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Growth of Single-Crystal Mesoporous Carbons with $Im\bar{3}m$ Symmetry

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Highly ordered mesoporous carbon FDU-16 rhombic dodecahedral single crystals with body-centered cubic structure (space group $Im\bar{3}m$) have been successfully synthesized by employing an organic−organic assembly of triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) and phenol/formaldehyde resol in basic aqueous solution. Synthetic factors (including reaction time, temperature, and stirring rate) are explored for controlling the formation of rhombic dodecahedral single crystals. The optimal stirring rate and the reaction temperature are 300 ± 10 rpm and ~66 °C, respectively. High-resolution scanning electron microscopy (HRSEM), scanning transmission electron microscopy (STEM), and ultramicrotomy are applied to study the fine structures of the carbon single crystals. The mesopores are arranged in body-centered cubic symmetry throughout the entire particle. Surface steps are clearly observed in the {110} surface, which suggests a layer-by-layer growth of the mesoporous carbon FDU-16 single crystals. Cryo-SEM results from the reactant solution confirm the formation of resol/F127 unit micelles, further supporting the layer-by-layer growth process. The mesoporous carbon FDU-16 single crystals grow up to the final size of 2−4 μm within 2 days. These findings may have consequences for the growth mechanism of other carbon materials in aqueous solution; moreover, the high-quality single crystals also have potential applications in nanodevice technologies.

1. Introduction

Mesoporous materials have attracted tremendous attention, because of their highly ordered structures,[1−6] variable compositions,[5,7−11] controllable morphologies,[12−16] and potential applications in catalysis, selective adsorption, drug delivery, etc. Single crystals of such materials offer good opportunities to understand the growth mechanism of mesostructures, leading to more rational design strategies for the synthesis of the mesoporous materials. However, it is quite difficult to synthesize mesoporous single crystals, because of the low energy penalty for the formation of defects.[17] Until now, several papers have reported on the fabrication of mesoporous single crystals of silica,[15,18−26] organosilicates,[27] and nonoxide composition

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(c-C_nPyPtSnSe, $n = 18, 20$).[28,29] Most of these single-crystals were prepared using ionic surfactants as a template. Only in a few studies were nonionic surfactants employed as templates at high ionic strength[15] or with very long crystallization times.[24] Furthermore, the formation of the mesoporous single crystals is significantly affected by various synthetic parameters, such as temperature, pH value, reaction time, concentration, and stirring rate.[30]

Carbon has different allotropes—graphite, diamond, fullerene, and nanotubes—and they are of great importance, because of their unique properties. Ordered mesoporous carbons have also attracted enormous interest because of their potential applications in catalysis, separation, electrochemical double-layer capacitors (EDLCs), fuel cells, and batteries.[7,9,31−37] Ordered mesoporous carbon was first prepared using a nanocasting strategy.[9] Not many silica materials are obtained as single crystals, and in the nanocasting route, it is difficult to completely fill the pore system of the hard template. Thus, it is almost impossible to obtain single-crystal replicas by nanocasting. Recently, an organic−organic assembly approach induced by solvent evaporation from block copolymers and phenolic resol solutions has been discovered to synthesize ordered mesoporous carbon films.[32,33,35,38] We have also reported a one-step aqueous route to synthesize ordered mesoporous carbons with controllable mesostructures and particle morphologies.[34,35] With this facile and low-cost aqueous method, we successfully synthesized ordered mesoporous carbon (FDU-16) single crystals with body-centered cubic symmetry ($Im\bar{3}m$).[39] Based on the observations of transmission electron microscopy (TEM) and scanning electron microscopy (SEM), a layer-by-layer growth was suggested to understand the formation of the mesoporous carbon crystals. Nevertheless, so far, there is no detailed study to understand this single-crystal growth process.

In this paper, we report, in detail, on the growth and single-crystal structure of ordered mesoporous carbon FDU-16 that has been analyzed using high-resolution scanning electron microscopy (HRSEM) and scanning transmission electron microscopy (STEM). Highly ordered mesoporous carbons FDU-16 with a three-dimensional (3-D) body-centered cubic structure ($Im\bar{3}m$) were obtained using triblock copolymer Pluronic F127 (EO_{106}-$PO_{70}EO_{106}$) as a template, and resol as a carbon precursor. The optimal stirring rate is controlled at 300 ± 10 rpm, and the most suitable reaction temperature is ~66 °C. After pyrolysis at 700 °C for 3 h in nitrogen, ordered mesoporous carbon single crystals with rhombic dodecahedral morphology were obtained. A detailed study of the relationship between the structure and parameters such as reaction time, temperature, stirring rate, etc. revealed a layer-by-layer growth and reorganization model as a suitable description of the growth process. A slicing technique was used to study the internal structure of the carbon crystals. By resolving the mesopore arrangement of each crystal section, we have further confirmed that these crystals are perfect single crystals with a body-centered cubic space group.

