

Fluorinated Carbon with Ordered Mesoporous Structure

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Because of their interesting structures and potential applications in separation, adsorption, or electronic devices, mesoporous carbons with ordered or uniform pore structures have been intensively studied in the past several years, primarily using templating synthetic route.^{1–5} Highly ordered mesoporous carbon was first reported by Ryoo's group, using ordered silica MCM-48 as a template and sucrose as a carbon precursor.¹ The carbonization of sucrose inside the pore channels of MCM-48 and removal of the silica framework have rendered a carbon material (CMK-1) with 3-D ordered pores ($I4_1/a$) and large surface areas.^{1,6} Subsequently, ordered mesoporous carbons with different mesostructures have been synthesized using varied templates and carbon precursors.^{7–13} More recently, carbons with controllable mesopore structures have also been synthesized using other methods.^{14–16} These studies significantly improve our ability to control the pore development process and widen the application areas of mesoporous carbons. On the other hand, the studies on the surface modification of ordered carbons are very limited.¹⁷ As an important modification method,^{18–20} fluorination has been used to modify the properties of graphite, activated carbons, and carbon nanotubes.¹⁸ Fluorinated carbons have found applications as lubricants or as cathode materials in lithium batteries. Here we report fluorination and structural change of highly ordered mesoporous carbons, which were synthesized by using ordered silica as a template and mesophase pitch as a carbon precursor.^{12,15} The mesoporous and fluorinated carbons with an ordered cubic structure were synthesized.

The ordered mesoporous carbon used here was synthesized using the ordered silica MCM-48 as a template. The MCM-48 template was synthesized with cetyltrimethylammonium bromide (CTAB) as a structure-directing agent, sodium silicate as a silica source, and tetraethylene glycol dodecyl ether (Brij30) as a modifier. The molar ratio used in this experiment was 8.3 $\text{Na}_2\text{Si}_4\text{O}_9$:5.7 CTAB:1 Brij30:2760 H_2O . A detailed synthetic procedure can be found in the Supporting Information. The obtained MCM-48 was then calcined at 550 °C in air to remove the surfactant. Subsequently, 1.1 g of MCM-48 was mixed in ethanol with 1.0 g of fine powder of mesophase pitch (Mitsubishi). After ethanol was gradually evaporated, the mixture was put into a tube furnace at 380 °C for 2 h under nitrogen protection, followed by the structure stabilization of pitch at 220 °C for 10 h in air.¹² The carbonization was carried out at 800 °C in a nitrogen atmosphere. Finally, the silica template was removed by hydrogen fluoride acid or concentrated NaOH solution, and the resulting carbon was denoted as C-48. The fluorination of dried ordered carbons was performed for 4 days in a U-shaped tube at room temperature (CF-1), 150 °C (CF-2), and 250 °C (CF-3), respectively, with a flow rate of 4.5 cm^3/min of diluted fluorine gas ($\text{F}_2/\text{He} = 5 \text{ vol } \%$). The color of the fluorinated carbon gradually changed from black to dark brown to gray to white for C-48, CF-1, CF-2, and CF-3, respectively.

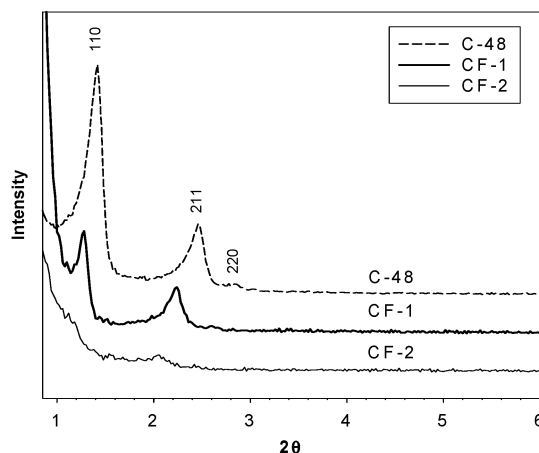


Figure 1. XRD diffraction patterns for carbon C-48 and the corresponding fluorinated samples CF-1 and CF-2.

