DOI: 10.1002/ange.200501561

Ordered Mesoporous Polymers and Homologous Carbon Frameworks: Amphiphilic Surfactant Templating and Direct Transformation**

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Organic porous materials—a class of advanced materials—possess enormous potential for many high-tech applications, such as bioreactors,[1] dielectrics,[2] sensors,[3] microelectrophoresis,[4] thermal insulation,[5] and catalysts.[6] In general, they can be prepared by phase separation,[7] and a hard templating approach, such as those employing colloidal particles.[8] Phase separation can be derived from organic–organic phases, while the pore structures can be formed after etching, or by dissolving one block (A) from the assembled block copolymer (A–B).[9] However, most of the resulting porous polymer structures are disordered with wide pore size distributions because of the contraction and swelling from changes in volume, as well as the structured defects formed during template removal.[10] Large porosities have rarely been reported.[11] Furthermore, the resistance of the pore structure to heat and solvents is rather low because the materials are formed by weak van der Waals forces and physical twists between polymer chains, which means that the framework is not connected by covalent bonds. Recently, a procedure for cross-linking lyotropic liquid crystals (LLC) in water was introduced to prepare periodic porous organic mesostructures.[12] Unfortunately, polymerization only occurs between nearest neighboring head groups, and the mesostructured channels are fully occupied with solution.[13] Therefore, it is not surprising that porosity has yet to be reported.

Carbon materials, including nanotubes and fullerenes, have attracted considerable attention because of their remarkable properties.[14] The traditional carbonization process for active carbon and related materials can only generate

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[**] This work was supported by the NSF of China (20233030 and 20421303), the State Key Basic Research Program of PRC (G200048001, 2001CB610506), Project 863 of the Sci. & Tech Ministry of China (2002 AA321010), the Shanghai Sci. & Tech. Committee (03J14004, 02A14005, 03527001, 04JC14087), LG Company, Unilever Research China, and the Shanghai HuaYi Chemical Group. We thank Dr. T. C. Li, S. H. Xie, and Dr. Y. Wan for experimental and characterization assistance.

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

porosity with a tunable pore size, but not regular pore structures. Ryoo et al. developed a nanocasting method to prepare mesoporous carbon replicas through carbonization of sucrose-filled ordered mesoporous silica, with subsequent removal of the silica frameworks by HF or NaOH.[15] The replicas obtained from these time-consuming and costly procedures are ordered arrays of carbon nanorods or nanowires with reverse structures to the parent mesoporous silica. It remains a challenge to prepare ordered mesoporous carbon materials with open frameworks which may find applications in hydrogen-storage, catalysis, adsorption, separations, electrochemical double capacitors, or even ordered carbon nanotube arrays.

The organic-templating pathway has been applied extremely successfully to the preparation of ordered mesoporous inorganic oxides.[16–18] Amphiphilic surfactants and block copolymers can be used as templates to achieve highly ordered mesoporous materials, with large surface areas and uniform pore sizes (1.5–30 nm) that are suitable for countless potential applications.[16–18] Among these periodic solids, mesoporous silica materials are the easiest to prepare and the most widely investigated as a result of their highly stable, covalently bonded frameworks.[19] Many silica mesostructures, such as 2D hexagonal ($p6m$)[17] and 3D cubic ($Ia\bar{3}d$, $Im\bar{3}m$, $Pm\bar{3}n$)[20–22] structures, have been synthesized. However, perhaps because of thermal instability resulting from noncovalently bonded frameworks, the preparation of ordered mesoporous organic materials by the amphiphilic surfactant-templating approach has seldom been reported.[23,24] Although Hillmyer and co-workers have obtained ordered epoxy resin/amphiphilic block copolymer nanocomposites, the porosity of the nanocomposites was not reported as a result of difficulties in removal of the amphiphilic block copolymer template.[23] More recently, Tanaka et al.[24] used resorcinol/formaldehyde, and triethyl orthoacetate (EOA) as the carbon co-precursor under strongly acidic conditions (5 M HCl) in a direct carbonization method to prepare ordered mesoporous carbon frameworks with channel structures. The resulting materials have a hexagonal mesostructure, mainly as a result of EOA, which might reduce the polymerization and interaction of the precursors derived from resorcinol/formaldehyde.

