Mesoporous Materials

DOI: 10.1002/anie.200603665

Formation of Mesoporous Carbon With a Face-Centered-Cubic $Fd\bar{3}m$ Structure and Bimodal Architectural Pores From the Reverse Amphiphilic Triblock Copolymer PPO-PEO-PPO**

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Diamond, a crystalline form of carbon, shows exceptional physical and chemical properties, such as the highest known hardness and elastic modulus. These characteristics have been attributed to its specific 3D atomic packing and strong sp^3 tetrahedral covalent bonds.[1,2] Attempts to design analogous materials, including molecular sieves and metal–organic frameworks (MOFs),[3,4] have centered on ensuring the same packing as that of diamond, which has 3D face-centered-cubic $Fd\bar{3}m$ symmetry.

Ordered mesoporous materials have received enormous attention owing to their high surface areas, regular frameworks, and large pore sizes with narrow distribution, all of which lead to multiple potential applications.[5,6] Ordered mesoporous carbon, which is one of the most promising materials, possesses both remarkable functional properties and excellent chemical/thermal stability, which makes it suitable for applications in catalysis,[7] sensing,[8] bioreactor construction,[9] and energy storage.[10] Recently, a family of highly ordered mesoporous carbon with $p6mm$, $Im\bar{3}m$, and $Ia\bar{3}d$ symmetries has been synthesized by an organic–organic self-assembly strategy with PEO-PPO-PEO triblock copolymers as templates (PPO: polypropyleneoxide; PEO: polyethyleneoxide).[11–15]

Among the various mesostructures, 3D cubic mesopore geometries are attractive owing to their promise, especially in host–guest chemistry.[16,17] However, the synthesis of mesoporous materials with a 3D cubic $Fd\bar{3}m$ structure, which is a unique structure with a bimodal pore size distribution, has not been reported to date by using triblock copolymers as templates. This attractive mesostructure with a silicate composition has only been obtained thus far by using laboratory-made tri-head-group cationic (for FDU-2)[18] and anionic (for AMS-8) surfactants as templates[19,20] under very strict synthetic conditions. In addition, the mesoporous silicas obtained have small lattice parameters and their bimodal mesopore systems cannot be detected by N_2 sorption measurements owing to the smaller size of the surfactant molecules compared to block copolymers.

Amphiphilic PEO-PPO-PEO triblock copolymers, which are commercially available as Pluronics or Synperonics, have been proven to be versatile and efficient templates for the fabrication of ordered mesoporous silicas with different symmetries.[21] PPO-PEO-PPO triblock copolymers are another family of commercial surfactants that have the hydrophilic PEO block located in the middle and the hydrophobic PPO blocks at either end of the polymer chain. They are rarely used in the synthesis of ordered mesoporous silicas, however, because of the difficulty of forming oil-in-water micelles.[22–24] Reverse PPO-PEO-PPO copolymers with long PEO segments can reduce the curving energy and result in micellar interconnected networks,[24] the possible fascinating phase behaviors of which may provide them with good structure-directing properties for the fabrication of face-centered-cubic $Fd\bar{3}m$ mesostructures with high curvature.

Herein, we report the synthesis of 3D face-centered-cubic ($Fd\bar{3}m$) mesostructures (designated as FDU-17) with open polymer and carbon frameworks from a phenolic resol precursor and the reverse amphiphilic triblock copolymer $PO_{53}EO_{136}PO_{53}$ (PO: propyleneoxide; EO: ethyleneoxide) as a template by the evaporation-induced self-assembly (EISA) method. The resultant polymeric and carbon materials are stable and feature a highly ordered mesostructure. Based on N_2 sorption and structure-modeling results, a tunable bimodal architecture consisting of small (3.2–4.0 nm) and large (5.4–6.9 nm) mesopores is produced. The BET surface areas of the

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[**] We thank Prof. Dr. Yong Tang of CAS for helpful suggestions and discussion during the preparation of the copolymers. This work was supported by the NSF of China (20233030, 20421303, 20407014, 20373013, and 20521140450), the State Key Basic Research Program of PRC (2006CB202502), the Shanghai Nanotech Promotion Center (0652nm024), the Shanghai Education Committee (02SG01, 04DB05), the Program for New Century Excellent Talents in University (NCET-04-03), and the Shanghai Science and Technology Committee (06J14006, 04JC14087, 055207078, 05DZ22313, and 03QF14037). Y.W. thanks the China Post-doc Scientific Fund for financial support. PPO: polypropyleneoxide; PEO: polyethyleneoxide.

