections. We can even modify the "interlayer distance" of the "macro-

[*] Prof. B.-L. Su, Dr. Z.-Y. Yuan
Laboratory of Inorganic Materials Chemistry (CMI)
Institute for Studies in Interface Sciences (ISIS)
The University of Namur (FUNDP)
61 rue de Bruxelles, 5000 Namur (Belgium)
Fax: (+32) 81-725414
E-mail: bao-lian.su@fundp.ac.be
M.-F. Six-Boulanger
Interfaculty Unit of Electron Microscopy
The University of Namur (FUNDP)
61 rue de Bruxelles, 5000 Namur (Belgium)

[**] The authors have chosen to use the term "macrolamellar" to describe the features observed in the materials presented herein. This choice is based on the IUPAC definition of macroporosity (larger than 50 nm in diameter) and microporosity (smaller than 2 nm in diameter).

  DOI: 10.1002/ange.200320060

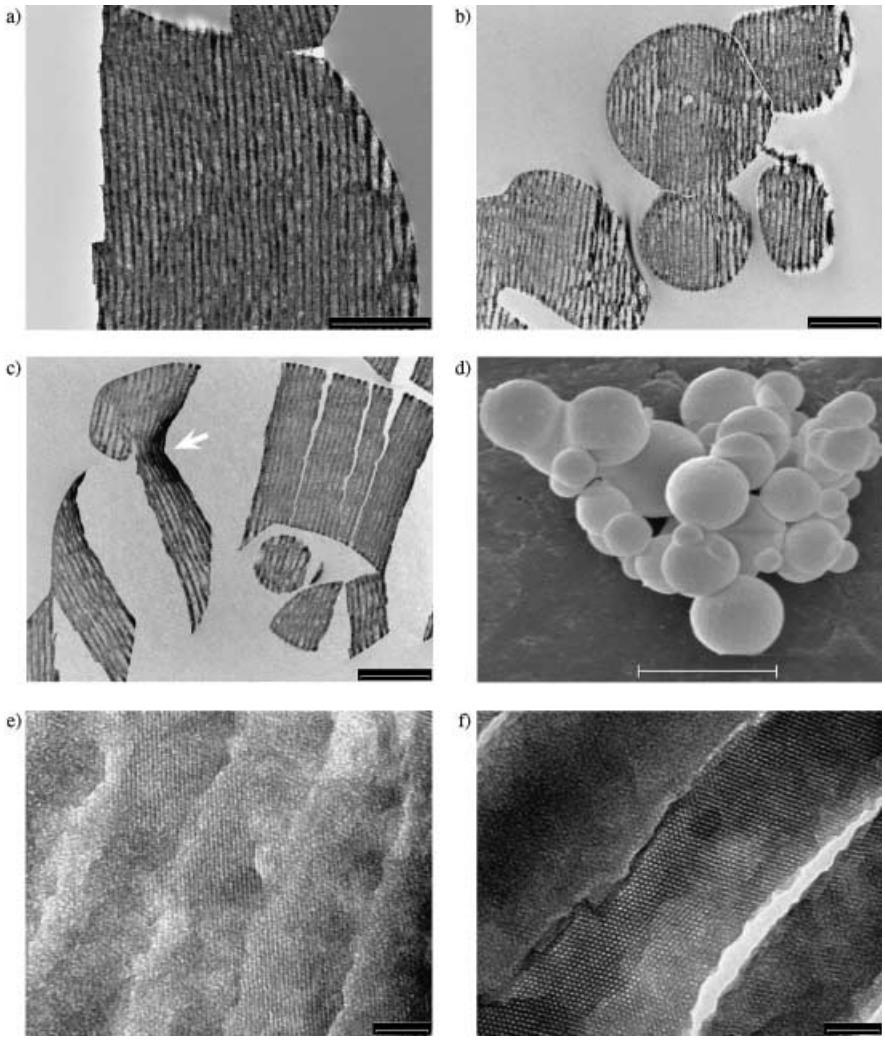

Figure 1. a,b) Low-magnification TEM images of ultrathin sections of mesoporous CMI-1 silica showing striped patterns with a wide interlayer distance (scale bar = 2 μm); c) low-magnification image showing that the particle slices are split up and constricted (marked with a white arrow) after electron-beam irradiation (scale bar = 2 μm); d) scanning electron micrograph of spherical CMI-1 particles (scale bar = 5 μm); e,f) high-magnification TEM images showing an ordered mesopore array when viewed perpendicular and parallel to the pore directions, respectively (scale bar = 50 nm).

lamellar structure" by changing the velocity of cutting during microtoming and altering the size of the blade of the diamond knife. In addition, wide striped patterns with the same orientation can be clearly observed even in the resin region of the ultramicrotomed specimens.

It is thus clear that the highly ordered macrolamellar structure described in the papers of Xu and co-workers is an artifact arising from the ultramicrotoming. Additional evidence to this effect can also be found in the TEM images within these papers. For example, in Figure 2 of ref. [4] and Figure 1 of ref. [6], the striped patterns in all of the randomly dispersed particle slices have the same directionality. It is impossible that the direction of the lamellar structure in such randomly dispersed particles can be the same (Figure 1 b and d) even if these materials had a true macrolamellar structure. Therefore, the so-called "hierarchically ordered silica mesophases" described in the papers of Xu and co-workers cannot be real, and the claimed "macrolamellar structure" is only an artifact.[3–11]. It is not surprising to see the same artifact on the amorphous samples prepared either by sol–gel or simple precipitation methods if the same sample preparation for TEM measurement is applied, that is, by ultramicrotoming.

[1] A. Sayari, P. Liu, *Microporous Mater.* **1997**, *12*, 149.
[2] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem.* **1999**, *111*, 58; *Angew. Chem. Int. Ed.* **1999**, *38*, 56.
[3] A. W. Xu, Y. P. Cai, H. X. Zhang, L. Z. Zhang, J. C. Yu, *Angew. Chem.* **2002**, *114*, 4000; *Angew. Chem. Int. Ed.* **2002**, *41*, 3844.
[4] A. W. Xu, *J. Phys. Chem. B* **2002**, *106*, 13161.
[5] A. W. Xu, J. C. Yu, Y. P. Cai, H. X. Zhang, L. Z. Zhang, *Chem. Commun.* **2002**, 1614.
[6] A. W. Xu, *Chem. Mater.* **2002**, *14*, 3625.
[7] A. W. Xu, Y. P. Cai, L. Z. Zhang, J. C. Yu, *Adv. Mater.* **2002**, *14*, 1064.
[8] A. W. Xu, *Chem. Lett.* **2002**, 878.
[9] A. W. Xu, *J. Phys. Chem. B* **2002**, *106*, 11713.
[10] A. W. Xu, J. C. Yu, H. X. Zhang, L. Z. Zhang, D. B. Kuang, Y. P. Fang, *Langmuir* **2002**, *18*, 9570.
[11] A. W. Xu, *Chem. Lett.* **2002**, 982.
[12] J. L. Blin, A. Léonard, B. L. Su, *Chem. Mater.* **2001**, *13*, 3542.