Herein, we report a simple and reproducible synthesis of highly ordered and stable mesoporous polymers by an amphiphilic surfactant-templating approach that is derived from examination of the successful assembly of mesoporous silica. We chose resol (phenol/formaldehyde) as a cheap precursor which can form three-connected covalently bonded zeolite-like frameworks by thermopolymerization. We also demonstrate that these polymers, with rigid networks, can be directly transformed by a careful carbonization process into well-ordered and ultrastable (> 1400 °C) open mesoporous carbon frameworks. The obtained mesoporous polymers have large uniform mesopores, surface areas, and pore volumes. Moreover, the mesostructures can be readily tuned from 2D hexagonal ($p6m$), to 3D caged cubic ($Im\bar{3}m$), and lamellar frameworks by simply adjusting the mass ratio of the polymer precursors and amphiphilic surfactants. The mesoporous carbon frameworks have homologous mesostructures with high surface areas, narrow pore size distributions, and large pore volumes.

Highly ordered mesoporous polymers can be synthesized by a solvent evaporation induced self-assembly method (EISA),[25] by using amphiphilic triblock copolymers (PEO-PPO-PEO) as templates, and a soluble low-molecular weight polymer of phenol and formaldehyde (resol; $M_w = 500–5000$) as precursors, followed by a thermopolymerization process (Figure 1). The choice of resol as a precursor is key to the successful organization of organic–organic mesostructures because resol has a large number of hydroxy groups (-OH) which can interact strongly with triblock copolymers through formation of H bonds.[26] Many kinds of amphiphilic surfactants, such as triblock copolymers containing a PEO segment, cationic surfactants,[27] and nonionic alkyl PEO oligomers[28] can be used as templates. Simple thermopolymerization of resol at low temperatures (100–140 °C) around the triblock copolymer can yield a rigid zeolite-like hydrocarbon network with three-connected benzene rings through formation of covalent bonds.[29] This feature makes the polymers stable and permits direct transformation to homologous carbon frameworks by carbonization to 900–1400 °C under nitrogen. The surfactant templates can be removed by solvent extraction assisted oxidation, or calcination at 300–500 °C under nitrogen. Low-cost, nontoxic, and commercially available copolymers are highly suitable templates because they contain a large amount of oxygen and can be easily decomposed. A carbonization process with a slow heating rate ($< 2\,°C\,min^{-1}$) under nitrogen is adopted to prepare ordered mesoporous carbon frameworks. The structures of the assembled frameworks can be controlled by varying the surfactant/resol ratio or choosing different surfactants. 2D hexagonal ($p6m$) and 3D cubic ($Im\bar{3}m$) structures can be obtained by using F127 (EO106PO70 EO106) as a template, whilst a lamellar mesostructure can be prepared using P123 ($EO_{20}PO_{70}\ EO_{20}$) as a template (see the Supporting Information). The ordered mesoporous carbon frameworks have the same structures as the parent polymers as well as high surface areas and uniform pores. The walls of the carbon frameworks are amorphous, very thick (ca. 7 nm), and ultrastable (> 1400 °C).

The X-ray diffraction (XRD) pattern (Figure 2a) for untreated mesoporous polymer (FDU-15) shows an intense diffraction peak and two weak peaks at a 2θ range of 0.5 to 2° that can be indexed as (10), (20), (21) reflections associated with 2D hexagonal $p6m$ symmetry.[17] This observation indicates that untreated FDU-15 has a high degree of hexagonal mesoscopic organization. The intense (10) peak reflects a d-spacing of 12.8 nm, which corresponds to a large unit-cell parameter ($a_0 = 14.8$ nm). Small-angle X-ray scattering (SAXS; see the Supporting Information) reveals four well-resolved reflections, further confirming a highly ordered hexagonal mesostructure. After calcination of the sample under nitrogen at 350 °C, the XRD pattern (Figure 2b) shows four well-resolved peaks of a hexagonal mesostructure that is similar to that of mesoporous silica SBA-15, thus suggesting that the $p6m$ morphology is preserved, although the XRD peaks appear at slightly larger 2θ values with a $d(10)$-spacing of 10.5 nm ($a_0 = 12.1$ nm). These results clearly indicate that the mesostructure is thermally stable in a nitrogen atmos-

