

## Synthesis of Mesoporous Carbon Materials via Enhanced Hydrogen-Bonding Interaction

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Porous carbon materials are ubiquitous in separation,<sup>1,2</sup> catalysis,<sup>3</sup> and energy storage/conversion.<sup>4</sup> The nanocasting method using mesoporous silicas as scaffolds has been intensively explored recently for the replication of porous carbon materials with controlled mesopore structures.<sup>3–9</sup> The silica scaffolds are usually presynthesized through the use of certain surfactant templates.<sup>5</sup> The key drawbacks associated with this nanocasting method are (1) the extra step needed to prepare the scaffolds and (2) the sacrificial use of not only the silica scaffolds themselves but also the surfactant templates used in the process for generation of the above scaffolds. Furthermore, because of the harsh carbonization conditions that can degenerate both the fidelity of the replication process and the structural integrity of the replicating scaffolds, the nanocasting method is extremely difficult to adapt to the fabrication of large-scale ordered nanoporous carbon films or monoliths. More recently, our group<sup>10,11</sup> and several others<sup>12–15</sup> have reported alternative methods for the synthesis of highly ordered mesoporous carbons via self-assembly. The essence of such methods is the direct use of the self-assembly of block copolymers as templates for generation of porous carbon structures without the extra step of generating templating silica structures.

Although the commercially available and inexpensive Pluronic block copolymers have been extensively used as templates to prepare mesoporous silicas with various pore structures,<sup>16</sup> their direct applications in synthesizing porous carbon materials have met with only limited successes<sup>10–14</sup> because of the stringent reaction conditions required. For example, the direct template synthesis of ordered porous carbons reported by Tanaka et al.<sup>12</sup> requires silicon wafer substrates and film morphologies, as well as the use of triethyl orthoacetate (for some unknown reasons). The porous carbon–particle synthesis developed by Zhao and co-workers<sup>13</sup> extends to only an extremely narrow pH range (8.5). Clearly, a general and robust method for the synthesis of ordered mesoporous carbons under a wide range of reaction conditions is yet to be developed. Herein, we report the synthesis of highly ordered mesoporous carbon structures based on a commercially available triblock copolymer (Pluronic F127, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>) as a structure-directing agent and a mixture of phloroglucinol and formaldehyde as an inexpensive carbon precursor under mild and widely variable processing conditions. The nanostructured carbons in the forms of monoliths, fibers, sheets, and films can be readily synthesized via this self-assembly method.

To probe the structural criteria for the self-assembly synthesis of ordered nanoporous carbons, we have examined the uses of three phenolic resin monomers for preparation of mesostructured resins: phenol, resorcinol, and phloroglucinol. The prerequisite for the generation of highly ordered mesostructures through self-assembly is the strong and collective interactions among the reacting species.<sup>10</sup> The three monomers used in this investigation can form single, double, and triple hydrogen bonding to the polyethylene (PEO)

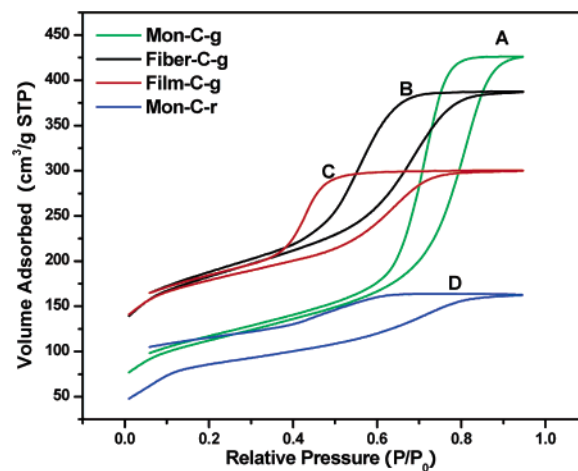


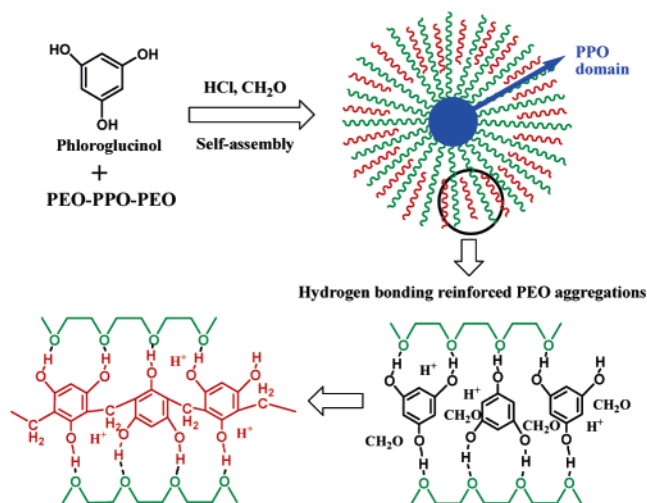
Figure 1. N<sub>2</sub> adsorption isotherms.

chains of F127 and thereby allow the study of the hydrogen-bonding effect on self-assembly.

The polymerization of phenol was very slow in the presence of F127 with HCl concentration lower than 10<sup>–2</sup> M.<sup>13</sup> In an ethanol/water mixed solvent containing 10<sup>–2</sup> M HCl, it took ~2 to 3 weeks to precipitate the phenol/formaldehyde polymer out of the solution at room temperature. The resulting polymer yielded porous carbons possessing very low surface areas (<5 m<sup>2</sup>/g). Resorcinol polymerized slightly faster than phenol. The polymerization time of resorcinol in 10<sup>–2</sup> M HCl at room temperature was ~1 week. The resulting soft polymers were further cured at 100 °C. Curve D in Figure 1 is the N<sub>2</sub> adsorption isotherm of a carbon made from resorcinol, which is denoted as Mon-C-r. The specific surface area of Mon-C-r is 288 m<sup>2</sup>/g, which is mainly contributed by micropore surfaces. The isotherm has a sharp slope at relative pressure from 0 to 0.1, which can be attributed to the presence of micropores, and a small slope at relative pressure from 0.4 to 0.8, which indicates a broad pore-size distribution in the mesopore range. The pore-size distributions are given in Figure S1 of the Supporting Information.

