Reply to Comment on "Spin-Coated Periodic Mesoporous Organosilica Thin Films with Molecular-Scale Order within the Organosilica Wall"

The comments raised by Dr. Inagaki and Takao Tani help us to reconsider our PMO thin films, and we see an interesting new perspective of this film system. After a thorough analysis of the comments, we still believe that our model of the film structure is the best explanation for the experimental results obtained and that long-range molecular-scale order is indeed present in the pore walls. We have no evidence to suggest that the PMO thin films contain amorphous pore walls along with a small fraction of nonporous Ph-triol particles having molecular-scale periodicity. Here are our responses to the comments. First of all, we never state that T^0 (R-Si(OH)$_3$: triol) species is a major species in our thin films. In fact, the organosilane molecules mostly exist as T^1, T^2, or T^3 species in the films, not as T^0 species. We mentioned silanetriol to refer to another study on the molecular packing structure of benzene-bridged bis-silanetriol (ref 21). The conception that our films contain Ph-triol molecules or particles is simply incorrect.

The next comment concerns the general observation that organosilica materials prepared under acidic conditions typically have a low degree of condensation and do not show any molecular-scale periodicity. However, the disordered molecular organization of benzene-bridged organosilane reported by Shea et al. contains alkoxy groups, while in our system the ethoxy groups have been fully hydrolyzed to hydroxyl groups, allowing our partially condensed BTEB molecules to link extensively via hydrogen bonding. In fact, this molecular self-assembly is so strong that the molecules spontaneously form such an ordered structure even in the absence of CTAB surfactant. The same high-angle XRD patterns of films made from sol prepared without the addition of CTAB surfactant can be obtained with strong and sharp peaks showing at exactly the same positions. Elongation of *d*-spacing of the molecular-scale periodicity to 10.1 Å is thus possible and favorable.

In the next comment, Dr. Inagaki reasons that broadening of XRD peaks should be observed for organosilane residing in the thin pore walls of a few nanometers, and very sharp XRD peaks should not be recorded. This seems to make sense. However, if one considers that the spontaneous and organized self-assembly of these partially condensed BTEB molecules is a major and competing driving force with the self-organization of surfactant molecules into hexagonally arranged micellar arrays, it is possible that an extensive regular intermolecular structure can still be established within the pore walls, hence, the observation of sharp XRD peaks. Perhaps the molecules do not arrange cylindrically around the micelles as those previously observed in other PMO materials, and this may explain why the lattice fringes observed in the TEM images are not perpendicular to the direction of the pore channels and why the same high-angle XRD peaks were recoded in the absence of CTAB surfactant.

Finally, Dr. Inagaki suspects that the TEM image shown (Figure 4b) with lattice fringes running in different directions may result from overlapping of two phases. First of all, one should not overinterpret this image. This image just represents our great effort to show the lattice fringes and verify the existence of molecular spacing of about 10 Å. Interestingly, it also reveals that the lattice fringes run at an angle of 45−60° with respect to the direction of the pore channels. However, this cross-sectional TEM sample is hard to prepare. If we have more TEM samples and images, we will be able to offer more insights. Again the molecular self-assembly into an ordered structure is such a major driving force that the lattice fringes can actually run independent of the pore channel directions. The change of lattice fringe direction may be related to the black stripe running across the film and the fact that this cross-sectional film sample may not be prepared perfectly. This image also suggests that the lattice fringes do not come from particles sitting on top of or below the film, but they actually are a part of the film structure. Thus, the lattice fringes and the TEM image do not result from overlapping of two phases.

Sheng-Ying Wu,
Han-Sheng Hsueh, and Michael H. Huang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

CM800014S

10.1021/cm800014s CCC: $40.75