Reply to the Comment on Spontaneously Ordered Sol−Gel Composites with Submicrometer Periodicity

In their Comment, A.-Y. Yuan and B.-L. Su suggest that the periodic microstructure observed in transmission electron micrographs (TEM) of microtomed sections of sol−gel derived silica−acrylate−zirconia (SZ) composites described in our Communication[1] might originate from diamond-knife-induced artifacts. However, we note here that our TEM studies of Pt/C replicas of fractured samples of SZ (Figure 1) show a persistent

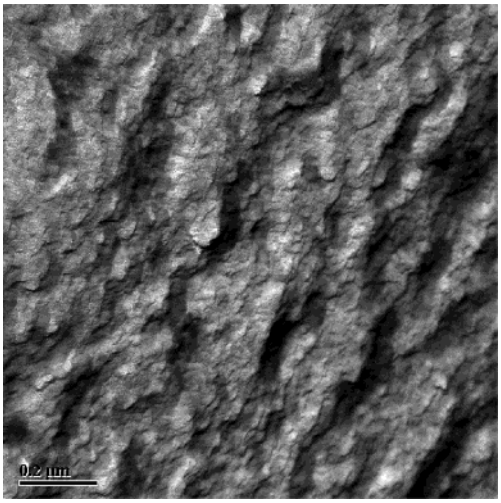

Figure 1. Pt/C replica TEM of the SZ composite. Scale bar = 0.2 μm. FFT of this image yields a periodicity of 240 nm (±30 nm).

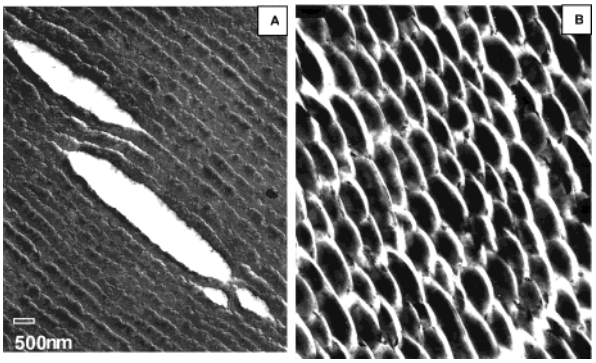

Figure 2. (A). Cross-sectional TEM of microtomed sections of a sol−gel derived monolith; (B) after heating in air at 700 °C for 10 h.

lamellar structure (note that there is a fine structure order as well).[2] Fast Fourier transform analysis of this structure yields a periodicity of 240 nm (±30 nm), which corresponds closely to the ∼250-nm spacing observed in ultrathin (microtomed) sections of the composite in our Communication.[1] Because the freeze-fracture technique does not involve microtoming, there can be no question in this instance of knife-induced artifacts.[3]

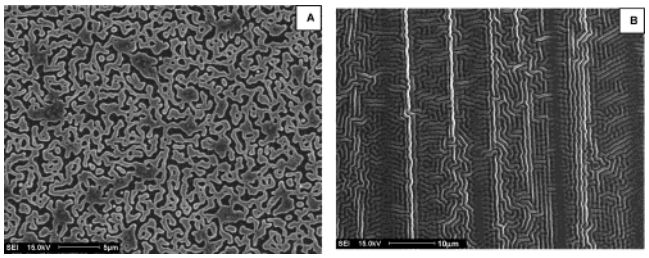

Figure 3. (A). Scanning electron micrograph of a spin-cast film of sol−gel derived silica−acrylate composite; (B) after irradiation with a waveguided Ar^+ laser beam (514.5 nm).

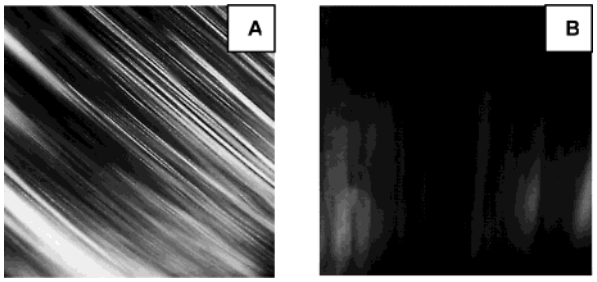

Figure 4. Polarized optical micrographs showing the birefringence of a sol−gel derived composite monolith; the optical anisotropy observed in (A) is extinguished when the sample is rotated by 45 °C (B).

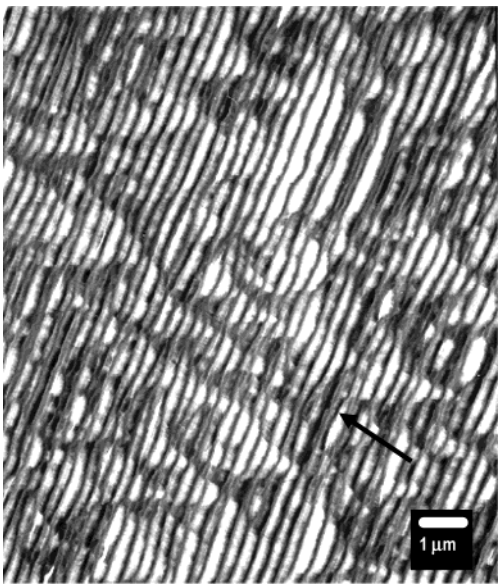

Figure 5. Transmission electron micrograph showing that shear-induced distortions of samples incurred during microtoming does not coincide with the orientation of domains (arrow indicates the direction of distortion).

The argument of Su et al. is based on their observation of macroperiodic order in various amorphous and surfactant-templated composites that are microtomed after embedding in epoxy resin. These composites differ from our materials, which (a) were prepared from

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

(2) Belanger, N.; Andrews, M. P. Unpublished results.

(3) Samples for TEM were prepared by plunge-freezing in liquid propane and etching under high vacuum (1 min) prior to coating with Pt/C.

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organosubstituted alkoxysilanes and not from only silicon or transition metal tetra alkoxides, (b) did not consist of particulate powders but were instead prepared as *spin-cast* films and optically transparent, solid monoliths, and (c) with the exception of pyrolyzed samples, were not embedded in epoxy resin. Being sensitive to the potential of artifacts created during sample preparation, we too have observed shear-induced distortions during microtoming, but these distortions did not coincide with the lamellar orientation of the sample (Figure 5). We also point out the dramatic difference in microstructure even between ultrathin sections of untreated and thermally treated samples of the same composite (Figures 1 and 4[1], Figure 2A and B)—although both samples were prepared through microtoming.

We also note that observations of self-organization in our samples are not based on evidence from TEM alone. The Comment by A.-Y. Yuan and B.-L. Su overlooks the bicontinuous organization at *submicrometer-length scales* observed by SEM (Figure 3[1], Figure 3A). Evidence of microstructural order at these length scales has also been observed through SEM of irradiated films (Figure 3B) and in polarized optical micrographs that show birefringence in monoliths (Figure 4).

We appreciate the concerns raised in the Comment by Su et al. who note the need to distinguish between material microstructure intrinsic to self-organization and microstructural artifacts caused by sample preparation. However, we emphasize here that experiments that do not require microtoming reinforce our assertion that self-organization is *inherent* to the SZ materials described in our Communication.[1]

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