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# Low-cost and facile synthesis of mesocellular carbon foams†

**Jinwoo Lee, Kwonnam Sohn and Taeghwan Hyeon***
*National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical Engineering, Seoul National University, Seoul 151-744, Korea. E-mail: thyeon@plaza.snu.ac.kr*

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**Mesocellular carbon foam composed of nanometer sized primary particles was synthesized using hydrothermally synthesized MSU-F silica as a template and poly(furfuryl alcohol) as a carbon source.**

Mesoporous carbons have attracted much attention because of their use as catalyst supports, adsorbents for bulky pollutants, and electrode materials.[1] Recently, new mesoporous carbons with connected pores have been synthesized using mesoporous silica materials as nano-scale templates.[2] Following the designed synthesis of MCM-48 templated mesoporous carbons by our group and by others, numerous ordered and disordered mesoporous carbons with connected pore structures have been synthesized using various mesoporous silicas as templates. To date, cubic,[2a] disordered,[2b] hexagonal,[2c] and foam-like[2d] mesostructured carbon materials have been synthesized. This technique of carbonization inside the pores of mesoporous materials has also allowed the elucidation of their pore structures. The 3-D wormhole-like pore structure in HMS silica[3] and the presence of complementary pores inside the channel walls of SBA-15 silica[4] were elucidated using this procedure. These novel mesoporous carbons have been successfully employed as electrodes for electrochemical double-layer capacitors[5] and fuel cells.[6] They have also been used as catalyst supports in the process of hydrogenation.[7] Generally, the pore sizes of these mesoporous carbons are limited by the wall thickness of the template silica materials, because these pores are generated from the dissolution of the silicate framework. Controlling the wall thickness of mesoporous silica has turned out to be a very difficult challenge, and the wall thickness is generally in the range of 2–4 nm.[8] In order to permit the facile diffusion and reaction of bulky molecules, mesocellular carbon foams with pore size ranging from 20 nm to 30 nm were synthesized by our group through the controlled incorporation of a carbon precursor (phenol resin) selectively into the complementary pores of the mesocellular silica foam templates.[2d] Although the mesocellular silica foam (MCF),[9] developed by Stucky and his coworkers, was successfully utilized as a template for mesocellular carbon foams, MCF is synthesized under strongly acidic conditions using an expensive silica source, TEOS. It is preferable to have a low-cost route for manufacturing silica templates, because the template has to be sacrificed when synthesizing the templated carbons. Recently, the preparation of C-MSU-H[10] was reported, whose structure is identical to that of the CMK-3 carbons, using MSU-H silicas[11] as templates. Because MSU-H is synthesized under neutral conditions using inexpensive sodium silicate as the silica source, the preparation of C-MSU-H is very cost-effective. The structure of MSU-F[11] is similar to that of MCF, and MSU-F is also synthesized under neutral conditions using inexpensive sodium silicate as the silica source. In our previous study, MCF carbons were synthesized by means of the vapor-phase infiltration of phenol, which is not a suitable method for large-scale production. Herein, we demonstrate the preparation of mesocellular carbon foams composed of nanometer-sized primary particles, designated as C-nano-MSU-F, using MSU-F silicas as templates, and through the use of a simple incipient wetness method using furfuryl alcohol. This MSU-F silica, with nanometer-sized primary particles, was synthesized by means of a modified version of the original synthetic procedure, employing post hydrothermal treatment at 100 °C. The nanometer-sized primary particles should allow better diffusion of large molecules to the active sites in the framework pores. For the purposes of comparison, we also synthesized mesocellular carbon foams using MCF silicas as templates and furfuryl alcohol as the carbon precursor.

MSU-F was synthesized following the procedure reported by Kim *et al.*,[10] except for the application of additional hydrothermal treatment at 100 °C for 24 h. After calcination at 550 °C for 4 h, alumination (Si/Al = 20) was performed, by means of the impregnation method, to generate acidic catalytic sites for the polymerization of furfuryl alcohol inside the mesopores. In a typical synthesis, 1 g of AlMSU-F is wetted with 2 ml furfuryl alcohol using the incipient wetness technique, and is then polymerized at 85 °C for 24 h. The resulting AlMSU-F/poly(furfuryl alcohol) composite is heated at 850 °C for 3 h under a nitrogen atmosphere. The dissolution of the AlMSU-F template using 3 M NaOH at 100 °C generates the mesocellular carbon foam designated as C-nano-MSU-F.

Fig. 1 shows the $N_2$ isotherms and pore size distributions of C-nano-MSU-F and MCF-carbon calculated using the BJH (Barrett–Joyner–Halenda) method. There are two types of pores which can be distinguished in C-nano-MSU-F. These are the 22 nm cellular pores and the 3.6 nm disordered pores. The BET surface area and single point total pore volume at $P/P_o$ = 0.98 are 716 m$^2$ g$^{-1}$ and 1.12 cm$^3$ g$^{-1}$, respectively. The cellular pores of the AlMSU-F template were preserved during the

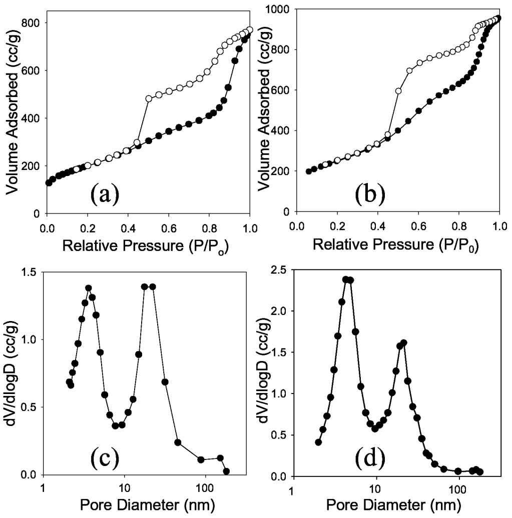

**Fig. 1** $N_2$ adsorption (filled circles) and desorption (empty circles) isotherms of (a) C-nano-MSU-F and (b) MCF-carbon. Corresponding pore size distributions of (c) C-Nano-MSU-F and (d) MCF-carbon, calculated from the BJH method.

