

Synthesis of New, Nanoporous Carbon with Hexagonally Ordered Mesostructure

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Nanostructured carbon materials such as carbon nanotubes^{1,2} attract rapidly growing attention due to the new possibilities for hydrogen storage in addition to the common applications as adsorbents,^{3,4} catalyst supports^{5,6} and electrode materials.⁷ Recently, Ryoo et al.⁸ reported the first synthesis of a new type of mesoscopically ordered nanoporous (or mesoporous) carbon molecular sieve designated as CMK-1 by carbonizing sucrose inside the pores of the MCM-48 mesoporous silica molecular sieve.⁹ The CMK-1 carbon, obtained after subsequent removal of the silica template with HF or NaOH solution, exhibited three narrow X-ray powder diffraction (XRD) peaks indicating the highly ordered pore arrangement. However, the XRD pattern indicated that the CMK-1 carbon underwent a systematic transformation into new structural symmetry from that of the silica template. Since then, there were no successful syntheses of ordered mesoporous carbon molecular sieves that could perfectly retain the structural symmetry for silica template.

Here we report the synthesis of ordered nanoporous carbon material designated as CMK-3 using the ordered mesoporous silica molecular sieve SBA-15¹⁰ instead of MCM-48. This synthesis is the first example of ordered mesoporous carbon molecular sieve retaining the structural symmetry for silica template. That is, unlike the previous case of CMK-1, the ordered structure of the CMK-3 carbon is exactly an inverse replica without involving structural transformation during the removal of the silica template.

The synthesis of CMK-3 was performed using SBA-15 silica as the template and sucrose as the carbon source. High-quality SBA-15 sample was prepared using the triblock copolymer, EO₂₀-PO₇₀-EO₂₀ (Pluronic P123, BASF), as the surfactant and tetraethyl orthosilicate (TEOS, 98%, Acros) as the silica source, following

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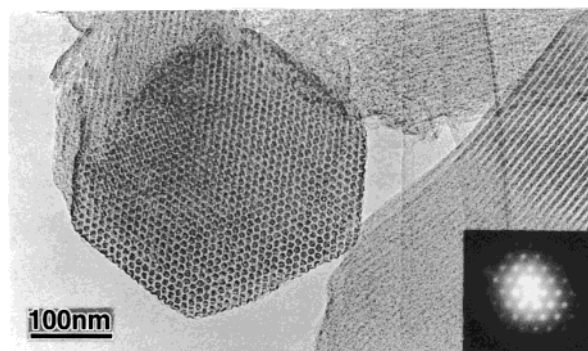


Figure 1. Typical TEM images of the ordered mesoporous carbon molecular sieve, CMK-3. This carbon was synthesized using sucrose as a carbon source and SBA-15 silica as a template. The TEM images were obtained with a JEM-4000 EX operated at 400 kV from the carbon material after silica template was completely removed with HF solution.

synthesis procedure reported by Zhao et al.¹⁰ except for the modifications of the starting composition and stirring mode. The starting composition was 10 g of P123:0.10 mol TEOS:0.60 mol HCl:20 mol H₂O. Typically, 1.1 g of TEOS was added to 19.0 mL of 1.6 M HCl containing 0.5 g of P123 at 308 K. The mixture was stirred with magnetic stirring until TEOS was completely dissolved. The mixture was placed in an oven for 24 h at 308 K, and subsequently for 6 h at 373 K. The product was filtered, dried without washing, and calcined at 823 K.

The calcined SBA-15 was impregnated with aqueous solution of sucrose containing sulfuric acid, similarly to the synthesis of CMK-1⁸ except for the different amounts of sucrose and H₂SO₄. Briefly, 1 g of SBA-15 was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H₂SO₄ in 5 g of H₂O. The mixture was placed in a drying oven for 6 h at 373 K, and subsequently the oven temperature was increased to 433 K and maintained there for 6 h. The sample turned dark brown or black during the treatment in the oven. The silica sample, containing partially polymerized and carbonized sucrose at the present step, was treated again at 373 and 433 K using the same drying oven after the addition of 0.8 g of sucrose, 0.09 g of H₂SO₄ and 5 g of H₂O. The carbonization was completed by pyrolysis with heating to typically 1173 K under vacuum. The carbon-silica composite obtained after pyrolysis was washed with 1 M NaOH solution (50 vol % ethanol-50 vol % H₂O) twice at 373 K or 5 wt % hydrofluoric acid at room temperature, to remove the silica template. The template-free carbon product thus obtained was filtered, washed with ethanol, and dried at 393 K. The energy-dispersive X-ray and thermogravimetric analyses showed that the silica content in the product was normally less than 5 wt % after the first washing with the NaOH solution. The second washing gave only trace amounts of silica, indicating that the treatment with NaOH or HF removed almost all of the silica.

