

## Fabrication of Novel Mesocellular Carbon Foams with Uniform Ultralarge Mesopores

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Received January 5, 2001

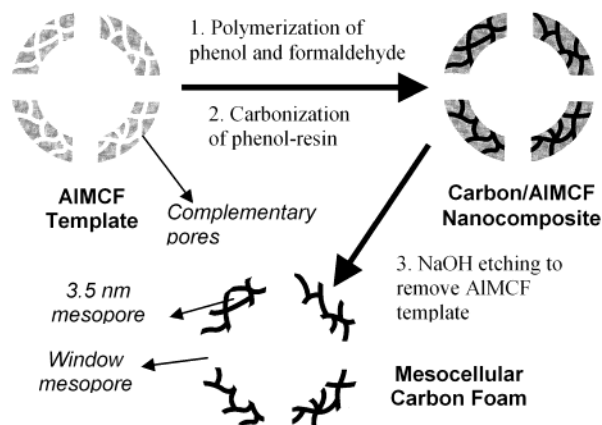
Revised Manuscript Received April 13, 2001

New mesocellular carbon foams with pore sizes of  $>20$  nm were synthesized. Template synthesis has been frequently applied to synthesize many porous materials. Several porous carbon materials have been fabricated using inorganic templates including zeolites,<sup>1</sup> alumina membranes,<sup>2</sup> opal,<sup>3</sup> and silica sols.<sup>4</sup> Recently, new mesoporous carbon materials were synthesized using mesoporous silica materials as templates.<sup>5,6</sup> These mesoporous carbons have been successfully applied as electrodes for the electrochemical double layer capacitor.<sup>7</sup> The pore diameter of these mesoporous carbons, however, is limited by the wall thickness of the template and is usually less than 5 nm. Our group synthesized mesoporous carbons with uniform  $\sim 10$  nm pores using surfactant-stabilized silica nanoparticles as templates.<sup>8</sup> These mesoporous carbons, however, possess isolated spherical pores, which severely limit their applications. Zakhidov et al. synthesized various macroporous carbons with closed-packed interconnected pores of  $>100$  nm using colloidal crystals of silicas as templates.<sup>3</sup> The pore dimensions of these macroporous carbons are too big for many chemical applications. For various applications including electrodes for supercapacitors and adsorption of bulky pollutants, ultralarge mesoporous carbons with well-interconnected pores of pore sizes ranging between 10 and 50 nm are necessary.<sup>9</sup> Herein we report on the synthesis of new mesocellular carbon foams with uniform ultralarge mesocells interconnected through uniform windows.

The overall synthetic procedure is described in Scheme 1. In the synthesis, mesocellular aluminosilicate foams were applied as template materials and in situ polymerized phenol-resin as the carbon source.<sup>10</sup> Mesocellular silica foams were synthesized by the reported method.<sup>11</sup>

Aluminum was incorporated into the silicate framework through the impregnation method to generate strong acid catalytic sites for the polymerization of phenol and formaldehyde.<sup>11</sup> Several

**Scheme 1.** Schematic Illustration for the Synthesis of Mesocellular Carbon Foam



different mesocellular aluminosilicate foams (AIMCF) with various cell and window dimensions were applied as templates.

The following procedure describes one typical synthesis of mesocellular carbon foam. Mesocellular aluminosilicate foam with a high Al/Si ratio of 11.5, cell diameter of 27 nm, window size of 11 nm, BET surface area of  $546 \text{ m}^2 \text{ g}^{-1}$ , and total pore volume of  $1.87 \text{ cm}^3 \text{ g}^{-1}$  was applied as the template. An excess 1.4 mL of phenol per gram of the template was incorporated into the pores of AIMCF by heating a mixture of AIMCF and phenol at 413 K under static vacuum. The resulting phenol-incorporated AIMCF and formaldehyde were reacted in an autoclave at 403 K for 2 days inside the pores of AIMCF to yield the phenol-resin/AIMCF nanocomposite. The nanocomposite was heated at  $1 \text{ K min}^{-1}$  to 433 K and held at that temperature for 5 h under nitrogen flowing. The temperature was then ramped at  $5 \text{ K min}^{-1}$  to 1123 K and held at that temperature for 7 h to carbonize phenol resin inside the pores of AIMCF to get the carbon/AIMCF nanocomposite. During the heat treatment, unreacted phenol and formaldehyde were evaporated. The dissolution of the AIMCF template using 1 N NaOH in a 1:1 mixture of EtOH and H<sub>2</sub>O generated mesocellular carbon foam. Thermogravimetric analysis of the carbon material under oxygen flow showed residue of 1 wt %, demonstrating that the aluminosilicate template was successfully removed.

