

Direct Preparation of Nanoporous Carbon by Nanocasting

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Porous carbon materials with high surface areas and large pore volumes are widely employed in many fields of science and technology, including water and air purification, separation, catalysis, and energy storage.^{1,2} They were originally prepared by carbonization of various raw materials, such as the naturally occurring precursors, wood, coal,^{3,4} lignite, coconut shell,⁵ and petroleum pitches,⁶ and lately synthetic polymers, for example, poly-(furfuryl alcohol)^{7,8} and phenol resin.⁹ These carbon materials often exhibit broad pore size distributions (PSDs) extending over the micro- and the mesopore range. Nevertheless, microporous carbon molecular sieves with extremely narrow PSDs were obtained via controlled pyrolysis of specific hydrocarbons over activated carbon.¹⁰

Templating techniques using inorganic materials with well-defined pore systems were introduced to produce carbon materials with narrow PSDs. This method is based on the pyrolysis of hydrocarbons, polymers, and other carbon precursors within the pore system of the template, followed by the selective elimination of the latter. Zeolites were used first as templates; however, the obtained carbon materials exhibited wide distributions of micro- and mesopore sizes.¹¹ The synthesis of macro- and mesoporous carbons with narrow PSDs using appropriate templates was far more successful. Periodic meso- and macroporous carbons were obtained using stabilized silica colloids^{12,13} and silica opals^{9,14} as templates. More recently, Ryoo et al.^{15–19} developed a templating method to prepare ordered mesoporous carbon molecular sieves, via carbonization of sucrose-filled ordered mesoporous silica using sulfuric acid as catalyst. They successfully obtained the carbon replicas of several silica mesophases.^{15–19} Employing phenol-formaldehyde resins instead of sucrose as carbon precursor, Hyeon and co-workers obtained the carbon replica of the MCM-48 mesophase,²⁰ as well as carbon with wormholelike pores²¹ and mesocellular carbon foams.²² Moreover, two groups were able to go back and forth from a mesoporous SBA-15 silica to its carbon replica.²³

The templating process using silica mesophases to generate periodic mesoporous carbon is quite tedious. It involves two main steps: (i) preparation and calcination of the silica mesophase, and (ii) filling the silica pore system by a carbon precursor, for example, sucrose or phenol resin, followed by the actual carbonization and selective removal of the silica framework. In addition, it would be difficult to make sure that the carbon precursor does not deposit on the external surface of the silica mesophase, thus leading to nontemplated carbon, most likely with a broad PSD. Here, we present a one-step preparation route to nanoporous carbon materials by the nanocasting technique. The method consists of preparing a cyclodextrin-templated silica mesophase via soft chemistry, followed by direct carbonization of the occluded cyclodextrins. In addition to being much simpler than the current templating approach, the nanocasting procedure affords purer nanoporous

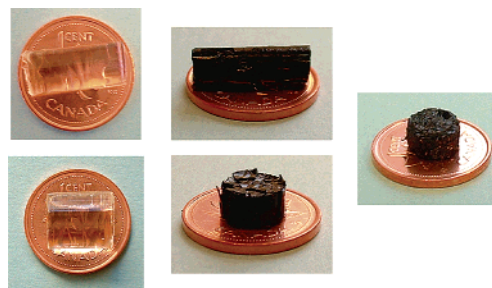


Figure 1. Images of monoliths at three stages.

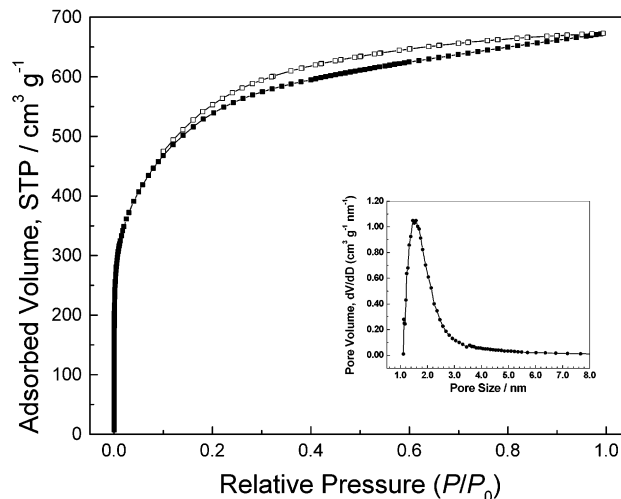


Figure 2. Nitrogen adsorption-desorption isotherm for nanoporous carbon (adsorption branch, ■; desorption branch, □). Inset: BJH pore size distribution obtained from the adsorption branch.

