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Synthesis of Mesoporous Carbon Using a Fullerenol-based Precursor Solution via Nanocasting with SBA-15

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Here, we demonstrate mesoporous carbons with different amounts of fullerene cage (MCF) by using a fullerenol-based precursor solution via a nanocasting method with SBA-15 mesoporous silica. The fullerene cages embedded in the frameworks are electrochemically active, showing high potential as an electrode material for an electric double-layer capacitor.

In recent years, nanoarchitectured carbon materials, such as nanoparticles, nanotubes, and nanoporous materials, have received considerable attention, since they show outstanding electrochemical and catalytic performances exceeding those of traditional carbon materials.[1] In particular, mesoporous carbons play a vital role in modern scientific applications in research fields such as electrochemical analysis, batteries, and catalyst supports, due to their novel physical and chemical properties, chemical inertness, and low background current.[2,3] Until now, many synthetic procedures (including direct synthesis from the self-assembly of the carbon precursor and surfactant) have been proposed.[4–7] Over broad synthetic procedures, replication synthesis (i.e., nanocasting) with a hard template, which results in highly ordered porous structures of carbon materials, has received considerable attention. Many studies have been conducted on ordered mesoporous carbon and the related carbon materials by using various carbon sources.[8–15]

Among the several applications noted above, the electrochemical behavior of mesoporous carbon materials has been of interest, and many intriguing and superior developments have emerged. To enhance the electrochemical and conducting performance, loading or doping nanocrystals (e.g., metals, metal oxides, and graphitized structures) in the mesoporous carbon have been reported.[16–20] Ryoo, Terasaki, et al. successfully prepared ordered mesoporous carbons that support the high dispersion of Pt nanoparticles, and they showed high electrocatalytic activity.[16] As another example, boron- and nitrogen-doped mesoporous carbon materials have been developed, in which the dopants enhanced the capacitance of ordered mesoporous carbon.[19,20] Consequently, the loading or doping of functional elements into the frameworks can provide many opportunities to develop new solid-state properties.

In this communication, we report the first synthesis of mesoporous carbons with different amounts of fullerene cage (MCF) via nanocasting with SBA-15 mesoporous silica. The fullerene structures have very attractive properties, i.e., high electrical conductivity and rapid charge transport.[21] Therefore, by loading the fullerene cages in the carbon-based frameworks, the electrochemical performances will be improved relative to those of mesoporous carbons prepared with only sucroses. In addition, we propose a new synthetic concept for the functionalization of mesoporous carbon frameworks; in other words, the fullerene cages can be directly embedded without any complex post-treatments by introducing fullerenol as a building block together with general carbon sources (e.g., sucrose) into mesopores. The direct use of fullerenes as building blocks is not applicable to the present study due to their very poor water solubility. Here, we selected fullerenols because fullerenols with numerous hydroxy groups (over 16 units) on the fullerene cage show excellent water solubility and can be easily dissolved with carbon sources in a water-based precursor solution.

In this experiment, water-soluble fullerenol ($C_{60}(OH)_{40}$) was prepared first according to the literature.[22,23] For the preparation of the mesoporous carbons with different amounts of fullerene cage (MCF), SBA-15 (28 mg) was immersed in a precursor solution prepared by mixing sucrose (36 mg), a 0.27 mol H_2SO_4 solution (0.14 mL), and fullerenol (0, 5, and 30 mg). The carbon mole ratios derived from fullerene cages were adjusted to be 0%, 17%, and 50% of the total carbon content, labeled as MCF_0%, MCF_17%, and MCF_50%, respectively. The mixture was placed into an oven at 60 °C for 6 h, and the temperature was increased to 100 °C and maintained for 6 h (Figure 1). The obtained black powders were immersed again in the precursor solution and reheated using the oven. After that, the carbonization progressed by pyrolysis at 600 °C for 6 h under an N_2 atmosphere. After the removal of SBA-15 by a 10 wt % HF solution, the MCFs were obtained as a final product.

From the SAXS profiles of MCF (Figure S1[24]), well-resolved peaks assignable to the (10), (11), and (20) peaks of a hexagonal symmetry were confirmed. None of the peak positions changed after the replication from mesoporous silica, indicating that both sucrose and fullerenol could be successfully introduced into the mesopore space and that mesopores were densely filled by the carbon content after the carbonization reaction. Therefore, no mesostructural distortions were confirmed. From the TEM observation, it was proved that MCF consists of uniformly sized nanorods arranged in a hexagonal pattern (Figure 2). None of the nanorods were isolated, and they were regularly packed in relation to each other due to their interconnection by small bridges[14] (Figure 2). N_2 adsorption–desorption measurements of MCF were carried out to characterize the average pore space between the rods and specific surface

Figure 1. Systematic illustration for the preparation of mesoporous carbon with fullerene cages (MCF).

