

Mesoporous Carbon Materials

A Synthetic Route to Ordered Mesoporous Carbon Materials with Graphitic Pore Walls***Tae-Wan Kim, In-Soo Park, and Ryong Ryoo**

Recently, it has been discovered that a new class of mesoporous carbons can be synthesized using ordered mesoporous silica as a template.^[1–5] The porous carbons are characterized by regular arrangements of uniform mesopores that exhibit Bragg X-ray diffraction (XRD) lines similar to those of the mesoporous silica templates. The various pore structures with tunable diameters (typically in the range of 2–10 nm) are attracting much attention for the development of new adsorbents,^[1] catalysts,^[1f] and electrode mate-

[*] Prof. R. Ryoo, T.-W. Kim, I.-S. Park
National Creative Research Initiative Center for Functional Nanomaterials and
Department of Chemistry (School of Molecular Science—BK21)
Korea Advanced Institute of Science and Technology
Daejeon, 305-701 (Republic of Korea)
Fax: (+ 82) 42-869-8130
E-mail: rryoo@kaist.ac.kr

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rials.^[1g-j,4a,5a] Similar to other carbon materials, it is expected that these mesoporous carbons should exhibit widely different physicochemical properties depending on the detailed structure of the frameworks. However, the synthesis of such mesoporous carbons with pore regularity was hitherto limited to carbon frameworks with an amorphous-carbon-like nature.^[1a,2a,4a]

Herein, we report a synthetic strategy to fabricate nanoporous carbon materials with graphitic framework structures through in situ conversion of aromatic compounds to mesophase pitch inside the silica templates. The carbon frameworks are composed of discoid graphene sheets, which self-align perpendicularly to the template walls during synthesis. We have confirmed that this synthetic principle can be applied with silica templates that have various pore structures, and can provide materials exhibiting greater mechanical strength under compression and thermal stability in air.

Various aromatic compounds such as acenaphthene, acenaphthylene, indene, indan, and substituted naphthalenes^[6] are suitable as carbon sources for the present synthesis. Aluminum is incorporated in silica templates following the post-synthesis procedure.^[7] First, the mesoporous template and the carbon source are placed into an autoclave. The aluminum sites on the silica wall act as catalysts to form in situ mesophase pitch in the silica template pores at a low pyrolysis temperature (400 °C). Subsequently, the temperature of the autoclave is increased to 750 °C for carbonization of the mesophase pitch in the template. After the autoclave was cooled down, the product is further heated to 900 °C under vacuum in a fused-quartz reactor for the complete carbonization of the carbon source. The carbon product is then recovered by the removal of the silica template using an aqueous solution of HF or NaOH.

We have confirmed that the synthesis method is applicable to mesoporous silica templates with various structures, such as MCM-48 (cubic *Ia3d*), SBA-1 (cubic *Pm3n*), and SBA-15 (2-dimensional hexagonal *p6mm*) mesoporous silicas. The resultant carbons using these silica templates with acenaphthene are referred to as CMK-1G, CMK-2G, and

CMK-3G, respectively. As shown in Figure 1, the CMK-*n*G carbons exhibit XRD peaks below $2\theta = 5^\circ$, which is characteristic of the highly ordered mesostructures, and similar to those for CMK-*n* carbons synthesized with sucrose^[1a,c,2a] or furfuryl alcohol.^[1b,4a] Furthermore, the CMK-*n*G carbons are characterized by intense peaks at around $2\theta = 26, 45, 53$, and 78° , which correspond to the (002), (101), (004), and (110) diffractions of the graphitic frameworks, respectively. The diffraction intensities and peak widths are comparable to those of multiwalled carbon nanotubes (MWCNT; Ijin Nanotech, Seoul), and thus much more intense than those of CMK-*n* carbons with amorphous frameworks, or activated carbons. The powder XRD results are consistent with the Raman spectra of different carbon species shown in Figure 2. That is, the CMK-3G and MWCNT samples exhibit a very narrow G-band as compared with the other carbons. The transmission electron microscopy (TEM) images of the CMK-3G mesoporous carbon in Figure 3 show hexagonal arrays of carbon rods, 7 nm in diameter and 3 nm apart, similar to the structure of CMK-3 reported in our previous work.^[2] Most interestingly, the TEM images indicate a stacking of the discoid graphene sheets oriented perpendicular to the direction of the rods.