2. Experimental Section

2.1. Chemicals. Triblock copolymer Pluronic F127 (EO_{106}-$PO_{70}EO_{106}$, $M_w = 12\,600$) was purchased from Acros Corp. Other chemicals were purchased from Shanghai Chemical Corp. All chemicals were used as received without any further purification. Millipore water was used in all experiments.

2.2. Synthesis of FDU-16 Single Crystals. Mesoporous carbon single crystals were synthesized under "hydrothermal" conditions at 66 °C, using triblock copolymer F127 as a template and phenol/formaldehyde resols as a carbon precursor. First, 2.0 g of phenol and 7.0 mL of formaldehyde solution (37 wt %) were dissolved in 50 mL of 0.1 M NaOH solution. The mixture then was stirred at 70 °C for 30 min. A clear resol precursor solution was obtained, denoted as Solution-P. On the other hand, 5.6 g of F127 was dissolved in 50 mL of water at room temperature. Solution-P then was added into the above solution, and a clear solution was obtained. The solution was reheated to 66 °C and stirred for 2−6 days with a stirring rate of 300 ± 10 rpm. The pale yellow precipitation was collected by sedimentation separation and centrifugation, washed with water for three times, and dried in air at room temperature. The products were pyrolyzed at 700 °C for 3 h in nitrogen with a heating rate of 1 °C/min. The products were denoted as FDU-16-X (where X represents the reaction time (in days): $X = 2, 3, 5$, or 6).

2.3. Characterization and Measurements. The small-angle X-ray scattering (SAXS) profiles were collected with a Nanostar U SAXS system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The d-spacing values were calculated using the formula $d = 2\pi/q$, where $q = 4\pi(\sin\theta)/\lambda$. Nitrogen sorption isotherms were measured at 77 K with an Autosorb-1MP gas sorption system (Quantachrome, USA). Before measurements, the samples were degassed under vacuum at 300 °C overnight. The Brunauer−Emmett−Teller (BET) method was used to calculate the BET equivalent specific surface areas (S_{BET}), using adsorption data in a relative pressure range from 0.008 to 0.057. This is rather low; however, this range gave the best linear fit. Using the non-local density functional theory (NLDFT) method mixed with the slit and cylinder pore model, the pore size distribution was derived from the adsorption branches of the isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure (P/P_0) of 0.998. The micropore surface area was calculated using the t-plot method in the relative pressure interval of $P/P_0 = 0.41−0.59$. SEM images

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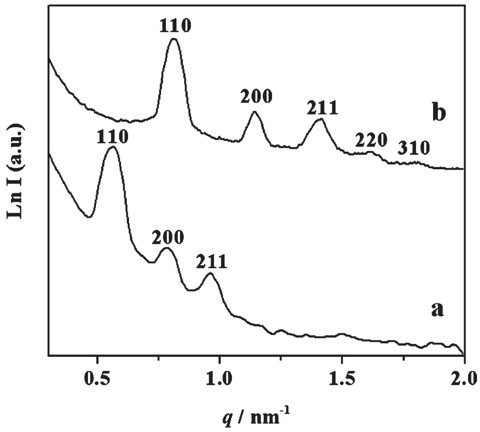

Figure 1. SAXS pattern of the (a) as-made and (b) pyrolyzed FDU-16-6 single crystals. The reaction conditions are 66 °C and 300 ± 10 rpm for 6 days.

were taken with a Philips XL30 system at 20 kV. HRSEM and STEM images were taken using a Hitachi S-5500 system with a cold-field field-emission gun (FEG) and an in-lens detector, operating at 1 and 30 kV, respectively. All samples were prepared on a lacey film supported on a copper grid without any surface coatings. Some of the mesoporous carbon FDU-16 single crystals were embedded in Spurr-resin with 1,2-propylenoxid as solvent for a special infiltration technique and then cut by a LEICA-Ultracut microtome with a 35° diamond knife for HRSEM and STEM analysis. Cryo-scanning electron microscopy (Cryo-SEM) images were taken using a Hitachi S-4800 system operating at 1 kV. The reactant water solution was dipped on a concave copper sample holder and dropped into soil nitrogen (a type of semisolid nitrogen made by treating liquid nitrogen under vacuum) before the images were obtained. TEM experiments were conducted on a JEM-2011 (JEOL, Tokyo, Japan) operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a lacey carbon film on a copper grid.