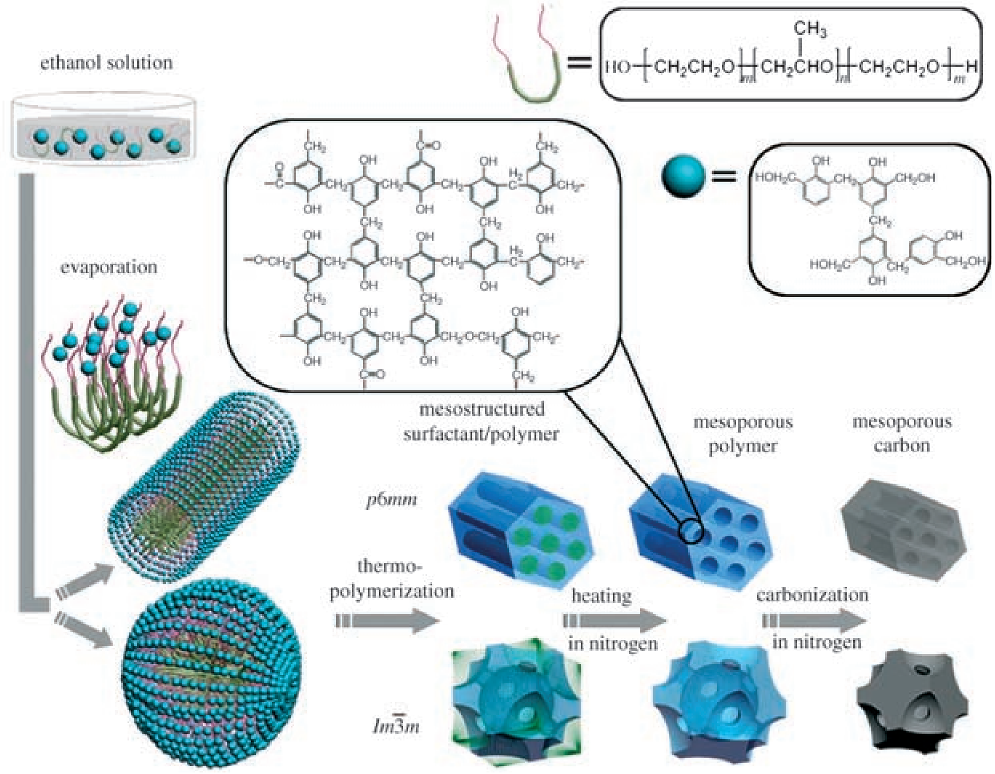

Figure 1. Schematic representation of the procedure used to prepare mesoporous polymers and carbon frameworks.

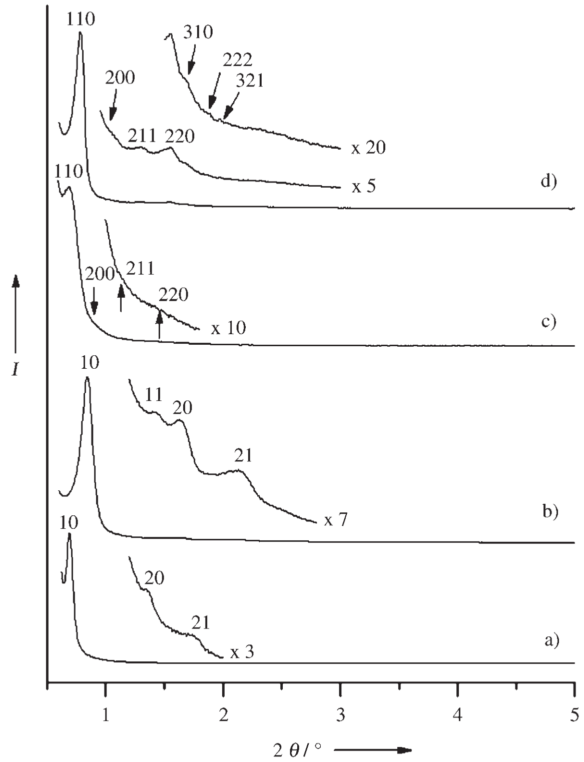

Figure 2. Powder XRD patterns of a) untreated FDU-15, b) FDU-15 calcined at 350 °C, c) untreated FDU-16, and d) FDU-16 calcined at 350 °C. The patterns were recorded on a Brucker D4 powder X-ray diffractometer using Cu$_{K\alpha}$ radiation.

phere, and the lattice of the framework shrinks by about 2.7 nm. The SAXS pattern shows three well-resolved peaks, thus providing evidence of thermal stability.