Figure 4 shows XRD patterns of the SBA-15 template containing carbonaceous products after the carbonization of acenaphthene at the given pyrolysis temperatures. The XRD pattern after pyrolysis at 400 °C shows a diffraction peak centered at $2\theta = 26^\circ$, which is very similar to the (002) diffraction of the graphite structure. A mesophase pitch is obtained by removing the SBA-15 template with HF. This result indicates that a liquid-crystalline mesophase with a *d* spacing of 0.36 nm is formed inside the SBA-15 channels during pyrolysis at around 400 °C. The mesophase pitch seems to lead to graphitic frameworks, as the carbonization is completed by further heating at 900 °C. The discoid alignment of the graphitic frameworks, as observed by TEM, is consistent with the general tendency of the edge-on anchoring of polycyclic aromatic hydrocarbons in mesophase pitch on silica surfaces.^[8]

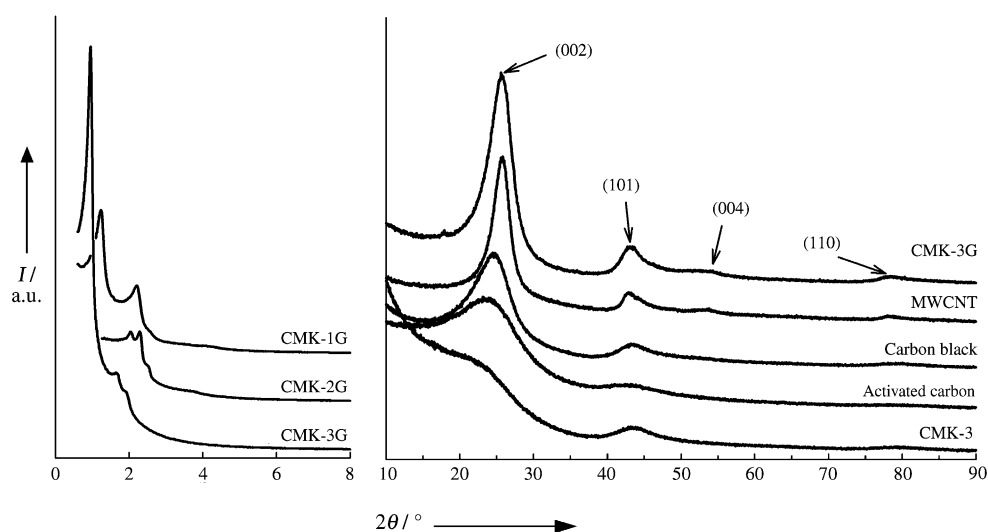


Figure 1. X-ray powder diffraction patterns for CMK-*n*G-type ordered mesoporous carbons in the low-angle region (below $2\theta = 8^\circ$), and other carbon materials in the wide-angle region ($10^\circ < 2\theta < 90^\circ$).

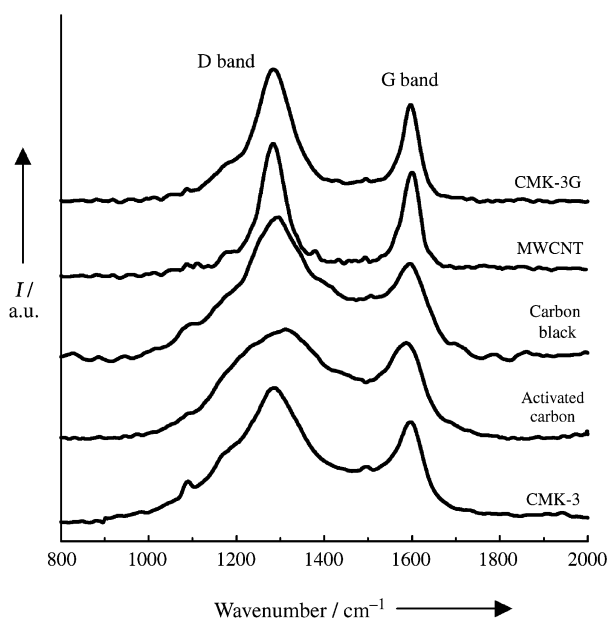


Figure 2. Raman spectra of CMK-3G ordered mesoporous carbon and other carbon materials.