3. Results and Discussion

Highly ordered mesoporous carbon FDU-16 single crystals can be prepared by a facile aqueous route from an organic−organic assembly of preformed resols and triblock copolymer Pluronic F127 in dilute NaOH solution at ~66 °C with a stirring rate of 300 ± 10 rpm. The as-made products are pale yellow fine powders. The SAXS pattern of as-made FDU-16 crystals shows three well-resolved scattering peaks at *q*-values of 0.56, 0.78, and 0.96 nm^{-1} (see Figure 1a), respectively. These scattering signals, where *q* behaves as $1:\sqrt{2}:\sqrt{3}$, can be indexed as the 110, 200, and 211 reflections of a body-centered cubic $Im\bar{3}m$ mesostructure. Pyrolyzing this sample at 700 °C for 3 h in nitrogen yields a better-resolved SAXS pattern (Figure 1b), suggesting that the highly ordered mesostructure is retained. More than five scattering peaks are observed at *q*-values of 0.81, 1.14, 1.41, 1.61, and 1.80 nm^{-1}, which can be indexed as the 110, 200, 211, 220, and 310 Bragg reflections of a cubic $Im\bar{3}m$ mesostructure, respectively. From SAXS measurements, unit-cell parameters (*a*) of 15.9 and 11.0 nm can be calculated for the as-made and pyrolyzed FDU-16-6 samples, respectively, which implies substantial shrinkage (31%) of the framework upon pyrolysis. The SEM image (Figure 2a) shows that the pyrolyzed FDU-16-6 sample is composed of single crystals 2−4 μm in size with uniform rhombic dodecahedral morphology. HRSEM images (see Figures 2b−d) show that the perfect carbon crystals have a symmetry with three 4-fold and four 3-fold axes, in agreement with the $m\bar{3}m$ point group. The 12 equivalent rhombic faces, which are composed of platelike thin layers, can be indexed as the {110} planes. Each surface of the 12 {110} planes has a terrace-like multilayer structure, with the hilltop at the center of the planes. Each thin layer on the surface of FDU-16-6 single crystals is composed of small spherical particles, which may transform from the resol/F127 nanocomposite micelles (Figure 2d, inset). The size of these spheres is ~10 nm, which is very close to the cell parameter *a* of the mesoporous carbon crystals.

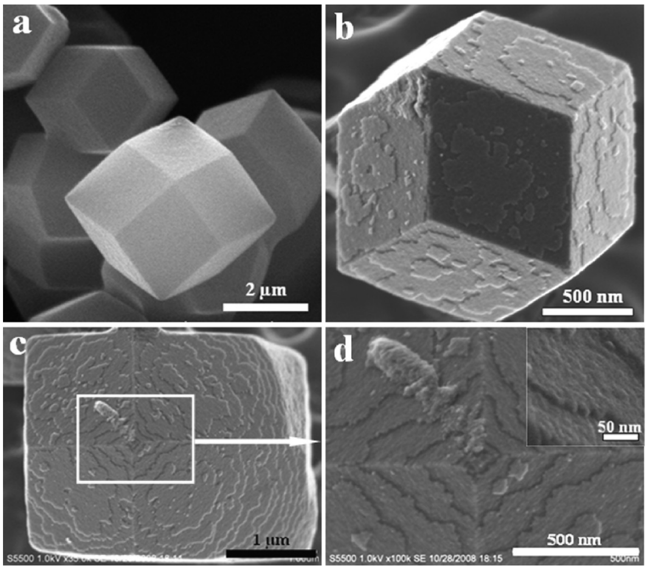

Figure 2. (a) Scanning electron microscopy (SEM) and (b, c, d and inset) HRSEM images of FDU-16-6 single crystals after pyrolysis at 700 °C in nitrogen. Synthesis conditions: 66 °C and 300 ± 10 rpm for 6 days.

