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Communication

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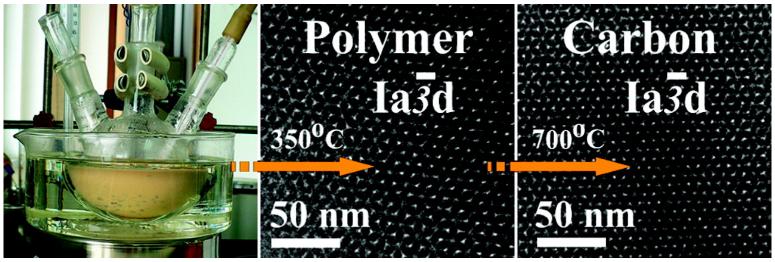

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A Facile Aqueous Route to Synthesize Highly Ordered Mesoporous Polymers and Carbon Frameworks with $Ia\bar{3}d$ Bicontinuous Cubic Structure

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Ordered mesoporous materials have attracted more and more attention owing to their potential applications in many fields, such as separation, adsorption, catalysis, etc. These materials are derived from the assembly of surfactants and inorganic precursors in a dilute surfactant aqueous solution.[1−5] Such method is now considered to be a facile, low-cost, and versatile approach for the synthesis of ordered mesoporous silica with various symmetries and has been demonstrated to be feasible in the industrial production. Among these mesostructures, MCM-48 with $Ia\bar{3}d$ symmetry has a more appealing structure for the applications. The center of the silica walls of MCM-48 is located on the gyroid infinite periodic minimal surface. It endows this material with a very open framework with two sets of pores of opposite handedness and thus great advantages in the applications.

By employing these mesoporous silica structures as hard templates, ordered mesoporous carbon replicas have been synthesized by Ryoo et al. from a nanocasting strategy.[6−11] Nevertheless, nanocasting is a very fussy, high-cost, and thus industrial unfeasible method. More recently, Tanaka et al.[12] used resorcinol/formaldehyde as co-precursor and direct carbonization of an organic−organic composite to prepare ordered mesoporous carbons with channel structure. On the basis of the consideration of framework construction of the zeolites, we simply used resol (phenol/formaldehyde) as a precursor, which can be a three-connected benzene ring framework, and independently demonstrated a reproducible synthesis of highly ordered mesoporous polymers and carbon frameworks with $p6m$ and $Im\bar{3}m$ symmetry via a solvent evaporation induced self-assembly (EISA) of triblock copolymers.[13] Unlike the nanorod/pipe array structures of the CMK carbon materials derived from a hard-template method, zeolite-like pore structures are observed in these novel mesoporous polymers and carbons, which may favor their applications. Since the mesostructures are formed on the surface by the EISA strategy, it meets the demands of preparing mesostructured films. However, it is not suitable for the industrial production of powder materials due to the engineering difficulties, such as sample collection, reactor design (large surface vessel), etc. It is therefore worth exploring an industrial feasible dilute aqueous solution induced self-assembly strategy for the fabrication of mesoporous polymers and carbons. In addition, mesoporous polymers or carbons with an appealing MCM-48-like framework have not yet been prepared following the EISA or other methods.

In this paper, we report a dilute aqueous route for the direct synthesis of novel bicontinuous cubic mesoporous polymer (FDU-14) and carbon (C-FDU-14) with $Ia\bar{3}d$ symmetry from the organic−organic self-assembly of triblock copolymer P123 with resols. The approach is quite similar to that of the mesoporous silica (MCM-41, SBA-15, etc.) and is considered to be more suitable for industrial production compared to the EISA method. Both FDU-14 and C-FDU-14 show an attractive bicontinuous cubic mesostructure of MCM-48.

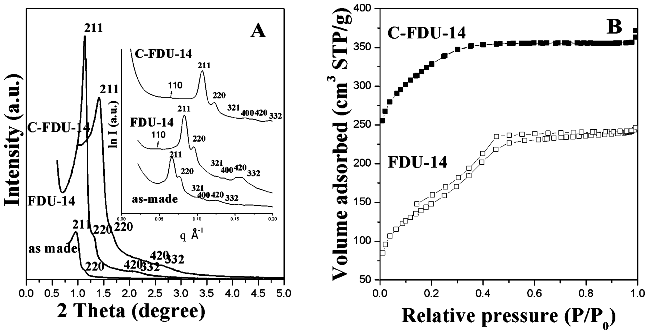

Figure 1. XRD (A) and SAXS (A inset) patterns of as-made FDU-14, FDU-14, and C-FDU-14. Nitrogen sorption isotherms (B) of FDU-14 and C-FDU-14.