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

mesoporous carbon materials are around 870 $m^2 g^{-1}$ and the pore volumes are 0.54 $cm^3 g^{-1}$.

The copolymer $PO_{53}EO_{136}PO_{53}$ was synthesized by anionic copolymerization of poly(ethylene glycol) (PEG6000) and propylene oxide (PO) monomers with potassium hydroxide as the catalyst. Its molecular structure was confirmed by ^{1}H NMR spectroscopy (Supporting Information, Figure S1), and it was found to have a dispersive value of 1.05 by gel permeation chromatography (GPC).

Phenolic resol precursors can interact with the reverse triblock copolymer template by forming hydrogen bonds between the hydroxy groups of the resol units and the PEO segments of the template. Upon solvent evaporation an organic–organic composite liquid-crystal mesophase with a high curvature is formed (Figure 1).[13,25] The phenolic resol precursors around the templates are thermopolymerized by heating at 100–160 °C and the mesostructured frameworks become rigid. A temperature of 350 °C was chosen to remove the template after an initial thermogravimetric (TG) analysis (Figure S2 in the Supporting Information). The mesoporous carbon frameworks were obtained in a subsequent carbonization step at 600–1000 °C with a very slow heating rate under nitrogen.

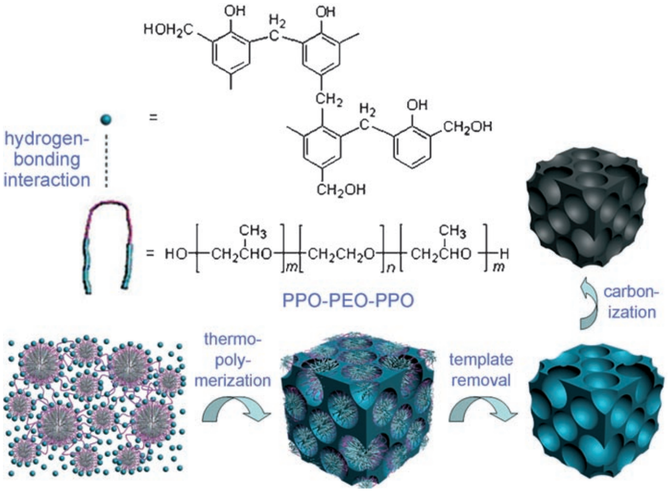

Figure 1. Organic–organic self-assembly process of the triblock copolymer PPO-PEO-PPO with a phenolic resol precursor to form 3D face-centered-cubic ($Fd\bar{3}m$) polymers and carbon mesostructures with bimodal architectural pores.

The small-angle X-ray scattering (SAXS) spectrum for as-synthesized FDU-17 exhibits an unusual pattern (Figure 2). Six poorly resolved diffraction peaks can be observed at q values of 0.2–1.5 nm^{-1}. After calcination at 350 or 450 °C under nitrogen, the patterns are more resolved and suggest the formation of a highly ordered mesostructure. This change can be ascribed to the increased electron-density contrast resulting from the removal of the templates. At least eight well-resolved diffraction peaks can be observed whose reciprocal d-spacing values follow the relationship $\sqrt{3}:\sqrt{8}:\sqrt{11}:\sqrt{19}:\sqrt{27}:\sqrt{36}:\sqrt{56}:\sqrt{76}$. These peaks can be indexed as the 111, 220, 311, 331, 333 (511), 442 (and/or 600), 642, and 662 reflections of the space group $Fd\bar{3}m$ (Q^{227}). The X-ray diffraction (XRD) patterns of these samples also show well-resolved reflections that indicate a highly ordered face-centered-cubic mesostructure (Figure S3 in the Supporting Information).