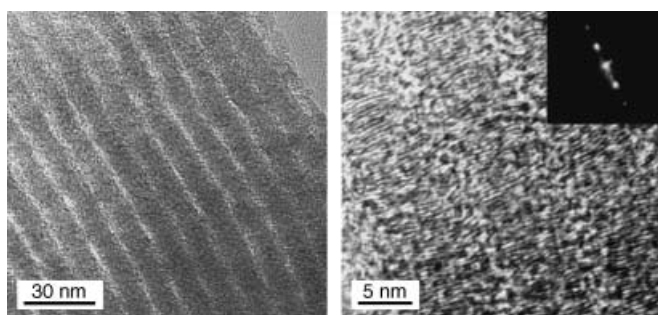


Figure 3. TEM image of CMK-3G (left) and its photomagnification (right) and the corresponding electron diffraction pattern (inset).

In Figure 5, the mechanical strength of the CMK-3G carbon is compared with those of other CMK-3 carbons prepared using furfuryl alcohol (CMK-3FA) and sucrose (CMK-3SC). The XRD intensity and peak resolution was monitored after subjecting the carbon powders to a pressure of 1.2 GPa for 1 hr in a mechanical press. This mechanical stability test showed almost no change in XRD pattern due to pressurizing in the case of CMK-3G. However, the XRD intensity was reduced very substantially for other CMK-3 carbons with amorphous frameworks (approximately 70% for CMK-3FA and 30% for CMK-3SC). This difference may be attributed mostly to differences in the nature of the carbon frameworks, either graphitic or amorphous.

Thermogravimetric weight changes were recorded in air to evaluate the thermal stability of the graphitic mesoporous carbon CMK-3G (Figure 6). The CMK-3G carbon and a reference MWCNT exhibited almost the same weight-change profiles. In contrast, CMK-3FA and CMK-3SC showed a comparable weight-loss profile at a lower temperature. Significant weight losses corresponding to the oxidation of

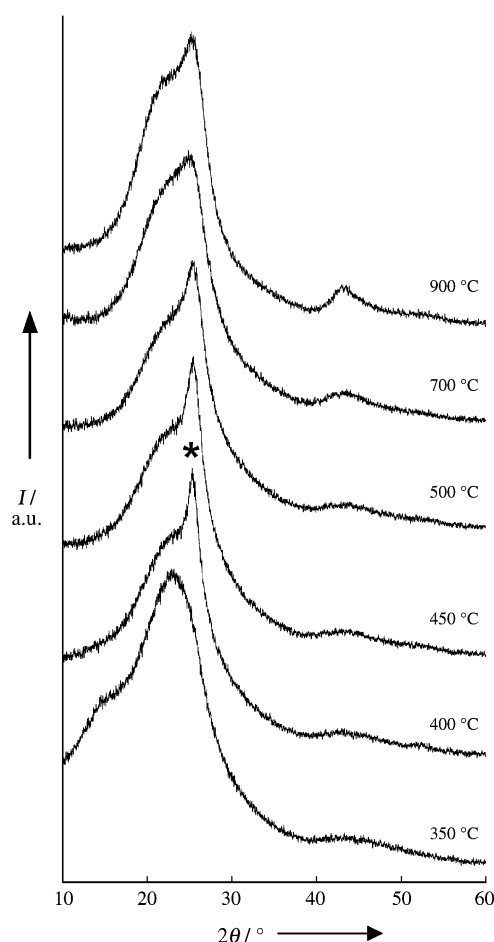


Figure 4. X-ray powder diffraction patterns for the SBA-15 template and acenaphthene composites during pyrolysis. The asterisk highlights the formation of a liquid-crystalline mesophase.

the carbons occurred in a narrow temperature range between 520 and 680 °C for CMK-3G and MWCNTs, and between 400 and 640 °C for CMK-3FA and CMK-3SC. Thus, the oxidation temperature for CMK-3G is similar to that of nanotubes, and significantly higher than that of mesoporous carbons with furfuryl alcohol and sucrose as carbon sources.^[1b,9] These results provide additional confirmation of the graphitized nature of the CMK-3G carbon frameworks, which is responsible for the much improved thermal stability in air.