Because of the extremely large size of the FDU-16-6 single crystals for proper TEM analysis, thin sections with a thickness of < 100 nm were produced by a diamond knife for *in situ* electron microscopic measurement. HRSEM images observed from the [111] and [100] directions show that the sections of the FDU-16-6 single crystals were cracked into striplike pieces normal to the cut direction (see Figures 3a and 3c, respectively). The STEM image (Figure 3b) viewed along the [111] direction of the cross section in Figure 3a exhibits the same packing pattern as the [111] face of the body-centered cubic $Im\bar{3}m$ structure. Different areas of the section in Figure 3a show the same packing patterns. These observations clearly show that the entire particle domain is a single crystal. Note that the section cut along the [100] direction gives the [100] face mesopore arrangement, which further confirms that the obtained carbon materials have a single-crystal structure. TEM images of the FDU-16-6 single-crystal slice are shown in Figure 3e, viewed along the [111] direction. The periodicity of the pattern extends

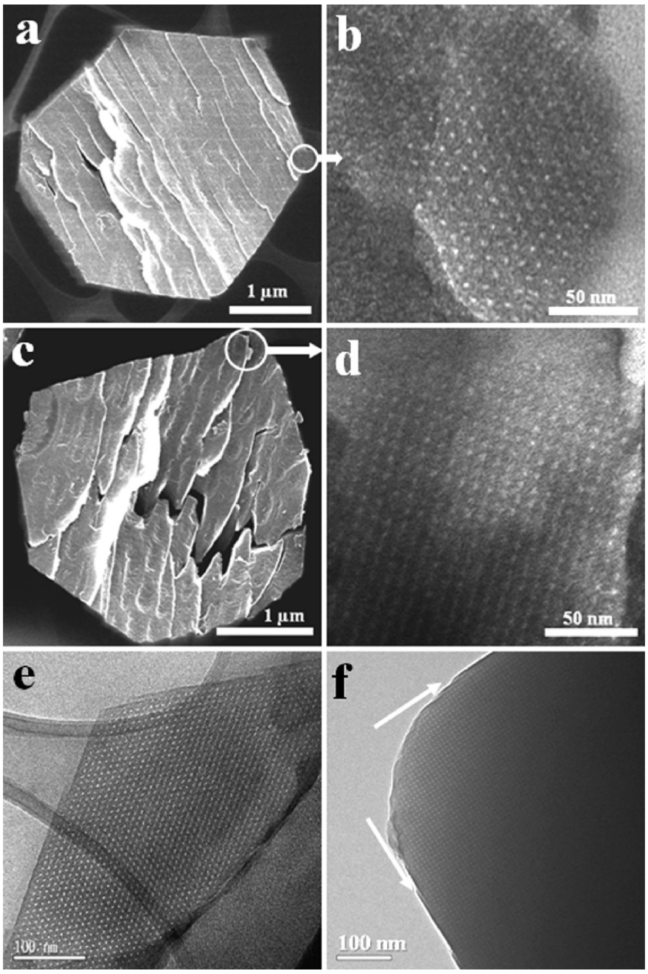

Figure 3. HRSEM and corresponding STEM images from the [111] direction (a, HRSEM image; b, STEM image), the [100] direction (c, HRSEM image; d, STEM image) of FDU-16-6 after pyrolysis at 700 °C in nitrogen. Also shown are TEM images from the [111] and [100] directions of FDU-16-6 after pyrolysis at 700 °C in nitrogen ((e) single-crystal slice and (f) bulk particle).

throughout the entire section, agreeing well with the STEM results. Furthermore, HRTEM images of a FDU-16-6 bulk single crystal in Figure 3f (white arrows), similar to the image of the slice in Figure 3e, show that the edges of the crystals seem to predominantly consist of collapsed and, thus, closed cages, which implies a difference between a defective surface and a rather well-developed inner structure of the carbon single crystals.

Nitrogen sorption isotherms (Figure 4a) of mesoporous carbon FDU-16-6 single crystals are predominantly Type I, with some Type IV characteristics. The BET equivalent surface area and the total pore volume are calculated to be 858 m^2/g and 0.42 cm^3/g, respectively. The isotherm shape suggests a micropore-rich material. The NLDFT pore size distribution is calculated from the adsorption branch mixed with a pore model of cylinder and slit shapes. The fitting error is as low as 0.074%. The pore size distribution curve (Figure 4b) reveals a multimodal distribution, which has one obvious and several weak maxima in the micropore range (<2 nm) and an obvious biomodal mesopore size distribution with maxima at 2.1 and 3.6 nm. The microporosity may be generated by both the thermal decomposition of the phenolic resin and the removal of PEO segments from the pore walls. The bimodal mesopores are generated by the decomposition of the Pluronic F127 templates, which represent the intrawall pores and the primary mesopores, respectively.[40] The weak maximum at ~5.5 nm may be related to structural defects.