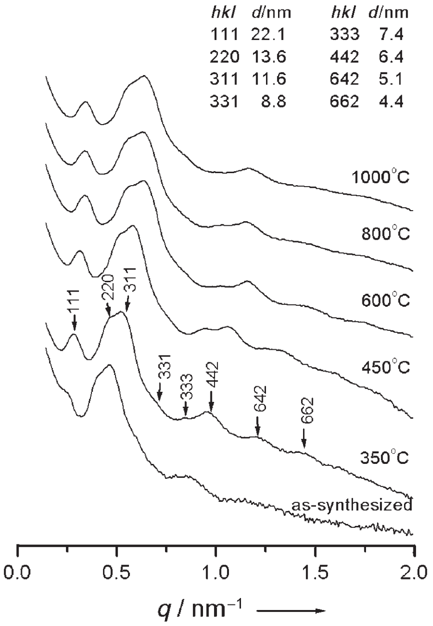

Figure 2. SAXS patterns (q vs. ln$I$) of as-synthesized FDU-17 and FDU-17 calcined at different temperatures.

The lattice parameter (a_0) of the as-synthesized FDU-17 calculated based on the SAXS data is as large as 45.1 nm. Upon calcination, the lattice parameters are calculated to be 38.3 (FDU-17-350) and 34.8 nm (FDU-17-450), which is a framework shrinkage of 15.1 and 22.8 %, respectively (Table 1). This result indicates that the polymer frameworks undergo a further polymerization and condensation during pyrolysis and template removal. A combination of ^{13}C cross-polarization/magic-angle spinning (CP/MAS) NMR and FT-IR spectroscopy (Figures S4 and S5 in the Supporting Information) and elemental analysis data revealed that the copolymer PPO-PEO-PPO can be eliminated by heating at 350 °C under N_2. The polymeric nature of the networks is maintained, with 71.1 wt % C, 4.1 wt % H, and 24.9 wt % O.

Table 1: Textural properties of the mesoporous polymer FDU-17 and the corresponding carbon frameworks.

Sample	d_{111} [nm]	a_0 [nm]	BET surface area [$m^2 g^{-1}$]	Micropore area [$m^2 g^{-1}$]	Pore size [nm]	Pore volume [$cm^3 g^{-1}$]
As-synthesized	26.0	45.1	–	–	–	–
FDU-17-350	22.1	38.3	–	–	–	–
FDU-17-450	20.1	34.8	510	280	4.0, 6.9	0.33
FDU-17-600	18.8	32.6	590	400	3.2, 5.4	0.35
FDU-17-800	18.8	32.6	780	530	3.5, 5.8	0.47
FDU-17-1000	18.8	32.6	870	550	3.9, 5.9	0.54

Well-resolved diffractions can also be detected in the SAXS patterns for FDU-17 samples after increasing the heating temperature to 600–1000 °C. This suggests that the highly ordered cubic $Fd\bar{3}m$ mesostructure is retained and is thermally stable. The carbonization can occur simultaneously with the increase in temperature and the polymer frameworks transform into carbon components. A 6.3 % shrinkage is observed between FDU-17-600 and FDU-17-450, as calculated from the cell parameters of 32.6 and 34.8 nm, respectively. Further raising the heating temperature to 800 and 1000 °C does not bring about any framework shrinkage (Table 1). The elemental analysis shows that FDU-17-800 is a carbon framework with the composition 90.0 wt % C, 0.8 wt % H, and 9.2 wt % O. All the observations taken together indicate that the carbon frameworks are rather rigid and stable.

The representative TEM images and corresponding Fourier diffractograms shown in Figure 3 indicate that both FDU-17-600 and FDU-17-800 possess a high degree of periodicity over large domains when viewed along the [100], [110], [111], and [211] directions. On the basis of observable reflections in the Fourier diffractograms and SAXS data, this can be summarized as $\{hkl\colon h+k, h+l, k+l=2n\}$, $\{0kl\colon k+l=4n\}$, and $\{h00\colon h=4n\}$, which confirms that the mesostructure is highly ordered and $Fd\bar{3}m$ (Q^{227}) symmetric. The 600 reflection is forbidden for $Fd\bar{3}m$ symmetry therefore it can be removed from the SAXS reflections. Planar defects can be observed in the TEM image viewed along the [110] direction as streaks in the Fourier diffractogram (Figure 3 b). These may be caused by nonhomogeneous shrinkage of the mesostructure during calcination. For both samples, the cell parameters estimated from the TEM images are approximately 31.9 nm, a value that is consistent with the data determined from the SAXS patterns.

