Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary data

Robust conductive mesoporous carbon-silica composite films with highly ordered and oriented orthorhombic structures from triblock-copolymer template co-assembly

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A. GISAXS data fits and unit cell parameters

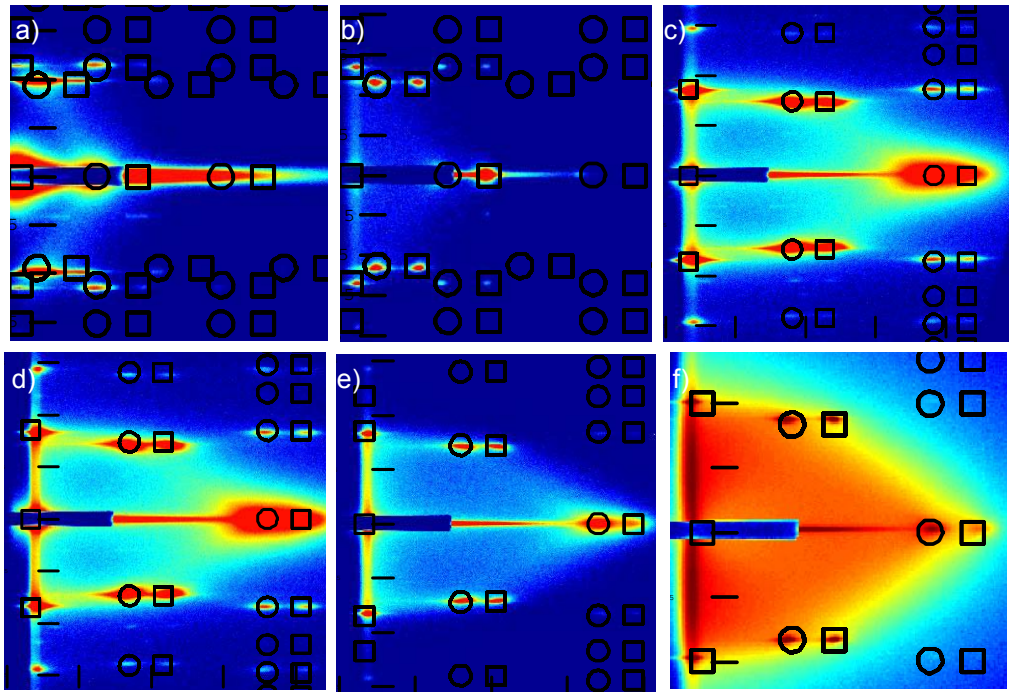

Figure S1. GISAXS patterns of the films. The overlay of simulated spots is from a NANOCELL simulation. The circles and squares represent the transmitted and reflected Bragg peaks, respectively. Simulation results show an (010) oriented *Fmmm* symmetry with many domain oriented normal to the substrate. The unit cell parameters of the films are shown in the table below:

Sample No	Sample Name	Unit Cell Parameters, nm		
		a	b	c
a)	FDU-16-AM	17	20	23
b)	FDU-16-350	17	17	23
c)	FDU-16-800	16	6.8	22.5
d)	CS-20-800	16	7.2	22.8
e)	CS-33-800	16.5	7.6	22.8
f)	CS-43-800	14.5	9.0	19.5

B. FTIR characterization

The FTIR spectra of the mesoporous polymer-silica composite films (350 ºC) and carbon-silica composite films (800 ºC) are shown in Figure S2. Following recognized peak identification of infrared spectra of organic compound [1-4] and inorganic compounds, such as silica,[5-8] and carbon,[9;10] the functional groups within these films have been identified by the absorption bands listed in Table S1 and S2. For the mesoporous polymeric films after being calcined at 350 ºC, the broad absorbance near 3500 cm^{-1} is attributed to the O-H stretching of phenolic groups and silanols from the incomplete condensation. Also, the bands at approximately 1226 cm^{-1} are assigned to C-O stretching of phenolic groups; this absorbance decreases with the increase of silica concentration in the films. As the silica concentration increased up to 38 and 56 wt%, this peak is no longer as well defined due to overlap with the strong Si-O-Si asymmetric stretching at 1100 cm^{-1}. The retained vibrations of phenolic resins and silicates indicate the coexistence of polymer and silica composites in the films. The absorbance at 980 cm^{-1} for the polymer-silica films with high silica content results from the silanol vibration. Absorbance in the range of 3100 ~ 2800 cm^{-1} is ascribed to the stretching of carbon-hydrogen bonds.

Increasing the pyrolysis temperature to 800 ºC induces dramatic changes in the FTIR spectra of the mesoporous composite films. Absorption near 3500 and 1226 cm^{-1} disappears, which suggests the total decomposition of phenol resins at this elevated temperature. The hydrocarbonaceous residues are greatly reduced, as the $-CH_3$ symmetrical deformation vibration at 1382 cm^{-1} is nearly vanished. Only aromatic C-H groups in the range of 3100 ~ 2800 cm^{-1} are detectable. The band multiplet in the range of 1600 – 1480 cm^{-1} transforms to a single symmetrical C=C band centered near 1600 cm^{-1} after heating polymeric nanocomposite to 800 ºC. These results suggest a formation of carbon materials. With the increase of silica content in the carbon-silica composite films, the Si-O-Si asymmetric stretching bands at 1100 cm^{-1}, and Si-O-Si bands at 468 cm^{-1} become better resolved.