The detailed synthesis procedure is shown in Supporting Information. FDU-14 can be synthesized at a temperature ranging from 60 to 70 °C and with a reactant molar ratio of P123:phenol: CH_2O:NaOH:H_2O = 8.27×10^{-2}:2.1:6.0−8.0:0.5:550. To obtain a rigid and stable thermoset framework, we synthesized FDU-14 at a basic condition. The pH value of the reaction solution is about 8.5, which is a key factor in the synthesis. FDU-14 cannot be obtained at a pH value higher than 9 and lower than 8.

XRD patterns of as-made FDU-14, FDU-14, and C-FDU-14 are shown in Figure 1A. The SAXS pattern of as-made FDU-14 displays six strong peaks associated with 211, 220, 321, 400, 420, and 332 reflections of a 3D bicontinuous cubic space group ($Ia\bar{3}d$), despite only two peaks in the XRD pattern. After template decomposition at 350 °C in nitrogen flow, four well-resolved peaks, indexed as 211, 220, 420, and 332 assigned to an $Ia\bar{3}d$ symmetry, are shown in the XRD pattern, indicating a highly ordered mesostructure of FDU-14. The SAXS pattern with six clear peaks further confirms the $Ia\bar{3}d$ symmetry. C-FDU-14 also reveals typical XRD and SAXS patterns of a highly ordered cubic $Ia\bar{3}d$ mesostructure. Nevertheless, a weak refection peak indexed as 110 in the SAXS patterns of both FDU-14 and C-FDU-14 suggests a little structural defect of $I4_132$ symmetry. The bicontinuous cubic structure of FDU-14 is mainly reserved after the surfactant removal and subsequent carbonization process. The lattice parameters of as-made FDU-14, FDU-14, and C-FDU-14 are calculated to be 23.0, 19.0, and 15.4 nm, respectively, which reflects a 17.4% shrinkage after template removal and a further 18.9% reduce after carbonization.

N_2 sorption isotherms (Figure 1B) of FDU-14 and C-FDU-14 are all type-IV curves with clear capillary condensation steps. Interestingly, the adsorption and desorption isotherms of FDU-14 are not close at low relative pressure, revealing typical isotherms of polymer materials. It can be calculated from the adsorption branch based on the Kruk−Jaroniec−Sayari (KJS) model[14] that FDU-14 has a pore size of 3.8 nm, a BET surface area of 550 m^2/g, and a pore volume of 0.4 cm^3/g. The pore wall thickness is

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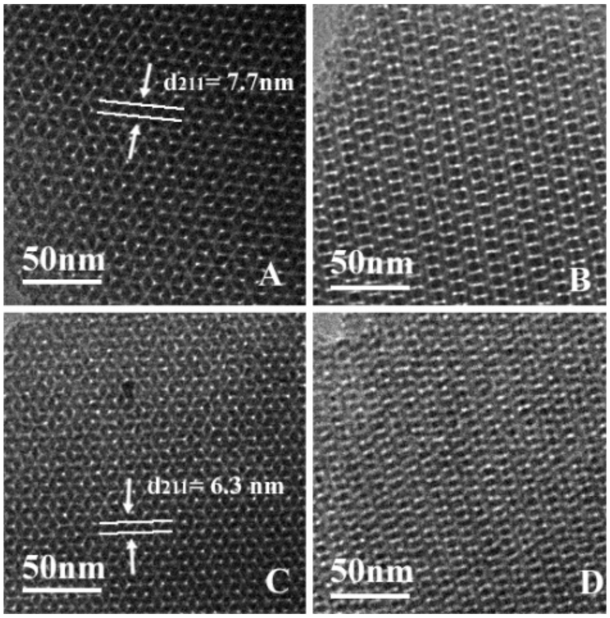


Figure 2. TEM images of FDU-14 view along [111] (A) and [311] (B) directions. TEM images of C-FDU-14 view along [111] (C) and [311] (D) directions.

