Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

Phenylene-bridged mesoporous organosilica films with uniaxially aligned mesochannels

Takashi Suzuki, Hirokatsu Miyata*, and Kazuyuki Kuroda*

Discussion of pore size.

The pore size can be discussed from the distance between mesopores determined by the XRD results and the reported wall thickness of phenylene-bridged mesoporous organosilica *powders* prepared under similar conditions.[26] The distance between mesopores of both films parallel to the substrate was estimated to be 6.8 nm by the in-plane ϕ-$2\theta\chi$ scanning profile (Fig. 3). On the other hand, the wall thicknesses of phenylene-bridged mesoporous organosilica *powders* prepared using Brij 56 under acidic conditions, calculated by the subtraction of pore size from the distance between mesopores, are estimated to be ~1.2 or 2.9 nm, depending on the methods of analysis (the density functional theory (DFT), Broekhoff-de Boer, Frenkel-Halsey-Hill (BdB-FHH), and the Barrett-Joyner-Halenda (BJH) methods).[26] Therefore, the pore diameter of both films parallel to the substrate is supposed to be ~5.6 nm or 3.9 nm. The shrinkage along the direction perpendicular to the substrate results in the ellipsoidal morphology of mesopores. Therefore, the diameter of short axis in the ellipsoidal pore may range between ~5.0 nm and 3.5 nm (hydrothermal film) and ~3.1 nm and 2.1 nm (EISA film), and these values were calculated by considering the degree of shrinkage. The TEM images of both films (Supplementary information Fig. S2) also provide us some rough data on the pore size. The pore size of both films was very roughly estimated to be 3 ~ 4 nm from the TEM images if the distance between mesopores is calibrated with the XRD results. Because the conditions for the

TEM measurement affect the results, the estimation of pore size by TEM should be very careful. However, the values are basically consistent with those reported for phenylene-bridged mesoporous organosilica powder prepared by using Brij 56.[26] Consequently, we think we can use these values as the rough estimates of pore size.

Influence of large shrinkage of mesostructure on the in-plane ϕ-$2\theta\chi$ scanning XRD profiles.

In this study, the in-plane ϕ-$2\theta\chi$ scanning XRD profile of the hydrothermal film is unchanged by the extraction of the surfactant. (trace **b** in Fig. 3A) However, the profiles of the EISA film are considerably changed by the surfactant removal, and the peak assigned to ($\bar{1}1$) is scarcely observed. (trace **d** in Fig. 3B) This does not result from the degradation of the mesostructure but does the large shrinkage of mesostructure along the direction of film thickness.

Because of the large shrinkage of mesostructure in the EISA film after the removal of the surfactant (traces **i** and **j** in Fig. 1B), the diffraction angle became large enough, compared to the divergence angle of the X-ray beam, not to be detected under the in-plane diffraction geometry. The position of the ($\bar{2}1$) peak is unchanged because this lattice plane is perpendicular to the film plane and is not influenced by the shrinkage of the mesostructure along the direction of film thickness.