The photographic image of untreated FDU-15 (Figure 3a) shows that it is a transparent and soft membrane, and indicates it is a homogeneous organic–organic composite. Transmission electron microscopy (TEM) images of FDU-15 calcined at 350 °C (C-FDU-15; Figure 3b,c) show well-ordered hexagonal arrays of mesopores with 1D channels that are similar to SBA-15,[17] further confirming a 2D ordered hexagonal mesostructure. The cell parameter (a_0) estimated from the TEM images is approximately 11.5 nm, which is in agreement with the value calculated from XRD data.

The N_2 sorption isotherms (shown as circles in Figure 4a) of FDU-15 calcined in a nitrogen atmosphere at 350 °C yield a type-IV curve with a sharp capillary condensation step at $P/P_0 = 0.6–0.7$ and an H_1-type hysteresis loop which is typical of large-pore mesoporous materials with cylindrical channels.[17] These results suggest that FDU-15 has uniform cylindrical mesoporous channels, similar to those of SBA-15.[17] The BET surface area and the total pore volume are calculated to be 652 $m^2 g^{-1}$ and 0.63 $cm^3 g^{-1}$, respectively. The pore diameter is about 6.8 nm with a narrow distribution. The wall thickness is estimated to be 5.3 nm, which indicates a thick organic network.

The ^{13}C solid-state NMR spectra (see the Supporting Information) reveal that calcination at 350 °C can decompose the triblock copolymers because they contain a large amount of oxygen, but the phenolic resin networks are preserved.

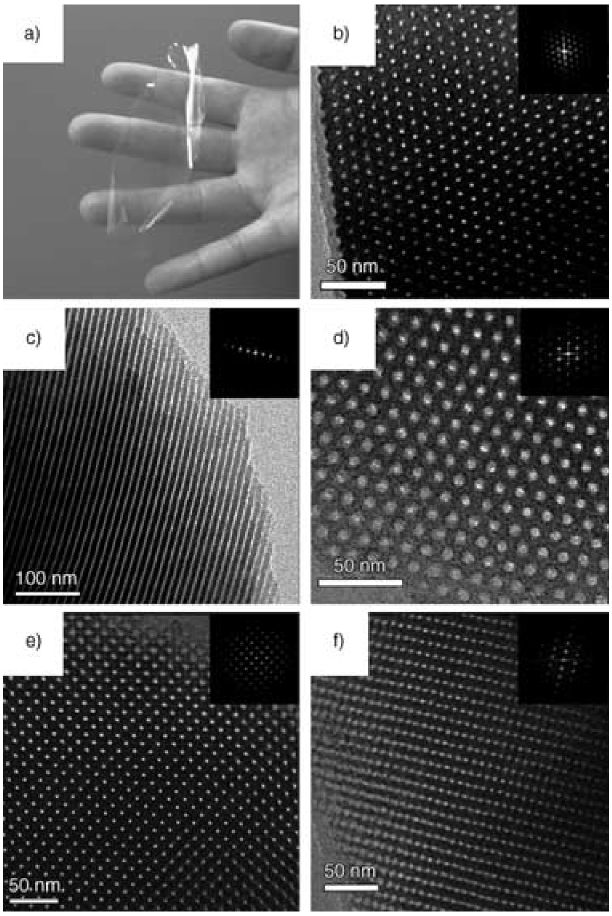

Figure 3. a) Photographic image of untreated FDU-15, b) TEM image of FDU-15 calcined at 350 °C viewed in the [001] direction, c) TEM image of FDU-15 calcined at 350 °C viewed in the [110] direction, d) TEM image of FDU-16 calcined at 350 °C viewed in the [111] direction, e) TEM image of FDU-16 calcined at 350 °C viewed in the [100] direction, and f) TEM image of FDU-16 calcined at 350 °C viewed in the [110] direction. TEM images were recorded on a JEOL 2011 microscope operated at 200 kV.

Elemental analysis reveals that calcined FDU-15 consists of C (77.97 %), H (5.20 %), O (16.8 %) with C/H/O molar ratio of 1:0.80:0.15, clearly suggesting a highly cross-linked phenol resin.