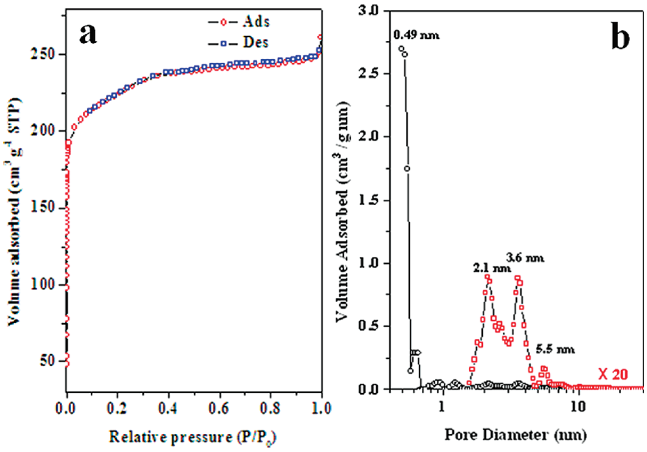

Figure 4. Nitrogen sorption isotherms and NLDFT pore size distribution of FDU-16-6 mesoporous carbon single crystals after pyrolysis at 700 °C in nitrogen. Sample synthesized at 66 °C and 300 ± 10 rpm for 6 days.

A simple aqueous route is employed here to prepare ordered mesoporous carbon single crystals. Preformed resols have a large number of hydroxy groups (−OH), which can interact with the PEO segments of Pluronic copolymer through hydrogen bonding. The formation of high-quality mesoporous carbon single crystals is dependent not only on the reaction temperature, but also on the stirring rate. The reaction temperature should be controlled as close as possible to the optimum of 66 °C, and the stirring rate should be ~300 rpm. A low temperature of ~60 °C gives products with a small particle size and irregular morphology. No precipitation could be obtained at ~70 °C. A low stirring rate can prolong the precipitation time and reduce the particle size, whereas a high stirring rate can lead to intergrowth, resulting in the formation of irregular mesoporous carbon particles.

The reaction time also plays a key role in the formation of uniform FDU-16 single crystals. No solid products can be observed within the first 48 h. The solution only changes from transparent and light yellow to opaque and dark red, because of the partial oxidation of resols. The SAXS pattern (Figure 5a) of the FDU-16 single crystals obtained after 2 days at 66 °C (FDU-16-2) shows only one broad scattering peak at a q-value of 0.77 nm^{-1}, suggesting the formation of only a poorly ordered mesostructure. As the reaction time increases, more-resolved scattering peaks can be observed in the SAXS patterns (see Figures 5b−d). This implies that the phenolic resin frameworks are not highly cross-linked when the resol/F127 composite coassembles into rhombic dodecahedron crystals with many defects. After a longer reaction at 66 °C, the polymer framework is further cross-linked and con-

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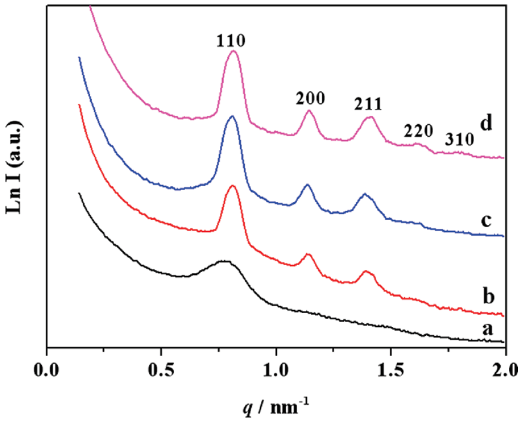


Figure 5. SAXS patterns of pyrolyzed (700 °C, nitrogen) FDU-16 single crystals after different reaction times ((a) 2 days, (b) 3 days, (c) 5 days, and (d) 6 days).