carbons as granules (in millimeter scale) or as monoliths (in centimeter scale). Cyclodextrins are cyclic oligosaccharides consisting of several $\alpha(1\rightarrow4)$ -linked glucopyranose units. Used as templates, they afford wormlike nanoporous silica materials.^{24–26} The supramolecular assembly (pseudopolyrotaxanes) from cyclodextrins and polymers was also found to regulate the pore structure of silica material via pH value, that is, from microporous to mesoporous.²⁶ Cyclodextrins can be employed not only as structure directing templates but also as carriers for metal nanoparticle precursors.²⁵

The cyclodextrin-silica organic-inorganic hybrid was prepared according to the reported procedure,^{24–26} except that sulfuric acid was used instead of hydrochloric acid. Sulfuric acid was preferred, because it catalyzes the carbonization of the cyclodextrin. The preparation procedure was as follows. Methylated β -cyclodextrin (Wacker Chem., 2.62 g) was dissolved in an aqueous pH 2.0 sulfuric acid solution (the concentration of methylated β -cyclodextrin was ca. 40 wt %) under stirring. Next, 5.12 g of tetramethyl orthosilicate (Aldrich, 99+%) was added under stirring. The mixture was stirred continuously until complete homogenization. The methanol formed

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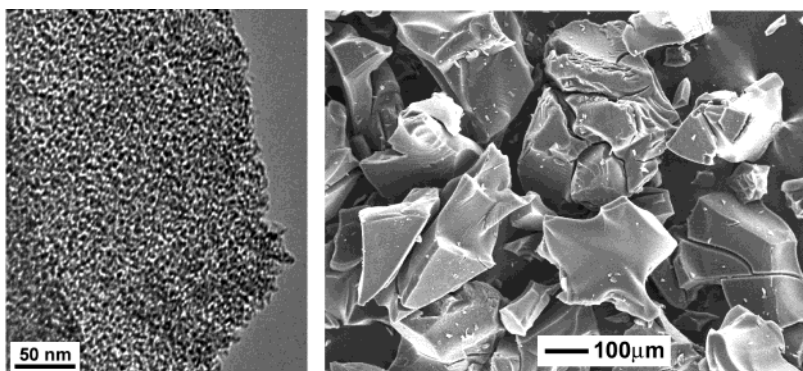


Figure 3. TEM (left) and SEM (right) images of nanoporous carbon.

during hydrolysis was removed via evaporation under reduced pressure until a thick transparent gel was obtained. The gel was aged in an open flask at room temperature for about 1 week. To obtain an organic–inorganic hybrid monolith, the same procedure was used except for the aging step. The gel was poured into a syringe, which was sealed by Parafilm with a small hole in the center, and was aged for several months.

The obtained colorless, transparent hybrid materials were subjected to carbonization in a tube oven with nitrogen flow (150 cm³/min) at high temperature (900 °C). The temperature was raised to 500 °C in 4 h, kept for 5 h, and then was increased to 900 °C in 7 h and kept constant for 4 h. A similar temperature program was used for the carbonization of the organic–inorganic hybrid monoliths, except that both temperature ramps lasted 24 h. After carbonization, the black carbon–silica composite was stirred gently in 5% HF solution to remove the silica template, followed by filtration and drying of the nanoporous carbon material. The removal of silica from the monolith composite was performed for a much longer time.

Monolith cyclodextrin–silica organic–inorganic hybrid samples with different sizes were prepared. Figure 1 shows images of monoliths at three different stages, that is, as prepared cyclodextrin–silica composites (colorless and transparent) (Figure 1, left), carbon–silica composites after carbonization (black) (Figure 1, center), and nanoporous carbon after removal of the silica template (black) (Figure 1, right).

A typical nitrogen adsorption–desorption isotherm is shown in Figure 2. The sorption data showed that the current carbon materials possess very high BET surface area (ca. 1970 m²/g) and high pore volumes (ca. 1.0 cm³/g). Using the BJH method combined with the recently proposed procedure for establishing the *t*-curve and calculating the film thickness of adsorbed nitrogen²⁷ (Figure 2, inset) showed that the current carbons exhibit a very narrow PSD with a maximum at 1.6 nm. Moreover, as shown in Figure 3, the TEM images for the porous carbon materials are similar to the images of the corresponding porous silica mesophases, showing a worm-holelike porous structure. X-ray diffraction showed that the obtained materials consisted of highly disordered, nongraphitic carbon.

Figure 3 (right) shows an SEM image for nanoporous carbon materials originating from a granular composite. The particles were crushed for SEM analysis, and yet their size was 100–300 μm, indicating that the original particles were essentially monoliths in nature. Therefore, the current one-step approach affords highly homogeneous porous carbon materials with millimeter to centimeter particle sizes using either granule or monolith cyclodextrin–silica precursors. The obtained carbon material was hard and dense and thus easy to handle. It can be used as a mold or template to produce other porous materials such as metals, metal oxides, and chalcogenides.

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