The 3D cubic mesoporous polymer structure (FDU-16) can be synthesized with a low F127/resol ratio. The XRD pattern for untreated FDU-16 (Figure 2 c) shows one intense and three weak diffraction peaks. This result, combined with the SAXS pattern (see the Supporting Information), suggests a cubic mesostructure.[21] After calcination of the sample at 350 °C in a nitrogen atmosphere, the XRD pattern (Figure 2 d) becomes more resolved, and seven diffraction peaks are observed. SAXS results (see the Supporting Information) show a well-resolved pattern. These reflection peaks can be indexed as (110), (200), (211), (220), (310), (222), and (321) of the body-centered cubic space group ($Im\bar{3}m$).[21] The lattice parameters are calculated to be 18.1 and 16.0 nm for untreated and calcined FDU-16, respectively. The lattice shrinkage is about 2.1 nm (11.6 %), which is slightly smaller than that for FDU-15 (18.2 %).

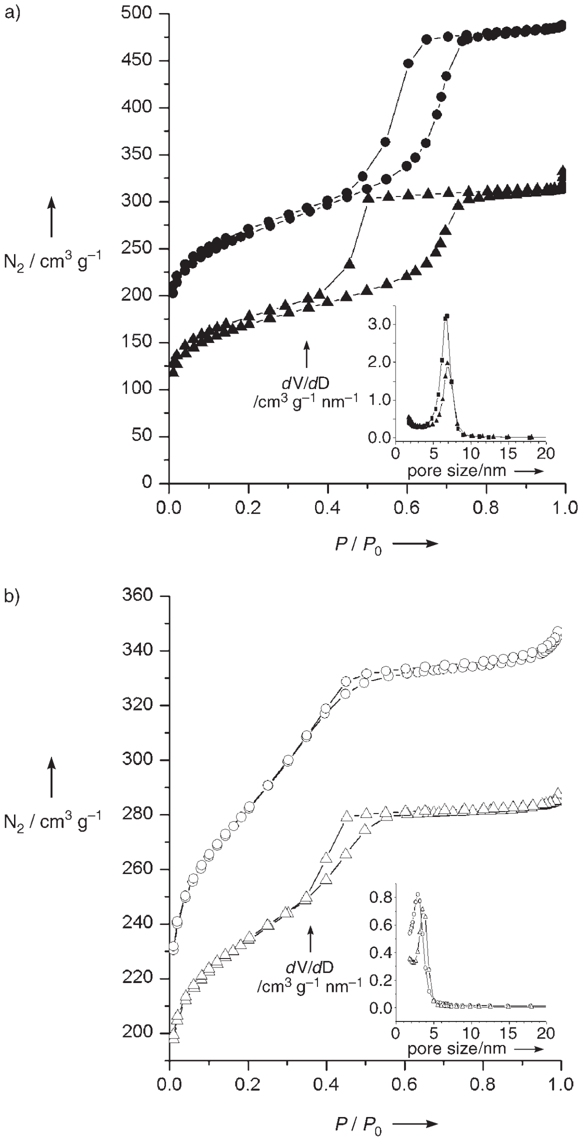

Figure 4. a) N_2 adsorption/desorption isotherms of FDU-15 (solid circles) calcined at 350 °C and FDU-16 (solid triangles) calcined at 350 °C, b) N_2 adsorption/desorption isotherms of C-FDU-15 (circles) calcined at 900 °C and C-FDU-16 (triangles) calcined at 900 °C. The pore-size distribution of FDU-15, FDU-16, C-FDU-15, and C-FDU-16 was determined by Barrett–Joyner–Halenda (BJH) analysis (inset). For clarity, the isotherms of C-FDU-15 in Figure 4 a are offset along the y axis by 100 $cm^3 g^{-1}$. N_2 sorption isotherms were measured using a Micromeritics Tristar 300 analyzer at 77 K.

The large domain regularity of calcined FDU-16 is verified by TEM images (Figure 3 d–f). These images viewed along the [111], [100], and [110] directions, together with electron diffraction data, further confirm an ordered cubic ($Im\bar{3}m$) mesostructure. The cell parameter estimated from the TEM images is approximately 15.9 nm, which is consistent with the value determined from the XRD data.

The N_2 sorption isotherms (shown as triangles in Figure 4 a) of C-FDU-16 show typical type-IV curves with an H_2-type hysteresis loop which imply a 3D caged pore structure with a small entrance size (< 4 nm).[30] C-FDU-16 has a BET surface area of 590 $m^2 g^{-1}$, a pore volume of 0.51 $cm^3 g^{-1}$, and a narrow pore distribution at about 6.8 nm. The pore size is identical to that of FDU-16, thus suggesting there is a dependence upon the template.