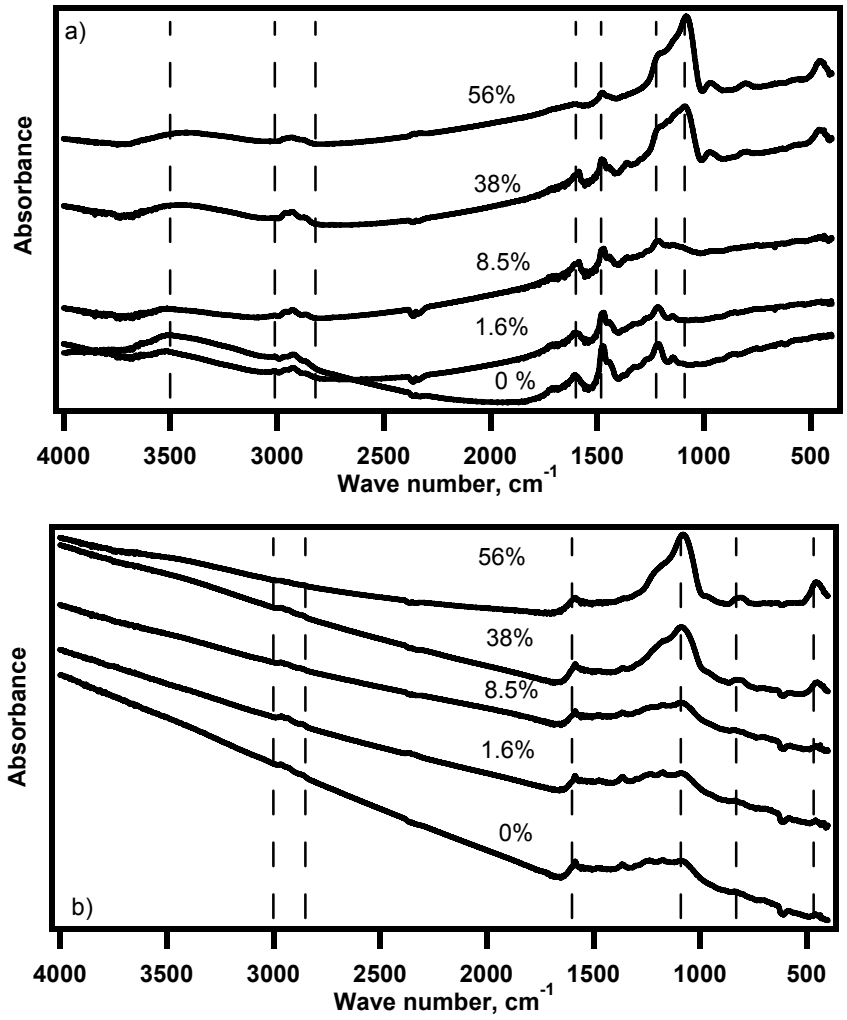

Figure S2. FTIR spectra of mesoporous nanocomposite films of (a) FDU-16, (b) CS-20, (c) CS-33, (d) CS-51 and (e) CS-68, after carbonization at (A) 350 ºC and (B) 800 ºC.

Table S1 FTIR vibration assignments of mesoporous polymer-silica films after pyrolyzed at 350ºC

Wavenumber, cm^{-1}	Functional group
Near 3500	O-H stretching of phenol group
3100-2800	C-H stretching
1600	C-C aromatic ring stretching
1481	C-H bending of aliphatic bridge structure
1226	C-O stretching of phenol group
1100	Si-O-Si asymmetric stretching
980	-Si-OH vibration
468	Si-O-Si band

Table S2 FTIR Vibration assignments of mesoporous carbon-silica films after pyrolyzed at 800ºC

Wavenumber, cm^{-1}	Functional group
3100-2800	C-H stretching
1600	C-C aromatic ring stretching
1382	$-CH_3$ symmetrical deformation vibration
1100	Si-O-Si asymmetric stretching
468	Si-O-Si band

References

1. Z. Lausevic and S. Marinkovic, *Carbon*, 1986**, 24**, 575.

2. C. Morterra and M. J. D. Low, *Carbon*, 1985**, 23**, 525.

3. K. Ouchi, *Carbon*, 1966**, 4**, 59.

4. K. A. Trick and T. E. Saliba, *Carbon*, 1995**, 33**, 1509.

5. Y. Gao, N. R. Choudhury, N. Dutta, J. Matisons, M. Reading, and L. Delmotte, *Chemistry of Materials*, 2001**, 13**, 3644.

6. G. H. Hsiue, W. J. Kuo, Y. P. Huang, and R. J. Jeng, *Polymer*, 2000**, 41**, 2813.

7. K. A. Mauritz and R. M. Warren, *Macromolecules*, 1989**, 22**, 1730.

8. D. H. Sun, R. Zhang, Z. M. Liu, Y. Huang, Y. Wang, J. He, B. X. Han, and G. Y. Yang, *Macromolecules*, 2005**, 38**, 5617.

9. J. Kim, J. Lee, and T. Hyeon, *Carbon*, 2004**, 42**, 2711.

10. R. L. Liu, Y. F. Shi, Y. Wan, Y. Meng, F. Q. Zhang, D. Gu, Z. X. Chen, B. Tu, and D. Y. Zhao, *Journal of the American Chemical Society*, 2006**, 128**, 11652.