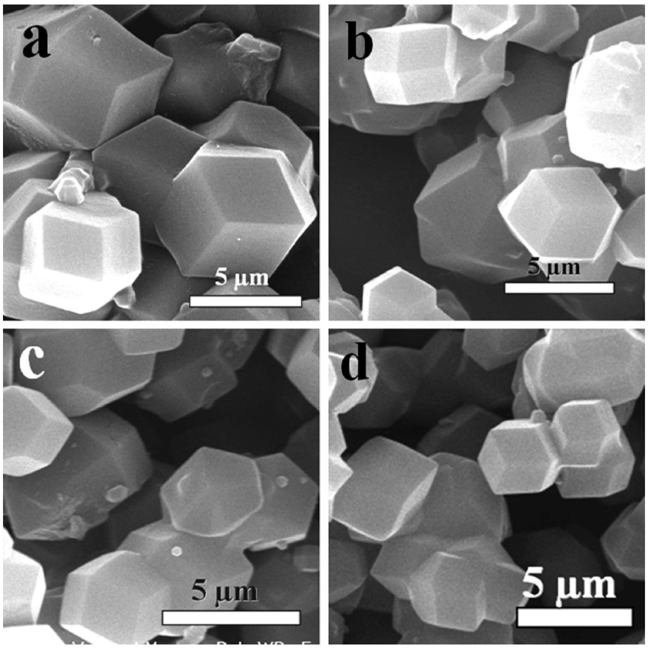


Figure 6. SEM images of pyrolyzed (700 °C, nitrogen) FDU-16 carbon single crystals after reaction times of (a) 2 days, (b) 3 days, (c) 4 days, and (d) 6 days. Synthesis conditions: 66 °C and 300 ± 10 rpm.

densed, and the mesostructure is reorganized from the F127 micelle/resol composite subunits. Therefore, the scattering peak intensity increases and the SAXS pattern becomes more distinct.

The SEM image (Figure 6a) shows that the mesoporous carbon FDU-16 single crystals obtained after 2 days have particle sizes of ∼3−5 μm. When the reaction time is extended to 6 days, the particle sizes do not change (see Figures 6b−d). This implies that the primary assembly occurs within the first 2 days, and the polymer framework cross-linking and reorganization of the mesostructure occur during the remaining time. Furthermore, all the particles stick together after separation from the solution, which results in a rough surface with many defects of all carbon crystals.

The Cryo-SEM image of the reactant solution after being reacted for 3 h (Figure 7a) shows spherical resol/F127 unit micelles (bright dots). The micelle size was calculated to be 10−18 nm, from the high-resolution cryo-SEM image (Figure 7b). Similar phenomena can be observed from the as-mixed resol/F127 solution. This result further confirms the formation of the resol/F127 unit micelles, suggesting a layer-by-layer growth of the unit resol/F127 micelles process.

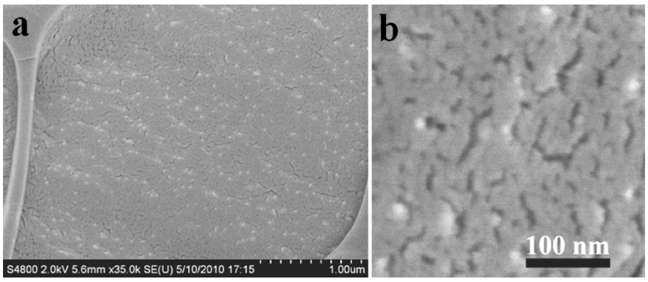
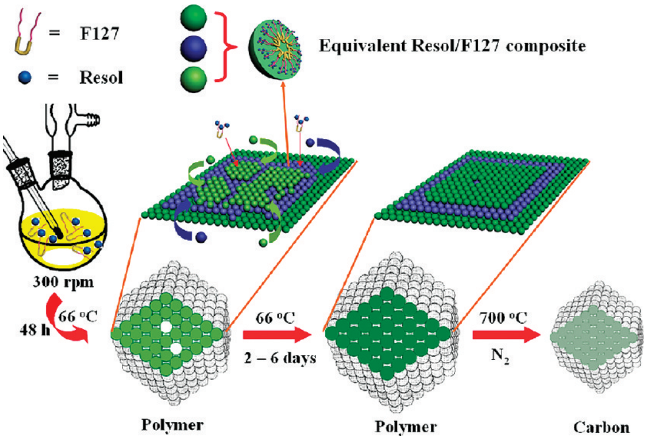


Figure 7. Cryo-SEM images of reactant solution after a reaction time of 3 h. Synthesis conditions: 66 °C and 300 ± 10 rpm.