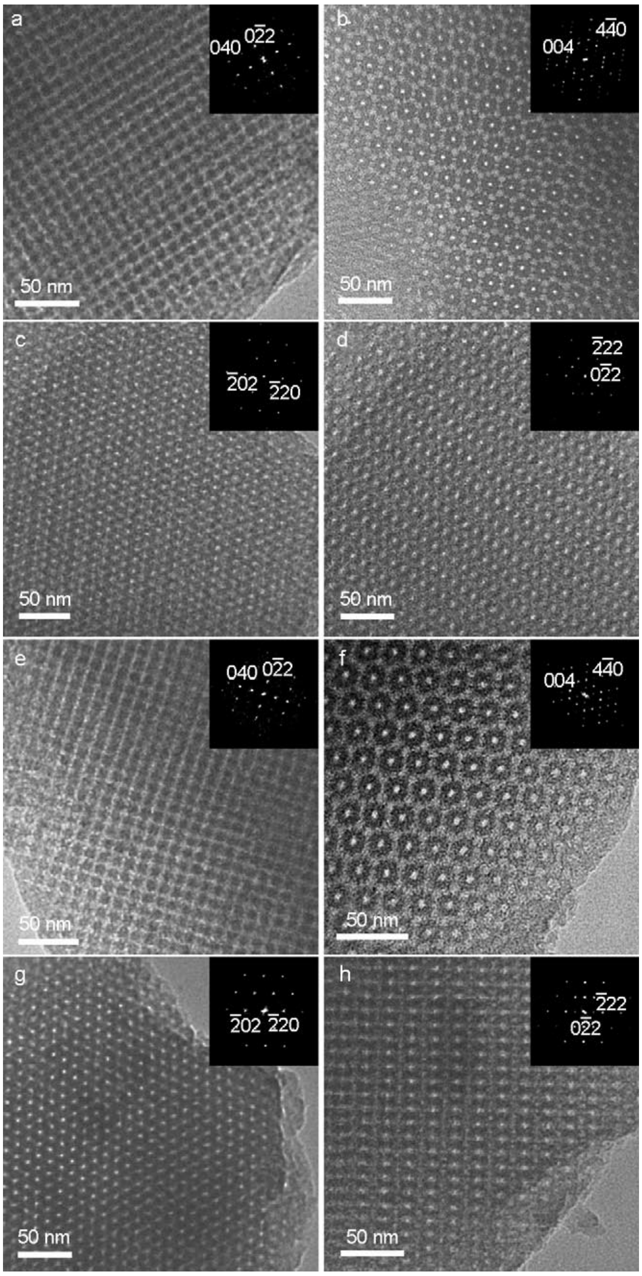

Figure 3. TEM images and corresponding Fourier diffractograms of FDU-17-600 (a–d) and FDU-17-800 (e–h) viewed along the [100] (a, e), [110] (b, f), [111] (c, g), and [211] (d, h) directions.

N_2 adsorption–desorption isotherms (Figure 4 a) of the calcined FDU-17 samples exhibit typical type-IV curves with a H_2-type hysteresis loop, which suggests that they contain caged mesopores with small windows. It is worth noting that a broad capillary condensation characteristic with two clear rapid-increase steps is observed in the adsorption branches at a relative pressure (P/P_0) of 0.4–0.7. Bimodal pore size distributions (Figure 4 b) are clearly observed for all calcined FDU-17 samples, which suggests that they have two caged mesopore systems related to the cubic $Fd\bar{3}m$ mesostructure.[19] The calculated sizes are 3.2–4.0 nm for the small and 5.4–6.9 nm for the large cages, both of which are larger than those in the AMS-8 mesostructure templated by a small anionic surfactant.[19] The BET surface areas and the total pore volumes of FDU-17-450 are low at around 500 m^2g^{-1} and 0.33 cm^3g^{-1}, respectively. This may be related to the mesostructure having thick walls. At the same time the pore size reduces upon heating, which can be explained by further condensation of the polymer frameworks. At heating temperatures above 600 °C the pore sizes expand a little and the BET surface areas and pore volumes increase to 870 m^2g^{-1} and 0.54 cm^3g^{-1}, respectively. As the d-spacing values and cell parameters remain unchanged, this suggests that the frameworks have transformed into carbon materials with thinner pore walls. This simultaneous change demonstrates that the thickness of the pore wall can be controlled by adjusting the calcination temperature.

