

Comments

Comment on Spontaneously Ordered Sol–Gel Composites with Submicrometer Periodicity

Saravanamuttu and Andrews¹ asserted a template-free, room-temperature sol–gel route to ordered composites with submicrometer periodicity. Their solid monoliths and composite films were prepared by sol–gel processing of simple silicon and transition metal alkoxides, and a close-packed, periodic array of 250-nm-wide domains was found in their TEM specimens of microtomed cross sections. We contend that their so-called findings of long-range microstructural organization with submicrometer periodicity are just an artifact, which arises from the ultramicrotoming of TEM specimen preparation.

In fact, such a macroperiodic organization described by Saravanamuttu and Andrews is often observed in the TEM specimens of ultrathin sections, whatever the compositions or microstructures of the specimens. We prepared amorphous silicas, titanias, and zirconias by simple hydrolysis of Si, Ti, and Zr alkoxides, respectively, at room-temperature, followed by TEM specimen preparation by embedding in epoxy resin and ultramicrotoming. The low-magnification TEM images of these amorphous oxide powders show that the particles are present in the form of a periodic array of many discrete and detachable domains, and each domain has a similar width of submicrometer scale and an identical orientation in the length direction (see Figure 1 of the Supporting Information). The array of these domains in all particles is the same. Such phenomena can also be seen in mesoporous materials,² such as silicas, titanias, and zirconias, prepared by surfactant templating (see Figure 2 of the Supporting Information). The long-range ordered pattern of submicrometer periodicity can be seen especially when the sample particles are large (e.g., monoliths and films). However, when we prepared the TEM specimens by dispersing the particles in alcohol by ultrasonic treatment, and dropping them onto a holey carbon film supported on a copper grid, followed by direct TEM observation, such macroperiodic patterns could *NOT* be seen in any of our materials, regardless of the compositions and whether they were nontemplated amorphous or surfactant-templated mesostructured materials. The only possible explanation for this is that the above macroperiodic pattern is artificial and due to the ultramicrotoming of specimen preparation. With careful examinations of various microtomed sections, it is found that the width of the macroperiodic pattern is affected by the velocity of cutting during microtoming, the scale of the blade of a diamond knife, and the density of the samples. The difference between Figures 1 and 4 in the paper of Saravanamuttu and Andrews should be due to the

increase of hardness of their composite after thermal treatment, but all the so-called macroperiodic structures described in these figures are knife-induced artifacts created during microtoming. The authors insisted in their reply that the fast Fourier transform (FFT) analysis of their TEM images on the microtomed specimen yields a periodicity of 240 nm which corresponds closely to the 250 nm spacing observed in the ultrathin (microtomed) section of their materials, and they argued that this “submicrometer periodicity” is inherent to their materials. However, it is well-known that the FFT analysis is only a treatment of image. When the image contains the striped line (this is the case for all the microtomed samples), the FFT analysis will give a line of spots. We carried out a series of FFT analyses with microtomed amorphous samples, and it is not surprising that this “submicrometer periodicity” artifact is really visible (Figure 2 of Supporting Information). So, it is clear that the “submicrometer periodicity” observed by Saravanamuttu and Andrews¹ is an artifact.

The same artifact is also present in the papers of Xu et al.^{3–11} in which their images are similar to those in the Supporting Information and in the paper of Saravanamuttu and Andrews. Evident proof can also be found in Xu's papers (e.g. Figures 1 and 2 of *Chem. Commun.* **2002**, 1614; Figure 1 of *Chem. Mater.* **2002**, *14*, 3625; and Figure 2 of *J. Phys. Chem. B* **2002**, *106*, 13161), as it is impossible that the striped patterns in all randomly dispersed particles have the same direction. Moreover, a wide striped pattern can be present simultaneously in the epoxy resin region, and the direction of striped pattern in resin region is the same as that in sample particles (see Figure 3 in the Supporting Information from the specimens provided by Xu himself^{3–11}). The distance between strips of resin region is larger than that of sample region because the resistance endured during ultramicrotoming is smaller in the resin region.

Supporting Information Available: Low-magnification TEM images of subject materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Zhong-Yong Yuan and Bao-Lian Su*

*Laboratory of Inorganic Materials Chemistry, I.S.I.S.,
The University of Namur (FUNDP), 61 rue de
Bruxelles, B-5000 Namur, Belgium*

Received January 22, 2003

CM031023Q

* To whom correspondence should be addressed. Fax: +32-81-725414. E-mail: bao-lian.su@fundp.ac.be.

(1) Saravanamuttu, K.; Andrews, M. P. *Chem. Mater.* **2003**, *15*, 14–16.

(2) Yuan, Z. Y.; Six-Boulanger, M. F.; Su, B. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 0000.

(3) Xu, A. W. *Chem. Mater.* **2002**, *14*, 3625–3627.

(4) Xu, A. W. *J. Phys. Chem. B* **2002**, *106*, 13161–13164.

(5) Xu, A. W.; Cai, Y. P.; Zhang, H. X.; Zhang, L. Z.; Yu, J. C. *Angew. Chem.* **2002**, *114*, 4000–4004; *Angew. Chem., Int. Ed.* **2002**, *41*, 3844–3848.

(6) Xu, A. W.; Yu, J. C.; Zhang, H. X.; Zhang, L. Z.; Kuang, D. B.; Fang, Y. P. *Langmuir* **2002**, *18*, 9570–9573.

(7) Xu, A. W. *Chem. Lett.* **2002**, 982–983.

(8) Xu, A. W. *J. Phys. Chem. B* **2002**, *106*, 11713–11715.

(9) Xu, A. W. *Chem. Lett.* **2002**, 878–879.

(10) Xu, A. W.; Cai, Y. P.; Zhang, L. Z.; Yu, J. C. *Adv. Mater.* **2002**, *14*, 1064–1068.

(11) Xu, A. W.; Yu, J. C.; Cai, Y. P.; Zhang, H. X.; Zhang, L. Z. *Chem. Commun.* **2002**, 1614–1615.