The ^{13}C solid-state NMR and FT-IR spectra of FDU-16 (see the Supporting Information) indicate that the copolymers can be decomposed and result in polymer networks after calcination at 350 °C. Elemental analysis shows a composition of calcined FDU-16 with a molar ratio of C/H/O = 1:0.70:0.20 (C 75.10, H 4.36, O 20.5 %).

Thermogravimetric curves (see the Supporting Information) show that significant weight losses of about 55 and 43 % occurred from 270 to 380 °C for FDU-15 and FDU-16, respectively. This weight loss can be mainly attributed to the decomposition of copolymer F127. Slow weight losses of 25.6 and 26.5 % between 380 and 900 °C as a result of carbonization is observed for FDU-15 and FDU-16, respectively. The carbonization yield, calculated on the basis of the phenol resin, is 43.0 and 65.9 % for FDU-15 and FDU-16, respectively. Elemental analysis data indicate that carbonization (> 900 °C) is almost completely achieved, with < 5 % oxygen and hydrogen remaining, thus suggesting that a pure carbon, homologous framework is obtained.

XRD patterns (Figure 5 a) show that the ordered mesostructures are preserved during the carbonization process, even up to 1400 °C. A 2D hexagonal mesoporous carbon framework (C-FDU-15) can be obtained from polymer FDU-15 after carbonization at 900 °C. XRD patterns show that C-FDU-15 has a highly ordered hexagonal (*p*6*m*) mesostructure which is the same as that of FDU-15, in contrast to the mesoporous carbon replicas (CMK-3) which are made up of carbon nanorods or arrays of nanowires and have the reverse structure of the mesoporous silica template.[31] The cell parameter (a_0) is calculated from XRD data to be 8.7 nm. Comparison of this value with that of its parent shows that shrinkage is as large as 28 %. TEM images (Figure 6 a, b) show that C-FDU-15 has well-ordered hexagonal arrays with 1D channels even after calcinations at 1400 °C, thus indicating a high thermal stability.

The N_2 sorption isotherms (shown as circles in Figure 4 b) of C-FDU-15 obtained at 900 °C also show typical curves for mesoporous materials, with a sharp capillary condensation step at low relative pressures ($P/P_0 = 0.2$–0.4). A small hysteresis loop is observed, which is similar to small-pore mesoporous silica MCM-41.[16] A narrow pore size distribution at about 2.9 nm is obtained, even though the pore size shrinkage is as large as approximately 57 %. The wall thickness is calculated to be 5.8 nm, which is similar to that of FDU-15. C-FDU-15 obtained at 900 °C has a large BET surface area of 968 $m^2 g^{-1}$, and a pore volume of 0.56 $cm^3 g^{-1}$.

Our results show that the successful formation of ordered mesoporous carbon frameworks is due to the rigid resin networks and a slow carbonization process. With increasing temperature, the a_0 and pore size decrease rapidly at first then decrease more slowly after 600 °C (see the Supporting Information), thus implying that heating at low temperature (< 600 °C) may be an important step for stabilizing the carbon frameworks.