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† Electronic supplementary information (ESI) available: $N_2$ adsorption–desorption isotherms, TEM and SEM images. See http://www.rsc.org/suppdata/cc/b2/b208642e/

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synthesis, because the furfuryl alcohol was polymerized around the acidic sites present in the surface of the AlMSU-F silicas. In contrast to CMK-5,[6] which is made using a similar method, it is not required that the unpolymerized furfuryl alcohol (FA) be removed before carbonization. The unpolymerized FA seems to be removed during heat treatment under an $N_2$ atmosphere. The 3.6 nm pores were generated by the dissolution of the silicate framework. MCF-carbon, synthesized using MCF silica as a template, also has 22 nm cellular pores and 4 nm disordered pores. The BET surface area and single point total pore volume of the MCF-carbon at $P/P_o = 0.98$ are 893 $m^2\ g^{-1}$ and 1.46 $cm^3\ g^{-1}$, respectively.

Fig. 2 shows transmission electron microscopic images (TEM) of C-nano-MSU-F and MCF-carbon. At low magnifications, the difference between C-nano-MSU-F and MCF-carbon is significant. The individual particles of C-nano-MSU-F are much smaller than those of MCF-carbon. The individual particle size of C-nano-MSU-F is around 300 nm. The presence of individual particles with a small size is highly desirable in mesoporous materials, because this favours the approach of large molecules to the framework pores. At higher magnifications, the two mesocellular carbons (C-nano-MSU-F and MCF-carbon) exhibit very similar pore structures. Both carbons have ~20 nm sized cellular pores and ~4 nm sized disordered pores. As expected, the smaller individual particle size of C-nano-MSU-F, compared to that of MCF-carbon, is derived from the smaller individual particle size of the MSU-F template in comparison to that of the MCF template (ESI† 2).

The smaller size of the individual particles in C-nano-MSU-F is confirmed by the scanning electron microscopy (SEM) images of C-nano-MSU-F (a) and MCF-carbon (b) (Fig. 3). The C-nano-MSU-F is comprised of 200–300 nm particles, while MCF-carbon is comprised of micrometer sized particles.

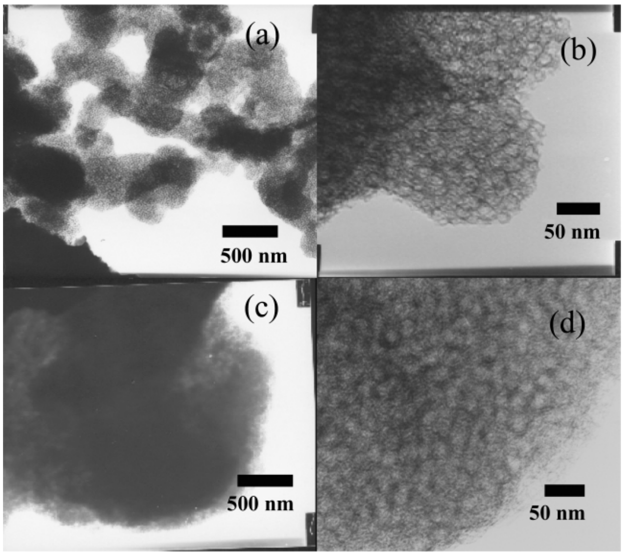

**Fig. 2** Transmission electron micrographic images (TEM) of C-nano-MSU-F (a, b) and MCF-carbon (c, d).

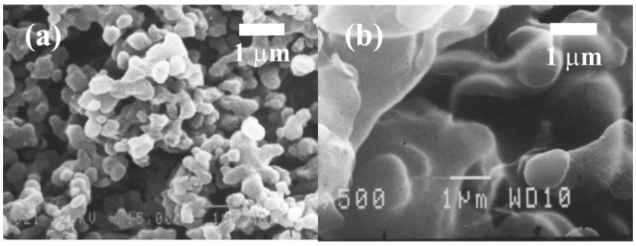

**Fig. 3** Scanning electron microscopic images (SEM) of C-nano-MSU-F (a) and MCF-carbon (b).

In conclusion, mesocellular carbon foams comprised of nanometer sized particles were fabricated using furfuryl alcohol as a carbon source and hydrothermally synthesized MSU-F silicas as templates. These mesocellular carbon foams possess large cellular pores (~20 nm) and disordered uniform pores (~4 nm), and are composed of nanometer sized primary particles. This combination of factors facilitates the diffusion of large molecules within these materials, thereby rendering them more effective for applications in catalysis and adsorption. The availability of an inexpensive and facile synthetic method for this novel mesocellular carbon foam will undoubtedly trigger research into its practical applications.

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