Figure 1 shows two transmission electron micrograph (TEM) images for CMK-3 viewed along and perpendicular to the direction of the hexagonal pore arrangement. As the TEM images show, the structure of the CMK-3 carbon is exactly an inverse replica of SBA-15. The structure of SBA-15 consists of the hexagonal arrangement of cylindrical mesoporous tubes 9 nm in diameter, which is similar to the structure of the honeycomb-like MCM-41 silica⁹ except for random interconnection of the tubes by micropores present in the pore walls.¹¹ The high-resolution TEM images show that the carbon nanorods in CMK-3 are 7 nm in diameter, the centers of adjacent rods are 10 nm apart, and the

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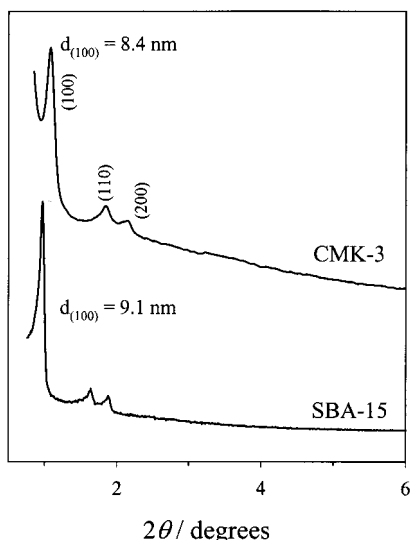


Figure 2. Powder XRD patterns of CMK-3 carbon and SBA-15 silica used as template for the CMK-3 synthesis. These XRD patterns were obtained using a Rigaku D/MAX-III (3 kW).

surface-to-surface distance is 3 nm. The carbon nanorods are interconnected by spacers, which are constituted by the carbon that filled the channel-interconnecting micropores within the SBA-15 wall. The TEM images in Figure 1 show that CMK-3 particles have exactly the same morphology as that of the SBA-15 silica particles.¹⁰ The fact that the carbon particles are not hollow indicates that the formation of the carbon structure occurred uniformly throughout the entire volume of SBA-15 particle. The synthesis experiment was repeated many times, increasing the synthesis scale from 1 to 20 g carbon per batch. The XRD pattern (vide infra), chemical analysis, and TEM images indicated not only that the sample was truly homogeneous within a selected batch but also that this synthesis was reproduced.

The ordered arrangement of the carbon nanorods in CMK-3 gives rise to the well-resolved XRD peaks shown in Figure 2, which can be assigned to (100), (110), and (200) diffractions of the 2-d hexagonal space group ($p6mm$), similar to the case of SBA-15. However, such fully ordered structures are difficult to obtain unless the pyrolysis temperature is increased to above 873 K. The carbon products obtained by pyrolysis below 773 K showed featureless XRD pattern or weak diffraction intensities, due to incomplete cross linking of the carbon frameworks. It is interesting that the hexagonal structural order is retained in CMK-3, while a featureless XRD pattern is obtained when carbon is synthesized using MCM-41 silica. This is because the main mesoporous channels in SBA-15 are interconnected through micropores inside the walls of the main channels, while the MCM-41 channels are not interconnected. In the case of MCM-41 silica, carbon infiltration leads to the formation of carbon rods that are not bonded to each other.

In Figure 3, the pore-size distribution obtained for CMK-3 from N_2 adsorption¹² is compared with that for SBA-15. The result indicates that the carbon is mostly nanoporous with quite narrow pore-size distribution centered at 4.5 nm, while the distribution for SBA-15 is centered at 9.2 nm. The 9.2-nm pores are larger

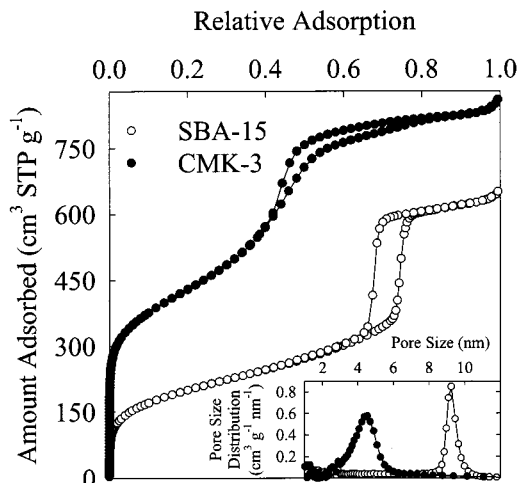


Figure 3. N_2 adsorption-desorption isotherm at 77 K for CMK-3 and SBA-15. Inset: The pore size distributions (calculated as described in ref 12).

by approximately 2 nm than the diameter of the carbon rods (7 nm) determined by high-resolution TEM. The difference may be related to the structural shrinkage during the carbonization process and perhaps to the existence of a certain distance between the SBA-15 pore walls and the carbon framework in the already formed SBA-15/carbon composite. The pore width of CMK-3 determined from nitrogen adsorption is consistent with the TEM data because the diameter of a cylinder, which can be placed in the void space between hexagonally arranged cylindrical rods with central axes 10 nm apart and surface distance of 3 nm would be 4.5 nm (or 3.5 nm in the case of hexagonal rods). The N_2 -adsorption data for CMK-3 provide the BET area of $1520 \text{ m}^2 \text{ g}^{-1}$ and the total pore volume of $1.3 \text{ cm}^3 \text{ g}^{-1}$, the latter being primarily related to the volume of the ordered pores, with minor contribution from micropores and secondary mesopores. The pore walls are constructed by disordered carbon networks similar to activated carbons prepared by pyrolysis of cellulose. The atomically disordered nature of the carbon frameworks is indicated by the appearance of two broad Raman peaks at 1350 and 1590 cm^{-1} .

In summary, a new, ordered, nanoporous carbon molecular sieve was synthesized using SBA-15 silica as the template, sucrose as the carbon source, and sulfuric acid as the carbonization catalyst. The advantage of this catalytic carbonization procedure is that the carbonization starts under mild conditions at low temperature, similarly to sol-gel processes. Uniform infiltration of carbon can be easily accomplished inside the silica nanopores so that the resultant carbon materials retain the mesostructural order of the silica templates. It is expected that this novel carbonization technique is suitable for the synthesis of other ordered, nanoporous carbon materials with interesting pore topologies. These nanostructured carbons will provide us with many new opportunities for applications as advanced materials.

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