In conclusion, ordered mesoporous carbons with various structures were synthesized through the in situ conversion of aromatic compounds to a mesophase pitch using mesoporous silicas MCM-48, SBA-1, and SBA-15 as templates. These nanoporous carbons with highly graphitic frameworks exhibit remarkably improved mechanical strength and thermal stability, in comparison with mesoporous carbons with amorphous frameworks. The underlying synthetic principle presented in this report may be important for the design of new mesostructured carbonaceous materials. Particularly, due to the graphitic nature of the frameworks, the resultant nanoporous carbons would attract much attention for the development of new electrochemical applications, such as fuel cells and lithium ion batteries. The edge-on graphitic structure

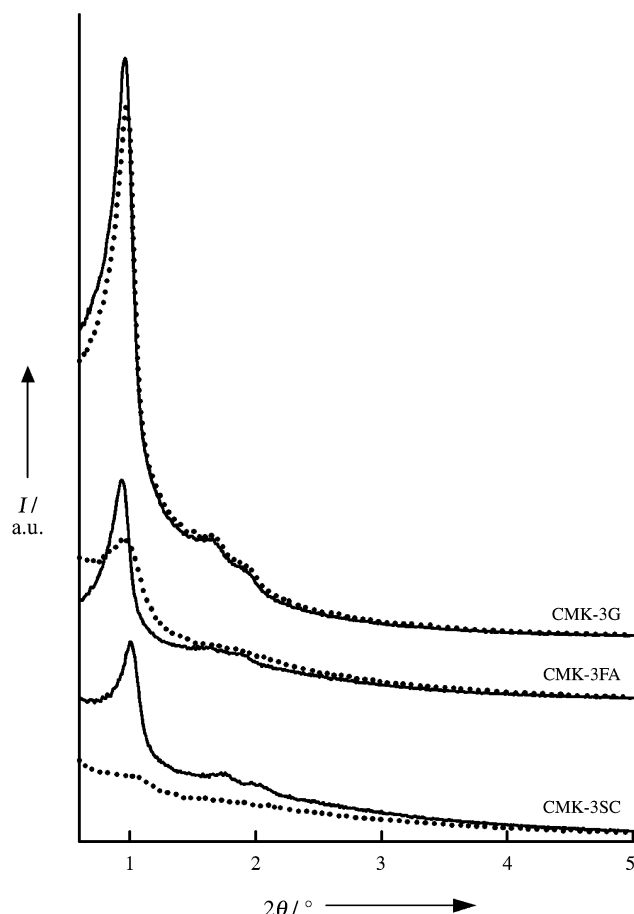


Figure 5. X-ray powder diffraction patterns before (—) and after (.....) pressurization (100 mg carbon, 10 mm palletized diameter; 1 hr at 1.2 GPa) for CMK-3G with acenaphthene as the carbon source, CMK-3FA with furfuryl alcohol, and CMK-3SC with sucrose.

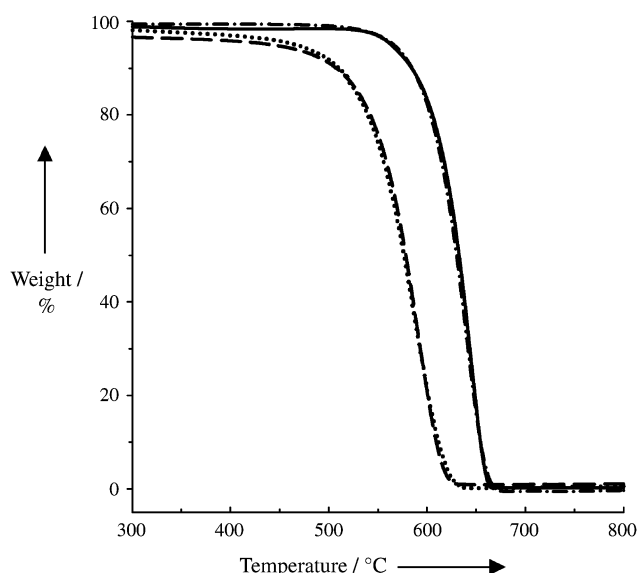


Figure 6. Thermogravimetric curves for the CMK-3G (—), MWCNT (---), CMK-3FA (.....), and CMK-3SC (-.-) carbon materials in air. The heating rate was $5.0^{\circ}\text{C min}^{-1}$.

exposed to pore surfaces may also give interesting properties as a support for catalytic metal clusters.