Scheme 1. Scheme for the Preparation of FDU-16 Mesoporous Carbon Single Crystals



On the basis of the above observations, we propose a layer-by-layer growth and reorganization process of mesoporous carbon FDU-16 single crystals, as shown in Scheme 1. First, the resol precursors interact with the PEO segments of the amphiphilic triblock copolymer F127 through hydrogen bonds to form spherical composite micelles as a structural unit for the single-crystal growth. With further cross-linking of resols, the resol/F127 composite micelles connect with each other through carbon−carbon bonds to form micelle aggregates as nuclei for the single-crystal growth. More and more micelles then transfer to the surface of the nuclei in a close-packed arrangement to form the body-centered cubic F127/resol composite mesostructure. Because of the moderate reaction temperature, slow stirring rate, and low resol concentration, the crystal growth is probably thermodynamically controlled. As the reaction time increases, along with the continuous condensation of phenolic resins, the inner layer micelles change into rigid structures. At the same time, the mesostructure of the single crystals reorganizes into the perfect $Im\bar{3}m$ structure, to reduce the overall energy. On the other hand, the outermost layer of the composite micelles remains flexible with a low degree of cross-linking, so that small carbon species and free Pluronic F127 molecules in the solution can "repair" the defects. Therefore, after calcination, the outermost layers cannot form highly ordered mesostructures. This can be observed from the TEM image (see areas denoted by white arrows in Figure 3f) of the FDU-16-6 single crystal.

The low degree of cross-linking of the phenolic resin at the beginning of the reaction makes the growth rate of the FDU-16 single crystals very slow. The small-sized crystals are suspended in the concentrated precursor solution. During the first 2 days, no products can be isolated, although particles are already present, as can be inferred from the turbidity of the solution. Attempts to isolate these particles failed, because the still high concentration of resol and F127 molecules lead to cross-linking during the solvent removal. During this period, the particles grow via continuous transfer of fresh resol/F127 composite micelles onto the surfaces of the small suspended crystals. After 2 days, the reagents have been consumed, and their solution concentration greatly decreases, which reduces the crystal growth rate. Therefore, the crystals almost stop growing after 2 days. However, the polymer framework continues to cross-link and condense after the initial particle formation, and the structural defects are repaired. During the calcination, triblock copolymer F127 templates are removed from the framework. The PPO micelle cores form the primary mesopore voids, while the PEO segments leave the microporosity. Because of the lower degree of cross-linking of the polymer products obtained from the aqueous route, compared to that from the evaporation induced self-assembly (EISA) method, larger structural shrinkage is observed for the former. It also results in a much smaller mesopore size of the FDU-16 single crystals, compared to materials from the EISA method.

Many synthetic factors can affect the formation of FDU-16 carbon crystals. The key issue is to well-separate the two processes of the F127/resol micelle assembly and the polymer condensation. If the polymerization rate of the phenolic resin was too fast, the process would be kinetically controlled and the particles would assemble into irregular shapes. In addition, if the stirring rate was too fast, the supply of F127/resol micelles from solution would be too fast for an ordered growth process; in addition, the high shear forces may also disturb the growth of well-developed particles, leading to irregular morphologies. At low temperature, slow stirring rate, and low polymer concentration, the crystallization is slow and proceeds under more thermodynamically controlled near-equilibrium conditions, leading to more isotropic growth. The FDU-16 carbon single crystals are always limited to micrometer size, mainly because, at larger particle sizes, more defects are formed and the times to heal them are longer. In addition, as the reaction time is extended, the crystals tend to cross-link with each other to form large particles of irregular shape.

4. Conclusion

Ordered mesoporous FDU-16 single crystals with body-centered cubic ($Im\bar{3}m$) structure have been successfully synthesized by an aqueous route with triblock copolymer F127 as a template and resols as a carbon precursor. These carbon single crystals are composed of 2−4 μm rhombic dodecahedral particles with 12 equivalent rhombic faces. HRSEM, STEM, cryo-SEM, and slicing techniques were applied to study the mesostructures of the carbon single crystals. These analyses revealed that the mesopores are present in a body-centered cubic arrangement throughout the entire particle. A layer-by-layer growth and reorganization mechanism is proposed, based on the detailed observations. This type of material does not only help to understand the growth mechanism of carbon materials in aqueous solution, it also has potential applications in nanodevice technologies.

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