Phloroglucinol, however, polymerized much faster than either resorcinol or phenol. It took only ~40 min to a few hours to polymerize phloroglucinol with formaldehyde in ethanol/water solution of F127 in 10<sup>–2</sup> M HCl. Mesoporous carbons with highly uniform mesopores can be made in a wide composition range of weight ratios of phloroglucinol:F127:formaldehyde:ethanol:water: HCl ≈ 1:1:0.26–0.48:150–1:90–10:0.03–0.003. As the reaction proceeded, the homogeneous reactant mixture separated into two layers within 30 min. The upper layer consisted mainly of water/ethanol, while the lower layer was a polymer-rich phase containing phloroglucinol/formaldehyde oligomers, F127, and a small amount of water/ethanol. The polymer phase was subsequently processed in three different ways to produce the mesoporous carbons with

Scheme 1. Localized Polymerization



Localized Polymerization in the PEO domain

monolith, fiber, and film morphologies, which were denoted as Mon-C-g, Fiber-C-g, and Film-C-g, respectively (see the Supporting Information). Their  $N_2$  adsorption isotherms (curves A, B, and C in Figure 1) clearly exhibit the isotherm steps corresponding to the mesopores, indicating that phloroglucinol is superior as a monomer for the preparation of mesoporous carbons in comparison to phenol and resorcinol. The BET surface areas of Mon-C-g, Fiber-C-g, and Film-C-g are 377.9, 593.0, and 569.1  $m^2/g$  and the corresponding average pore sizes are 9.5, 6.1, and 5.4 nm, respectively.

The phase separation of the polymer-rich solution from the ethanol/water solvent is the key to the wide processing conditions for synthesizing mesoporous carbons based on phloroglucinol. Phenolic resins, such as novolacs and resols, are known to form hydrogen-bonding networks with PEO-containing polymers (Scheme 1).<sup>17</sup> As shown in our previous work,<sup>10</sup> the hydrogen bonding is an important factor for the preferential organization of the carbon precursors according to the spatial arrangement of the hydrophilic blocks of F127. Therefore, the high hydroxy density in the oligomers formed from phloroglucinol provides the greater driving force for the self-assembly interaction with the PEO blocks, as compared with those provided by the oligomers from phenol and resorcinol. High-resolution scanning electron microscopic (SEM) images confirm that the pore structures of the carbon samples vary with the carbon precursors and the processing methods. Panels A and B of Figure 2 are the SEM images of monolithic samples Mon-C-r and Mon-C-g. In agreement with the BET measurements, no uniform mesopores were found for Mon-C-r, while Mon-C-g has a wormy structure with uniform mesopores. The wormy mesostructures can be assembled to more ordered hexagonal mesostructures through controlled solvent evaporation or shear force. Both spin coating and fiber extrusion were employed to provide the shear force for synthesizing the mesoporous carbon films and fibers with more ordered mesostructures. The SEM images (Figure 2C,D) confirm that samples Film-C-g and Fiber-C-g have more ordered structures. The synthesis of Fiber-C-g can be scaled up to 100 g. Flexible carbon sheets were woven with the ordered mesoporous carbon fibers (Figure s2 of the Supporting Information). Also, as shown in the Supporting Information, the X-ray diffraction (XRD) pattern of Fiber-C-g confirms the ordered hexagonal mesostructure.

In conclusion, phloroglucinol was found to be an excellent precursor for the synthesis of mesoporous carbons when commercially available triblock copolymers were used as structure-

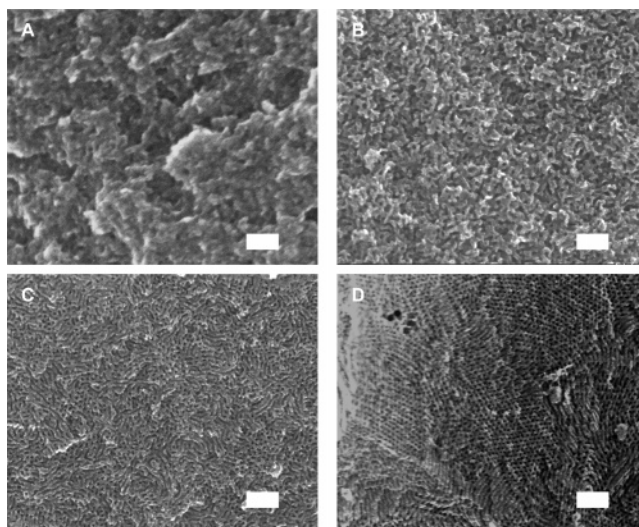


Figure 2. High-resolution SEM images of (A) Mon-C-r, (B) Mon-C-g, (C) Film-C-g, and (D) Fiber-C-g. The scale bar is 100 nm.

directing agents. The enhanced hydrogen bonding is the key to the preferential arrangement of carbon precursors in the selected domains of PEO-PPO-PEO triblock copolymers. Ordered structures can be achieved by shearing the polymer precursors before curing. Mild reacting conditions and wide composition ranges are the obvious advantages of this method over the techniques previously reported.

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**Supporting Information Available:** Experimental details, pore-size distributions, XRD, TEM, and photos of mesoporous carbon sheets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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