A structural model for the cubic $Fd\bar{3}m$ mesostructure can be proposed in line with the TEM, SAXS, and N_2 adsorption–desorption data. It consists of a 3D periodically ordered packing of two types of spheres (Figure 1). Eight large-caged pores and sixteen small pores exist in one unit cell. The eight large spheres have $\bar{4}3m$ symmetry and are arranged tetrahedrally on a diamond lattice and the sixteen small spheres have $\bar{3}m$ symmetry.[26] The formation of this cubic $Fd\bar{3}m$ mesostructure may be closely related to the characteristic phase behaviors of reverse PPO-PEO-PPO copolymers

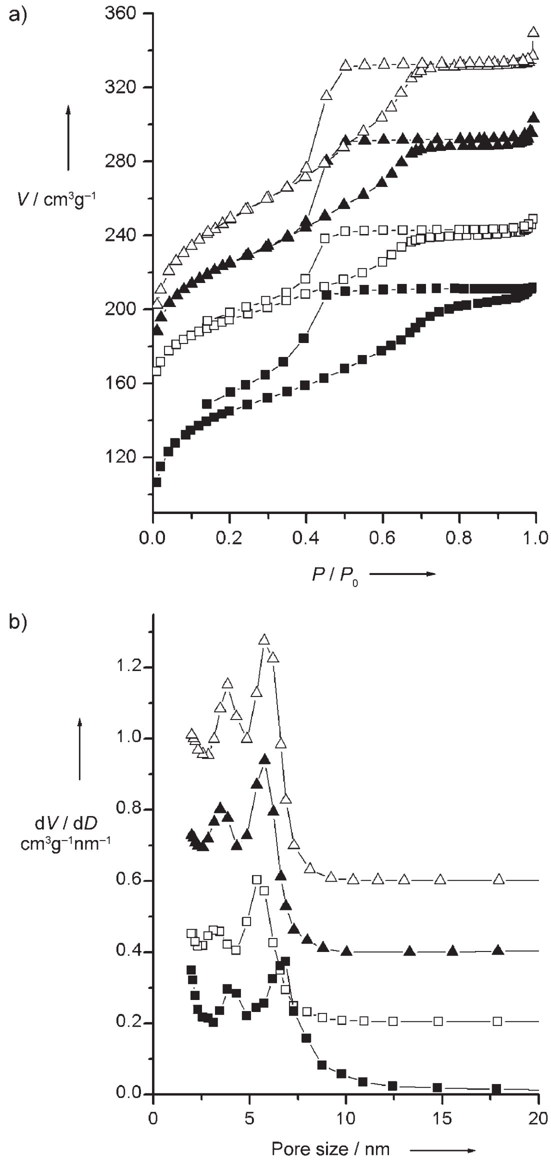

Figure 4. N_2 adsorption–desorption isotherms (a) and pore-size distribution plots (b) of FDU-17 calcined at different temperatures (■ 450 °C; □ 600 °C; ▲ 800 °C; △ 1000 °C). The isotherms for FDU-17-600 are offset vertically by 25 $cm^3 g^{-1}$. The pore-size-distribution curves for FDU-17-600, FDU-17-800, and FDU-17-1000 are offset vertically by 0.2, 0.4, and 0.6 $cm^3 g^{-1} nm^{-1}$, respectively.

(Figure 1).[27] The sequence of PPO and PEO segments greatly influences the physicochemical behaviors of these copolymers in water, therefore the reverse PPO-PEO-PPO copolymers are very different from PEO-PPO-PEO not only in configuration but also in their micellization properties.