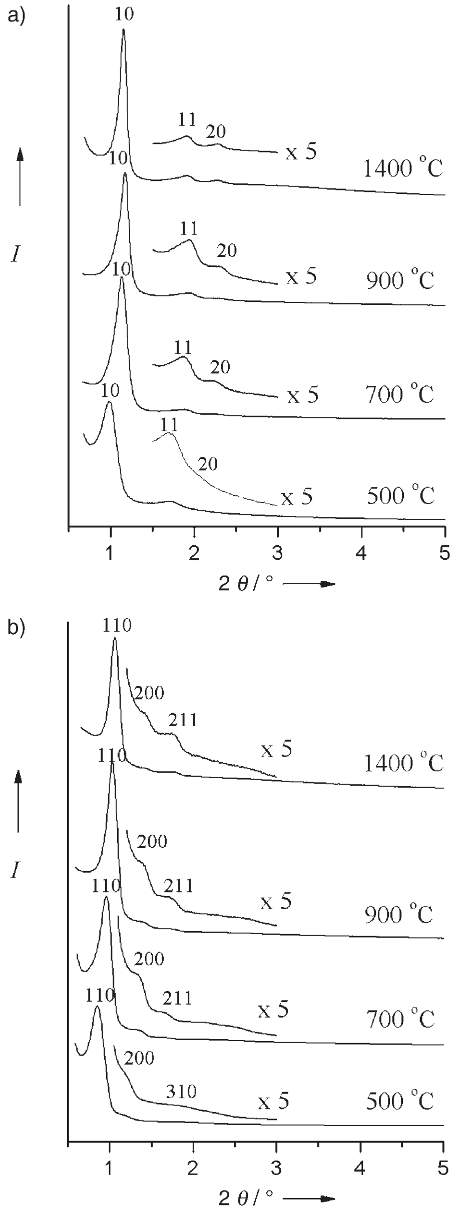

Figure 5. a) XRD patterns of C-FDU-15 calcined at temperatures ranging from 500 to 1400 °C, and b) XRD patterns of C-FDU-16 calcined at temperatures ranging from 500 to 1400 °C.

C-FDU-16 has a well-ordered cubic ($Im\bar{3}m$) mesostructure. Three well-resolved peaks can be observed in the XRD patterns (Figure 5 b). SAXS patterns (see the Supporting Information) confirm that the cubic mesostructure is retained during carbonization. The cell parameter (a_0) for the sample obtained at 900 °C is estimated to be 12.1 nm, and the shrinkage is about 24 %, which is slightly smaller than that for C-FDU-15. This observation implies that the 3D framework is more rigid than the 2D hexagonal structure. TEM images (Figure 6 c, d) show that C-FDU-16 has a large domain regularity with body-centered cubic symmetry ($Im\bar{3}m$) even after calcination at 1400 °C, which indicates ultrahigh thermal stability.

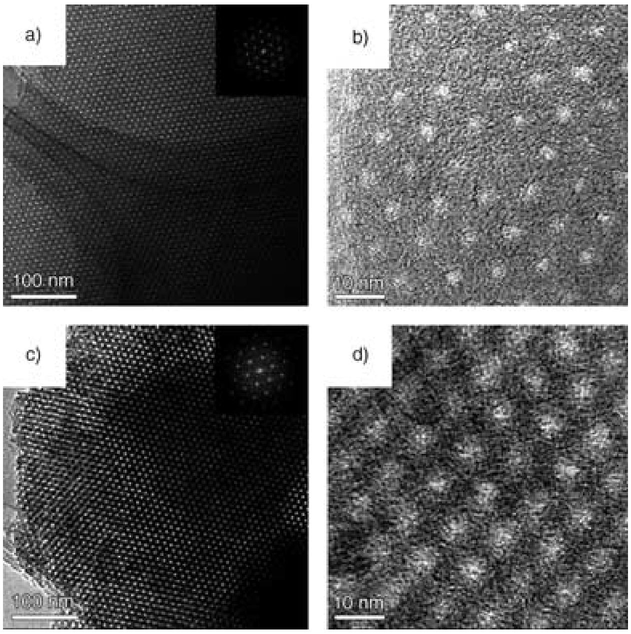

Figure 6. a) TEM image of C-FDU-15 calcined at 1400 °C, b) HRTEM image of FDU-15 calcined at 1400 °C, c) TEM image of C-FDU-16 calcined at 1400 °C, and d) HRTEM image of C-FDU-16 calcined at 1400 °C.

C-FDU-16 obtained at 900 °C also shows type-IV isotherms with a small H_2-hysteresis loop (shown as triangles in Figure 4b), thus implying small cage-like mesopores.[28] The pore size (ca. 3.7 nm), with a narrow distribution range, is smaller than that for its parent and the shrinkage (about ca. 45 %) is lower than that for C-FDU-15 which implies the cubic framework is more stable, and may be related to the 3D frameworks. C-FDU-16 obtained at 900 °C has a surface area of 778 $m^2 g^{-1}$ and a pore volume of 0.44 $cm^3 g^{-1}$.

The wide-angle XRD patterns (see the Supporting Information) for the carbon homologues are characteristic of amorphous carbon frameworks even after carbonization at 1400 °C.[32] The Raman spectra results (see the Supporting Information) also suggest an amorphous carbon framework.[32] High-resolution TEM (HRTEM) images (Figure 3d) of mesoporous carbon obtained at 1400 °C show that most of the carbon is amorphous, which suggests that graphitization is difficult.