The structure of the mesocellular carbon foam and the mesocellular aluminosilicate foam were investigated by gas adsorption measurement, transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS) measurements.

The nitrogen adsorption/desorption isotherms of the mesocellular carbon foam (Figure 1) exhibited large hysteresis with sharp adsorption and desorption branches at high relative pressure, which is similar to the isotherms from the AIMCF template (see Supporting Information).<sup>10</sup> The sharpness of the isotherms indicates the narrow pore size distribution of large mesoporous

(11) In a typical preparation, 4 g of poly(ethylene oxide)-*block*-poly(propylene)-*block*-poly(ethylene oxide) triblock copolymer (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Pluronic P123, BASF) was dissolved in 150 mL of aqueous 1.6 N HCl at room temperature. 23 mg of NH<sub>4</sub>F and 3 g of trimethylbenzene (TMB) were added into the mixture. After stirring for 1 h at 313 K, 8.5 g of tetraethoxyorthosilicate (TEOS) was added to the mixture. The resulting reaction mixture was stirred at 313 K for 20 h followed by aging at 373 K for 24 h to get a white precipitate. The precipitate was filtered, dried in air, and finally calcined at 773 K for 8 h in air to get mesocellular silica foam. Aluminum was incorporated into the silicate framework through the impregnation method. 1 g of MCF was added into an aqueous solution containing 0.34 g of AlCl<sub>3</sub>·6H<sub>2</sub>O in 10 mL of water. The resulting slurry was stirred for 30 min. The powder was retrieved by filtration and was dried at 353 K in air. Finally, the Al-impregnated MCF was calcined at 823 K for 4 h in air to yield AIMCF. Si/Al ratio was derived from the XRF (X-ray fluorescence) measurement and was found out to be 11.5.

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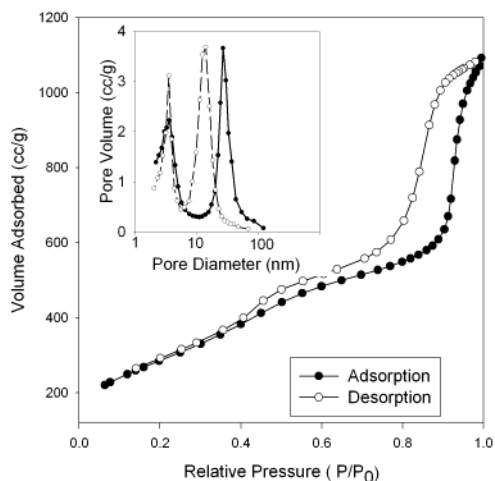
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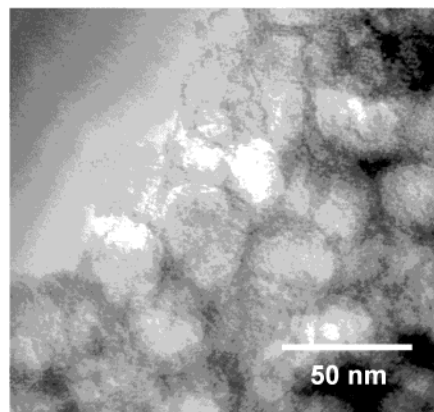


**Figure 1.** Nitrogen adsorption/desorption isotherms and the corresponding pore size distributions (inset) of mesocellular carbon foam. The isotherms were measured at 77 K using a Micromeritics ASAP2000 analyzer.