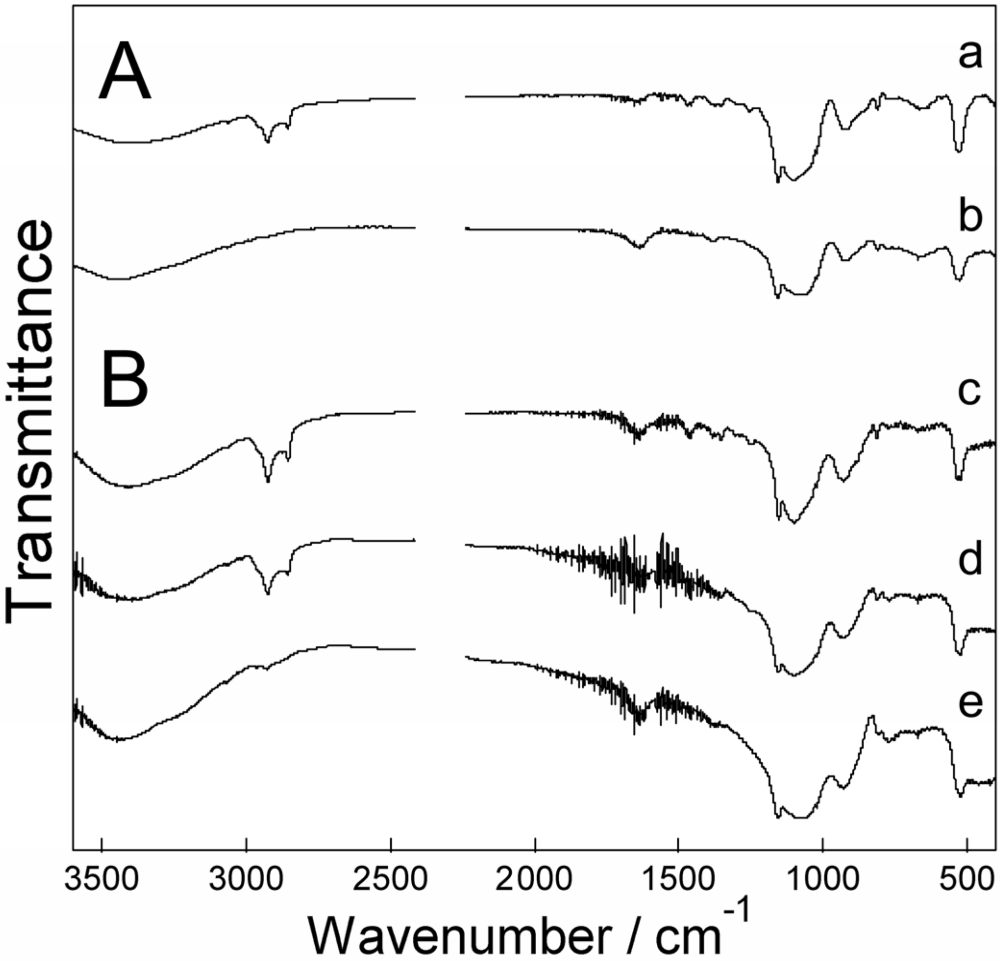

Figure S1. IR spectra of phenylene-bridged mesoporous organosilica thin films prepared by **A**) hydrothermal deposition process and **B**) EISA process. **a,c**) As-deposited, **b,e**) after surfactant removal, and **d**) after thermal treatment.