In summary, highly ordered mesoporous polymers and carbon frameworks, with large uniform pores and surface areas, have been synthesized successfully. Two examples, FDU-15 and FDU-16, with hexagonal and cubic mesostructures, synthesized from triblock copolymers have been demonstrated. Ordered mesoporous carbon structures can be directly prepared from the polymers without defects. The resulting open carbon frameworks, connected by covalent bonds, have ultrahigh stability ($>$1400 °C). The two new families of ordered mesoporous organic polymers and inorganic carbon solids, whose physical and chemical properties are quite easily distinguished from those of mesoporous silica, could have many potential applications in catalysis, separation, hydrogen storage, drug delivery, electrode materials, microdevices, and even in bioengineering.

Experimental Section

Resol precursor preparation: A soluble low-molecular-weight polymer ($M_w = 500$–5000) derived from phenol and formaldehyde (resol) was prepared by a basic polymerization method. Typical preparation procedure: Phenol (0.61 g, 6.50 mmol) was melted at 40–42 °C before 20 % NaOH (aq; 0.13 g, 0.65 mmol) was added slowly over 10 min with stirring. Formalin (37 wt %, 1.05 g) containing formaldehyde (13.0 mmol) was added dropwise, and the reaction mixture was stirred at 70 °C for 60 min. After cooling the mixture to room temperature, the pH of the reaction mixture was adjusted to neutral (7.0) using 0.6 M HCl solution. Water was then removed under vaccum below 50 °C. The final product ($M_w < 500$ measured by GPC) was redissolved in ethanol before use.

Synthesis of mesoporous polymer FDU-15 and FDU-16: Typical synthetic procedure of FDU-15: triblock copolymer poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO, pluronic 127; 1.00 g) was dissolved in ethanol (20.0 g), then the ethanol solution of the above precursors containing phenol (0.61 g, 6.50 mmol) and (0.39 g, 13.0 mmol) formaldehyde was added by stirring for 10 min to form a homogeneous solution with the molar composition of F127/phenol/formaldehyde/ethanol of 0.012:1:2:67. The solution was transferred to a dish and the ethanol evaporated at room temperature over 5–8 h to produce a transparent membrane. The membrane was then heated in an oven at 100 °C for 24 h to thermopolymerize the phenolic resins. The products were calcined at 350 °C under nitrogen for 5 h with a temperature increase rate of 1 °C min^{-1} to obtain the porosity and decomposition of the amiphiphilic triblock copolymer template.

Cubic mesostructured resin polymers FDU-16 were synthesized by a procedure similar to that above, using triblock copolymer F127 (1.00 g), ethanol (15.0 g), resol precursor solution containing phenol (1.22 g, 13.0 mmol), and formaldehyde (0.78 g, 26.0 mmol). F127/phenol/formaldehyde/ethanol = 0.005–0.006:1:2:50.

Synthesis of lamellar mesostructured polymers from P123: Lamellar mesostructured polymer was prepared by using triblock copolymer pluronic P123 according to the above procedure. A homogeneous solution with the molar composition of P123/phenol/formaldehyde/ethanol = 0.022:1:1.2:50 was obtained and transferred into a dish to evaporate the ethanol. The resulting membrane was then heated in an oven at 100 °C for 24 h.

Synthesis of mesoporous carbon frameworks C-FDU-15 and C-FDU-16: Mesoporous carbon materials, C-FDU-15 and C-FDU-16, were prepared by direct transformation of the corresponding mesostructured polymers by carbonization under nitrogen. Carbonization was carried out in a tube oven under nitrogen at 700–1400 °C for 5 h. The temperature was increased at a rate of about 1 °C min^{-1} and held at 200, 350, and 500 °C for 2 h before reaching the final temperature. Elemental analysis results showed that the products contained $>$90 wt % carbon, $<$1.9 wt % H after carbonization at $>$700 °C.

Measurements: XRD patterns were recorded on a Brucker D4 powder X-ray diffractometer by using $Cu_{K\alpha}$ radiation (40 kV, 40 mA). TEM images were obtained with a JEOL 2011 microscope operated at 200 kV. Samples for TEM measurements were suspended in ethanol and supported on a carbon-coated copper grid. N_2 adsorption isotherms were measured using a Micromeritics Tristar 3000 analyzer at 77 K. Before measurements were taken, all samples were degassed at 473 K for more than 12 h.

Received: May 7, 2005

Keywords: mesoporous materials · self-assembly · synthesis design · template synthesis

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