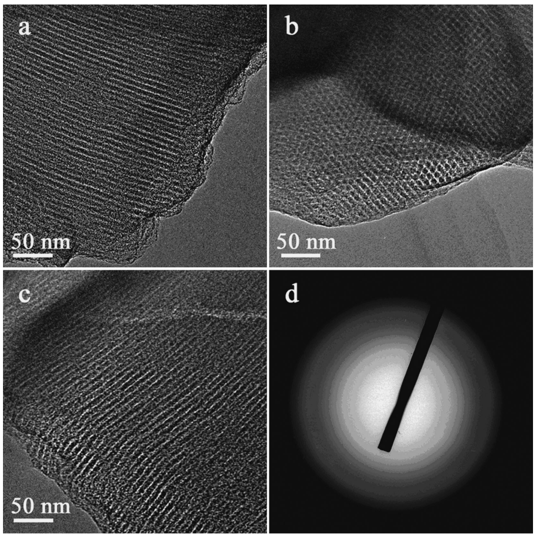

Figure 2. TEM images of (a) mesoporous carbon without fullerene cages and (b and c) mesoporous carbon with different amounts of fullerene cage ((b) MCF_17% and (c) MCF_50%). (d) Selected-area electron diffraction (ED) of MCF_50%. The *d* spacings of each of the two patterns are around 0.2 and 0.1 nm, respectively.

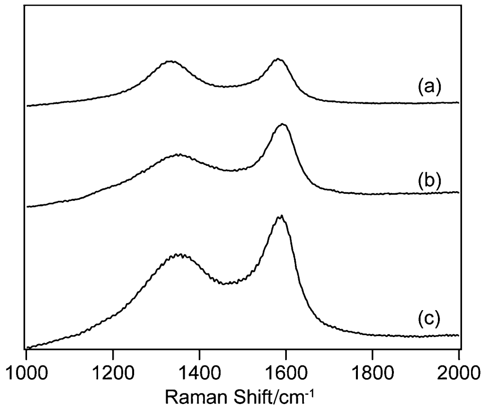

Figure 3. Raman spectra of (a) mesoporous carbon without fullerene cages (MCF_0%) and (b and c) mesoporous carbon with different amounts of fullerene cage ((b) MCF_17% and (c) MCF_50%).

Table 1. Comparison of the chemical compositions of MCF_0%, MCF_17%, and CMK-3

Samples	C (Carbon)	H (Hydrogen)	N (Nitrogen)	O (Oxygen)
MCF_0%	88.6	1.7	0.0	7.7
MCF_17%	88.1	1.5	0.0	8.4
CMK-3[a]	92.5	0.2	0.0	4.5

[a] As a reference, CMK-3 was prepared under carbonization conditions at 900 °C.

areas (Figure S2[24]). The nitrogen adsorption–desorption isotherms of the MCF were determined to be type IV with a small hysteresis loop, which is characteristic of mesoporous materials. The average pore space was measured to be around 4.9 nm using the NLDFT method. Even after doping fullerene cages, the average pore spaces did not change, indicating perfect replication from mesoporous silica. With the increase of the doped amount of fullerene, the BET surface areas gradually decreased. The respective surface areas of MCF_0%, MCF_17%, and MCF_50% were 1800, 1000, and 870 $\mathrm{m^2\,g^{-1}}$. Such a decrease of the surface areas may be due to reduction of mesostructural ordering by the addition of fullerene cages.