Figure S1

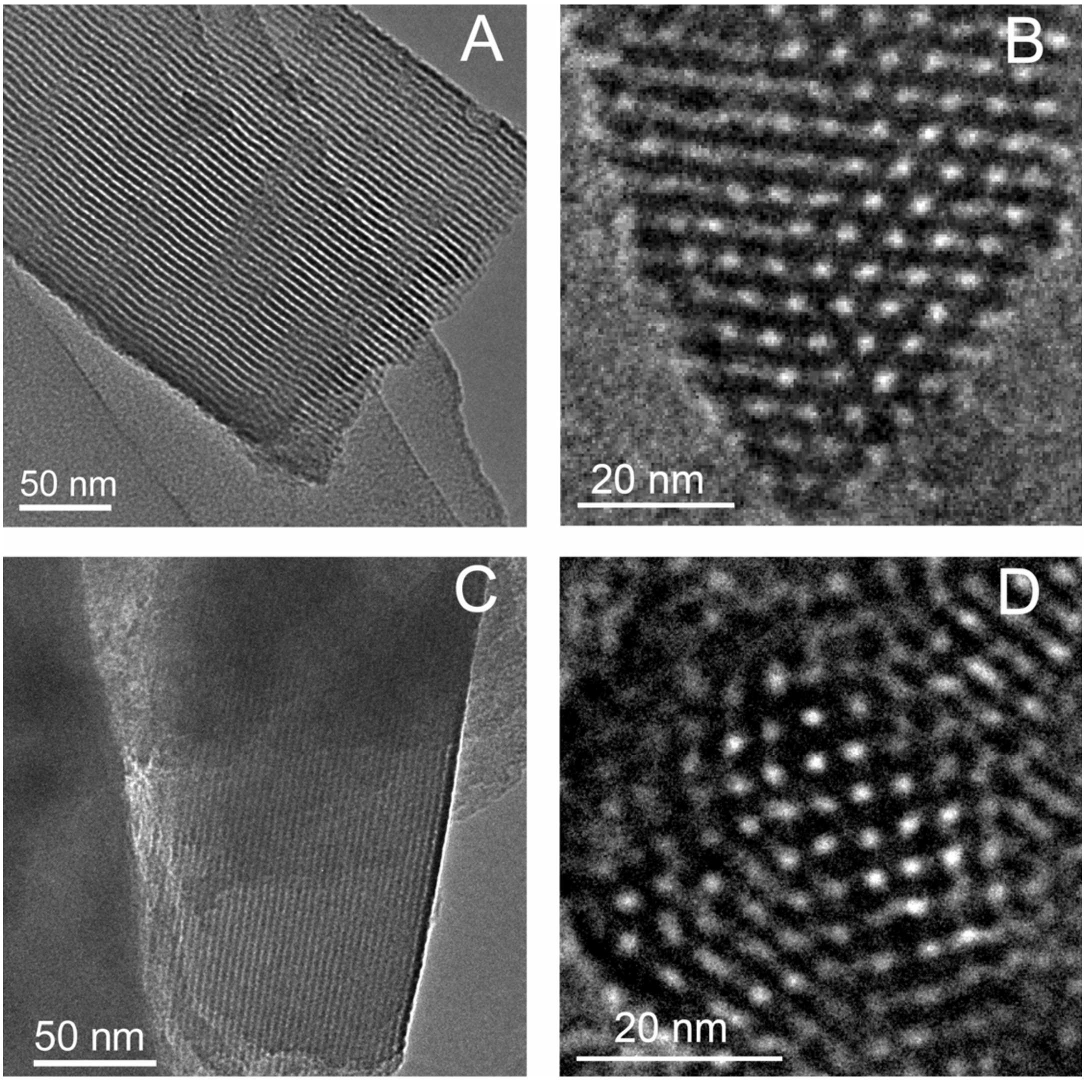

Figure S2. TEM images of the phenylene-bridged mesoporous organosilica thin films prepared by **A, B**) hydrothermal deposition process and **C, D**) EISA process.

Figure S2

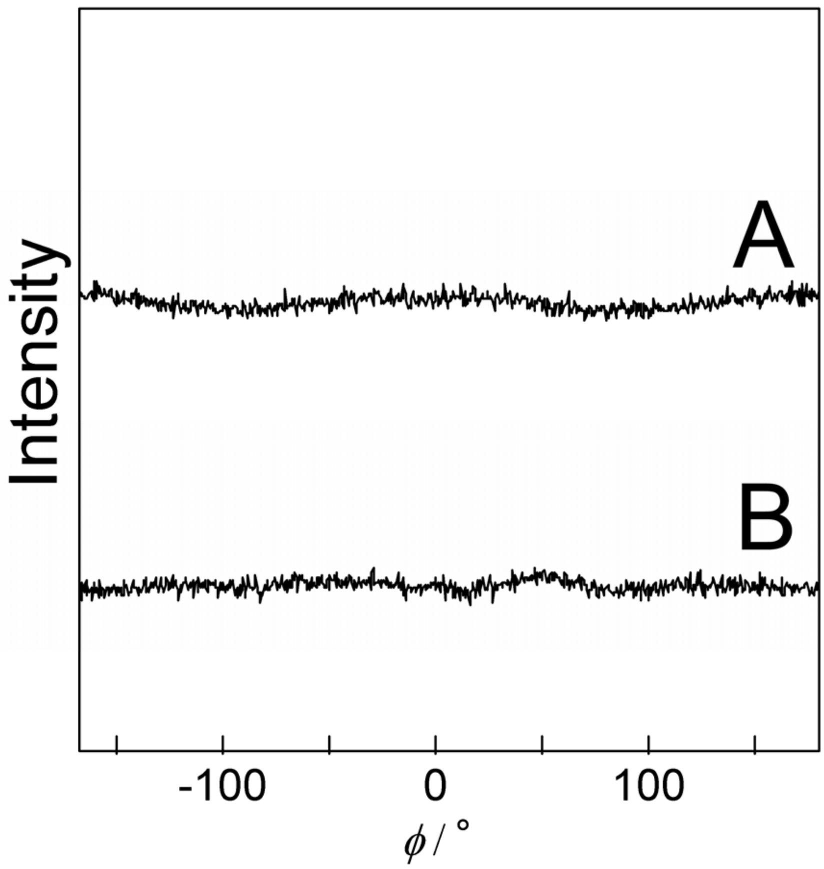

Figure S3. Wide-angle in-plane ϕ scanning XRD profiles of phenylene-bridged mesoporous organosilica films prepared by **A**) hydrothermal deposition process and **B**) EISA process.