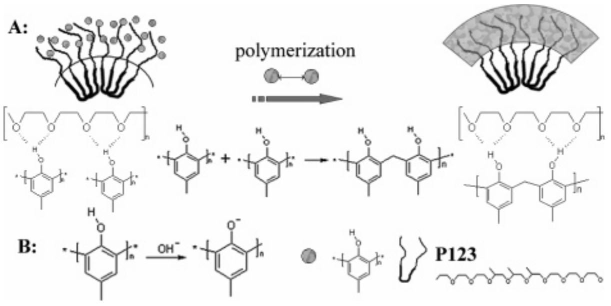
4.2 nm, calculated according to a reported method.[15] During the carbonization process from 400 to 700 °C, a significant weight loss (~16 wt %) can be observed in the TGA curves (Figure 1, Supporting Information) of as-made FDU-14, which can be attributed to the mass loss on the wall. The framework may shrink a lot, and many micropores will be derived on the pore wall. As a result, the pore size and the wall thickness of FDU-14 changed from 3.8 to 2.7 nm and from 4.2 to 3.6 nm, respectively. Meanwhile, the surface area and pore volume increase distinctly to 1150 m^2/g and 0.57 m^3/g, respectively.

TEM images of FDU-14 and C-FDU-14 show typical patterns of mesostructure of $Ia\bar{3}d$ symmetry. Although there is a weak 110 diffraction peak in the SAXS patterns, no typical pattern of $I4_132$ symmetry is observed, suggesting that the large domains are of $Ia\bar{3}d$ symmetry. The TEM images clearly reveal the homologous structure of FDU-14 and C-FDU-14 with a pore shrinkage after carbonization, which is consistent with the N_2 adsorption results.

The framework components were characterized using ^{13}C solid-state NMR, FTIR, and C:H:O elemental analysis. The ^{13}C solid-state NMR and FTIR spectra (Figures 2 and 3 in Supporting Information) show that as-made FDU-14 is composed by phenolic resin and triblock copolymer P123. After decomposition of the template at 350 °C in nitrogen, all of the typical signals and bands of triblock copolymer P123 in NMR and FTIR spectra disappear and only those of phenolic resin are detected. It indicates the almost complete removal of triblock copolymer and the formation of a polymer framework. The framework consists of 78.1% C, 4.3% H, and 16.1% O, with a molar ratio C:H:O of 6.5:4.3:1, which is in good agreement with that of phenolic resin. Homologous C-FDU-14 possesses a carbon framework composed of C (92.1%), H (1.9%), and O (6.0%).

We proposed a possible formation mechanism of FDU-14 in Scheme 1, which is constructed on the basis of the well-defined structure of phenolic resin. Condensation polymerization of phenol and formaldehyde forms polymethylenephenol, as shown in Scheme 1A, in a weak basic solution. The resols can interact with the hydrophilic PEO blocks of P123 by hydrogen bond interactions.[16] Cooperative assembly results in resol-*block*-copolymer mesophase in the dilute solution. Further polymerization of resols leads to the formation of the polymer framework of the mesostructure. In the case of relatively strong basic condition (pH > 9), the resols may transform to resol anions (Scheme 1B). Interaction between resol and template is destroyed due to the weak hydrogen bond between anions and P123. At neutral or weak acidic media (pH 4−8), the polymerization is too slow. This process is similar to the formation of mesostructured silicates; however, one-layer closed H-bonding may occur in the polymer case.

Scheme 1. (A) Possible Formation Mechanism of FDU-14. (B) Resol Anions Formed in Strong Basic Media



In summary, a dilute aqueous strategy has, for the first time, been conducted to fabricate a novel bicontinuous cubic mesoporous polymer and carbon with $Ia\bar{3}d$ symmetry. The simplicity of this synthetic method can generate a family of mesoporous polymers with a variety of properties. Moreover, the obtained mesoporous polymer and carbon have large surface area (up to 1150 m^2/g) and uniform pore size (~3 nm) and may have excellent properties in many application fields.

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Supporting Information Available: Synthesis detail, ^{13}C solid-state NMR spectra, and FTIR spectra of as-made FDU-14 and FDU-14, and TG analysis of as-made FDU-14. This material is available free of charge via the Internet at http://pubs.acs.org.

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