In the selected-area electron diffraction (ED), the arc-like patterns are indicative of the presence of carbon (Figure 2d). To obtain further important information on the microstructure of the carbons, Raman microprobe spectroscopy was carried out. The Raman spectra of MCF (MCF_17% and MCF_50%) are displayed in Figure 3. A lower-intensity broad D-band signal and a higher-intensity G-band were observed at 1351 and 1592 $\mathrm{cm^{-1}}$, respectively. The D-band is a characteristic peak of the disordered amorphous carbon state, while the G-band is attributed to the vibration mode of the hexagonal unit of carbon atoms.[25] In both cases (MCF_17% and MCF_50%), the ratios of the intensities of the G-band to the D-band were around 2. In the case of mesoporous carbon without fullerene cages (MCF_0%), the intensities of the G-band and the D-band were almost identical, meaning the mesoporous carbon prepared with sucrose was partially composed of graphite layers. Such a phenomenon has always been confirmed in general mesoporous carbon materials. The noteworthy point is that, with an increase in the amount of doped fullerene cages, the integrated areas of the G-band gradually increased (i.e., the number of the hexagonal units of carbon atoms increased). This is definitive evidence that the fullerene cage structures were well retained even after the carbonization of the frameworks.

The degree of carbonization of the MCF was confirmed by elemental analysis of C (carbon), H (hydrogen), N (nitrogen), and O (oxygen) (Table 1). One sucrose molecule has 11 hydroxy groups for each 12 carbon atoms, while one fullerenol has about 40 hydroxy groups for each 60 carbon atoms. The oxygen atomic ratio for one carbon atom of sucrose was relatively higher than that of fullerenol. Therefore, we expected that the relative amount of the oxygen atoms should be reduced by doping fullerenol. However, the actual amount of oxygen atoms in MCF was higher than that of fullerene-undoped mesoporous carbon even though exactly the same carbonization conditions

Table 2. Gravimetric and specific capacitances at 2 mV s^{-1} in 0.5 M H_2SO_4 of various samples

Samples	Capacitance	
	/F g^{-1}	/µF cm^{-2}
MCF_0%	50	28
MCF_17%	80	80
MCF_50%	57	65
MCF_17% before silica removal	6	—

were used. Not all of the hydroxy groups on the fullerene cages could effectively react during the carbonization process because fullerene is a very rigid and highly stable structure without any conformation changes due to its larger molecular size than that of sucrose. To achieve a high degree of carbonization, a thermal treatment over 900 °C under an N_2 atmosphere is needed, but the fullerene structure collapsed above 650 °C. Therefore, we used a carbonization process at 600 °C in this study.

Our MCF is expected to show enhanced electrochemical performance relative to that of general mesoporous carbons (prepared with sucrose) due to the electronic properties of the fullerene cages. As an example of preliminary applications, we demonstrate here an electrochemical application toward an electric double-layer capacitor.[26] The cyclic voltammograms (CVs) of the MCF materials (before and after the removal of silica) and fullerene-undoped mesoporous carbons (MCF_0% and CMK-3) are given in Table 2 and Figure S3.[24] They all showed clear peaks at ca. 0.6 V, which is generally attributed to the quinone/hydroquinone redox pair. Rectangular-shaped CVs, which are typical of a carbon-based electrical double-layer capacitor, were not obtained due to the low degree of carbonization (Table 1). The gravimetric capacitances were 50 (for MCF_0%), 80 (for MCF_17%), and 57 F g^{-1} (for MCF_50%). In comparison with MCF_0%, the gravimetric capacitances were increased by doping the fullerene cages. MCF_50% showed smaller capacitance than MCF_17% due to the decrease of the specific surface area (Figure S2[24]). MCF_17%, with the retention of a high surface area, exhibited the highest capacitance. The capacitance of MCF_17% reached the same degree of CMK-3 carbonized at 900 °C (77 F g^{-1}) despite of the low degree of carbonization. This result shows the potential usefulness of our MCF. A higher capacitance of MCF will be expected in the future by considering a preservation method of fullerene cages under a high-temperature carbonization process.

These results indicate that the fullerene cages in the pore walls of the MCF materials are easily accessible to guest ions in an electrolyte solution, increasing the total electrochemical double-layer capacitance. Considering the capacitance of pure fullerenes,[27] however, the capacitance of MCF was lower than we expected because not all fullerenes were exposed to the outer surface of the pore walls. From the theoretical calculation, it was expected that over 60% of all doped fullerenes in MCF_17% were exposed to the outer pore surface and reacted with the electrolyte.

In conclusion, we obtained novel mesoporous carbon by using a fullerenol-based precursor solution via the nanocasting method with SBA-15 mesoporous silica. The synthesis strategy can be extended to carbon nanomaterials of various shapes, such as other fullerenes (C_{70}), carbon nanotubes and graphenes with different physical and chemical properties. The resultant mesoporous materials can provide new possibilities for advanced applications. They can find applications in molecular sieves, gas storage, catalysts, adsorbents, battery electrodes, and supercapacitors.

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