cells. The isotherms also showed a small hysteresis loop at medium relative pressure. The pore size distribution of the mesocellular carbon foam calculated from the adsorption branch of the isotherm using the BJH (Barrett–Joyner–Halenda) method exhibited two different pores centered at 27 and 3.6 nm (inset of Figure 1). The pore size analysis derived from the desorption branch of the isotherms showed bimodal pore arrangement with pores centered at 14 and 3.5 nm. These nitrogen adsorption/desorption isotherms and the corresponding pore size distribution data reveal that the mesocellular carbon foam possesses ink-bottle-like pores (similar to the AIMCF template, see Supporting Information) composed of main cells with a diameter of 27 nm that are interconnected by uniform 14 nm windows.<sup>10</sup> The carbon foam also possesses small mesopores centered at 3.6 nm resulting from the replica of AIMCF walls, which is consistent with small hysteresis at medium relative pressure in the isotherms.<sup>5,6</sup> The existence of these small mesopores of 3.6 nm which interconnect main cells is very important for the application perspective, because these interconnecting mesopores can facilitate better diffusion and transport of molecules between main mesocells.

The spherical cells of  $\sim 27$  nm are evident in the TEM image of the carbon material (Figure 2). The uniformity of these mesocells was also confirmed by the strong peak at  $2\theta$  of  $\sim 0.5^\circ$  in the small-angle X-ray scattering pattern of the carbon (see Supporting Information). The equal cell dimensions of the template and the carbon foam suggest that phenol-resin formation and the subsequent carbonization did not occur inside the main cells of AIMCF, instead these processes proceed inside complementary pores that interconnect main mesocells.<sup>12</sup> The result was also confirmed by the fact that the nitrogen adsorption/desorption isotherms and the corresponding pore distribution of the carbon/AIMCF nanocomposite are nearly identical to those of the AIMCF

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**Figure 2.** Transmission electron micrograph of mesocellular carbon foam. The image was obtained with a Phillips CM-20 electron microscope.

template (see Supporting Information). Phenol vapor can be incorporated into complementary pores at low vapor pressure, whereas it cannot be infiltrated into the main cells of AIMCF, because very high vapor pressure is required to be incorporated into large 27 nm pores with wide 11 nm pore windows. The result also demonstrates that carbon framework, formed inside the complementary pores of AIMCF, was well interconnected and strong enough to survive even after the removal of the template. The slight increase in the window dimension from 11 nm of the AIMCF to 14 nm of the carbon foam might result from the structure change during the carbonization step. The mesocellular carbon foam exhibited the BET surface area of  $1037 \text{ m}^2 \text{ g}^{-1}$  and the total pore volume of  $1.66 \text{ cm}^3 \text{ g}^{-1}$ .

We have made several other mesocellular carbon foams using mesocellular silica foam templates with different cell and window sizes. For example, using AIMCF with 30 nm cells and 14 nm windows as a template, mesocellular carbon foam with 30 nm cells and 18 nm windows was obtained. The mesocellular carbon foam possesses uniform mesopores of  $\sim 3.5$  nm, which were generated from the removal of aluminosilicate templates.

In summary, new mesocellular carbon foams were fabricated through the carbonization of phenol-resin inside the pores of mesocellular aluminosilicate foam templates, followed by the removal of the templates. The carbon foams could be applied to electrode materials for supercapacitors, catalyst supports, and adsorbents for bulky water-pollutants.

**Acknowledgment.** We are grateful to the Brain Korea 21 Program supported by the Korean Ministry of Education and the Korea Science and Engineering Foundation (Basic Research Program No. 98-05-02-03-01-3) for financial support.

**Supporting Information Available:** Nitrogen adsorption/desorption isotherms and the corresponding pore size distribution of the AIMCF template and the carbon/AIMCF nanocomposite and small-angle X-ray scattering patterns of the AIMCF template and the corresponding mesocellular carbon foam. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA015510N