It has been suggested that the reverse copolymers facilitate the formation of interconnected micelles[23,24] in which the two outer PPO blocks of a chain participate in two different micelles or aggregates.[27] Highly curved copolymer–resol networks with a cubic $Fd\bar{3}m$ mesostructure are possibly formed in the reverse $PO_{53}EO_{136}PO_{53}$ system with a long PEO chain but not with PEO-PPO-PEO copolymers. Our results show that the ratio of $PO_{53}EO_{136}PO_{53}$ template to phenolic resol precursor is a critical factor in the formation of the cubic $Fd\bar{3}m$ mesostructure, which can only be formed in a narrow range around a copolymer/phenol/formaldehyde molar ratio of 0.0063/1/2. A stable, mesostructured carbon with hexagonal (*p6mm*) symmetry is obtained upon increasing this ratio (Figure S6 in the Supporting Information).

In summary, highly ordered mesoporous resin and carbon frameworks with face-centered-cubic $Fd\bar{3}m$ symmetry have been synthesized by using $PO_{53}EO_{136}PO_{53}$ as a template in an EISA process. A clear bimodal pore size distribution is detected with mean values of 3.2–4.0 and 5.4–6.9 nm, respectively, with small window sizes. This mesostructure may be related to the characteristic phase behavior of reverse triblock PPO-PEO-PPO copolymers. The use of PPO-PEO-PPO copolymers as templates is thus shown to be an effective way to fabricate new mesostructures that were only thought to occur in inverse lyotropic phases.

Experimental Section

Soluble phenolic resol was prepared under basic conditions according to a reported procedure.[13] Thus, phenol (1.0 g, 10.6 mmol) was melted at 50 °C and then an NaOH solution (20 wt %; 0.21 g, 1.06 mmol) was added with stirring over 10 min. After dropwise addition of formalin (37 wt %; 1.725 g, 21.2 mmol), the mixture was stirred at 75 °C for 1 h and then cooled to room temperature. HCl solution (0.6 M) was used to adjust the pH value to neutral and the water was removed. The obtained phenolic resol ($M < 500$, as determined by GPC) was re-dissolved in ethanol for further use.

FDU-17: In a typical synthesis, $PO_{53}EO_{136}PO_{53}$ (0.30 g) was dissolved in ethanol (5.0 g). Then, the resol precursor (5.0 g) containing phenol (0.37 g, 3.8 mmol) and formaldehyde (0.23 g, 7.6 mmol) was added with stirring over 10 min to form a homogeneous solution. A transparent film was obtained by pouring the solution into a dish and allowing the ethanol to evaporate at room temperature for 5–8 h, then heating in an oven at 100–160 °C for 24 h. The as-synthesized product was collected and calcined at 350 or 450 °C for 4 h at a heating rate of 1 $K min^{-1}$ under N_2 to remove the templates. Mesoporous carbon was obtained by direct carbonization of the corresponding mesoporous polymer. The process was carried out in a tube oven at 600–1000 °C for 4 h at a heating rate of 1 $K min^{-1}$ under N_2. FDU-17-X represents the FDU-17 sample calcined at X °C.

The SAXS patterns were recorded with a Nanostar U small-angle X-ray scattering system (Bruker) using $Cu_{K\alpha}$ radiation (40 kV, 35 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer. Before measurement, the samples were degassed in vacuo at 200 °C for at least 6 h. TEM images were obtained with a JEOL 2011 microscope operating at 200 kV. TG analysis was carried out using a Mettler Toledo TGA-SDTA851 analyzer from 25 to 900 °C, at a heating rate of 10 $K min^{-1}$, under nitrogen or air. Solid-state ^{13}C NMR experiments were performed at room temperature with a Bruker DSX300 spectrometer under conditions of cross polarization (CP) and magic-angle spinning (MAS) with a frequency of 75 MHz (2 s recycle, 2.5 ms contact time; adamantane as reference).

Received: September 7, 2006

Keywords: carbon · mesoporous materials · molecular sieves · self-assembly · triblock copolymers

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