Figure S3

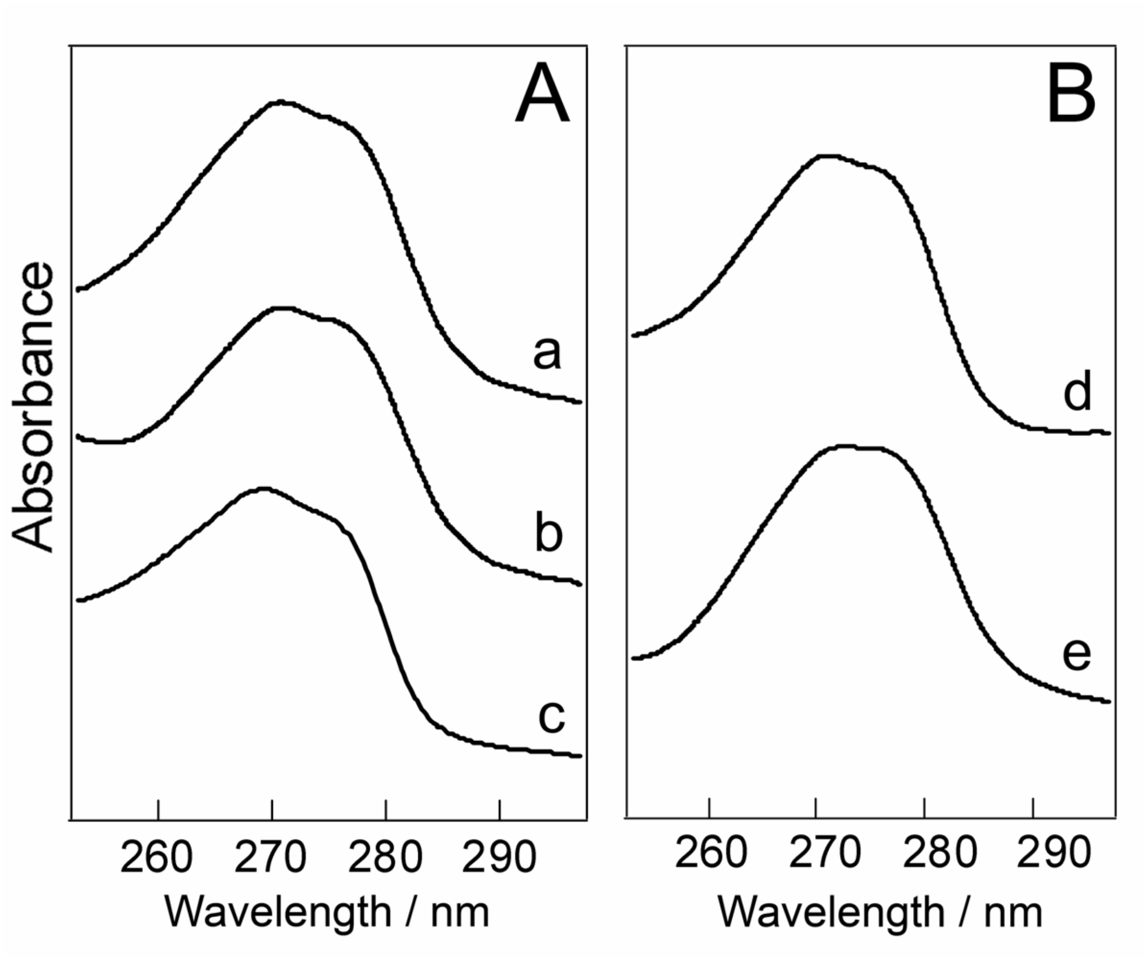

Figure S4. Absorption spectra of the mesoporous phenylene-bridged mesoporous organosilica films prepared by **A**) hydrothermal deposition process and **B**) EISA process. **a, d**) as-deposited films, **b, e**) films after surfactant removal, **c**) monomeric BTEB in 2-propanol ($2.5 \cdot 10^{-5}$ M).

Figure S4