Experimental Section

SBA-15 silica was prepared using $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, BASF) and tetraethylorthosilicate (TEOS, Acros) according to the procedure described elsewhere.^[2a,10] In a typical synthesis batch, P123 (4.0 g) was dissolved in HCl solution (1.6 M, 150 g) at 35°C . TEOS (8.50 g) was added to the solution while stirring at 35°C , which was continued for 15 min at the same temperature. The mixture was placed under static conditions in an oven at 35°C for 24 h, and then heated to 100°C for 24 h. The SBA-15 product was filtered without washing and dried in an oven at 100°C . The product was washed with ethanol and calcined to remove the surfactant. Calcination was performed in air by heating the sample to 400°C under static conditions. Aluminum was incorporated within the calcined silica to obtain AISBA-15 with a Si:Al ratio of 20, following the impregnation procedure using an aqueous solution of AlCl_3 (98%, Junsei).^[7] The impregnation was carried out in a rotary evaporator at about 60°C . The aluminated sample was then immediately calcined in air at 550°C .

Other template samples such as MCM-48 and SBA-1 were synthesized following the synthesis procedures reported in the literature.^[11,12] Aluminum was incorporated in the same way as for SBA-15.

In a typical synthesis batch of CMK-3G, AISBA-15 (3 g) and acenaphthene (99%, Aldrich; 3.72 g) were combined in an autoclave (7 cm³ capacity) that can withstand high temperatures and pressures (made of INCONEL alloy 601). After being purged with Ar and closed tightly, the autoclave was heated in a furnace while the temperature was increased to 750°C at a rate of $2.5^{\circ}\text{C min}^{-1}$, and then maintained for 2 h. The product was collected after the autoclave was cooled to room temperature. (Care must be taken due to high-pressure generation in the autoclave.) Subsequently, the product was heated to 900°C under vacuum in a fused-quartz reactor. The carbon product was released by the removal of the silica template with a HF solution. The autoclave may be substituted with sealed quartz tubing in cases where small amounts of sample are prepared.

A sample of CMK-3FA was prepared with furfuryl alcohol (FA). Typically, AISBA-15 (1 g) was infiltrated with FA (0.9 mL; Aldrich) by incipient wetness at room temperature. The FA/AISBA-15 composite thus prepared was heated overnight in a closed vial at 90°C to polymerize the FA. Then, the FA/AISBA-15 composite was heated under vacuum to 350°C at a rate of $1.8^{\circ}\text{C min}^{-1}$ in a fused-quartz reactor. The sample was cooled to room temperature after remaining at 350°C for 6 h. To this sample, FA (0.63 mL) was subsequently added. The FA polymerization and heating to 350°C was repeated once again. Carbonization of the carbon source was completed in vacuum by heating to 900°C at a rate of $1.6^{\circ}\text{C min}^{-1}$. The carbon product was recovered by HF washing. A CMK-3SC sample was synthesized with SBA-15 and sucrose, following the procedure described elsewhere.^[2a]

XRD patterns were recorded with a Rigaku MultiFlex diffractometer operating with $\text{Cu K}\alpha$ radiation at 2.0 kW. The 2θ step width was 0.01° . Acquisition time was 1.2 s below 10° , and 1.0 s elsewhere. Raman spectra were recorded with a Bruker RFS 100/S spectrometer. A DPY421 diode laser pumped Nd:YAG laser operating at a wavelength of 1050–1060 nm and a power of 100 mW was used as the radiation source. TEM images were obtained with Philips F20 Tecnai transmission electron microscope taken at $490000\times$ magnification at an operating voltage of 160 kV. The TEM images were taken from thin edges of carbon particles mounted on a porous carbon grid. The mechanical stability was tested with a 12 Ton E-Z Press (ICL) with a 10 mm die set. Carbon samples (100 mg) were pressurized to 1.2 GPa and maintained for 1 h. Thermal stability of the carbon materials was investigated by recording weight changes on

a thermogravimetric analyzer (TA Instruments TGA 2050). Analysis under air was carried out at a heating rate of $5.0^{\circ}\text{C min}^{-1}$.

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