Shown in Figure 1 is the X-ray diffraction pattern for the templated carbon C-48, fluorinated carbon at room temperature (CF-1), and 150 °C (CF-2). The templated carbon C-48 shows strong XRD peaks at $2\theta = 1.42^\circ$, 2.46° , and 2.84° , indicating the ordered pore structure of this carbon material. According to previous studies,^{1,6} the space group for carbon templated with silica MCM-48 is changed to $I4_1/a$, in comparison to the $Ia\bar{3}d$ space group for MCM-48. This structural change was explained in terms of the displacement model by Kaneda et al.⁶ Accordingly, the peaks for C-48 carbon can be assigned to the (110), (211), and (220) diffractions, respectively. Fluorination of C-48 at room temperature rendered a mesoporous fluorinated carbon with ordered pore structure, as evidenced by the XRD pattern for the fluorinated carbon sample CF-1 in Figure 1. One interesting finding is that the peak positions for (110) and (211) diffractions were gradually shifted to lower angles as the degree of fluorination gradually increased. The (110) and (211) diffractions for the fluorinated carbon CF-1 was shifted to $2\theta = 1.28^\circ$ and 2.24° , respectively, while for CF-2 the (110) diffraction became very weak and the (211) diffraction was shifted to 2.04° . The corresponding unit cell parameter, a_0 , changed from 8.80 nm for C-48 to 9.70 nm for CF-1 and 10.60 nm for CF-2. The shifts of peak positions and the increases in unit cell dimensions should be related to the framework expansion of the ordered mesoporous structure, caused by the fluorination of sp^2 and sp^3 carbons.^{20,21} Fluorine can react not only with H in CH bonds ($\text{CH} \rightarrow \text{CF}$) but also with the unsaturated bonds in the graphitic microdomains in carbons.^{20,21} The reaction of fluorine with unsaturated carbon will form sp^3 -hybridized carbon atoms and inevitably increase the bond length as well as the dimension of carbon framework, resulting in gradual structural degradation as shown in Figure 1.

Shown in Figure 2 is the transmission electron microscopy (TEM) image of the fluorinated carbon CF-1 prepared at room

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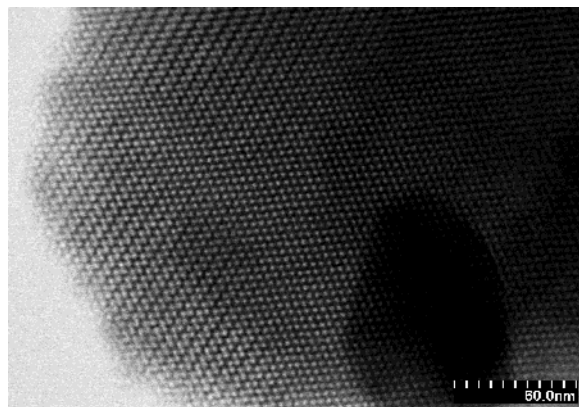


Figure 2. TEM image of the fluorinated carbon CF-1 prepared at room temperature.

temperature. The ordered structure of the fluorinated sample can be clearly observed. Even for the sample fluorinated at 150 °C (CF-2), the ordered structure was partially retained (see Supporting Information Figure S2). The energy-dispersive X-ray (EDX) spectra for CF-1, CF-2, and CF-3 (Supporting Information Figure S3) confirm that the degree of fluorination gradually increases with the reaction temperature. Both gravimetric measurement and EDX analysis showed that the conservative estimates for the F/C ratios are about 0.1 for CF-1, 0.5 for CF-2, and 0.8 for CF-3, respectively. Although there are some reports concerning the fluorination of carbon nanotubes,^{18,19,22} the current work has demonstrated that the fluorinated carbons with ordered mesoporous structure can be readily synthesized by reacting ordered carbons with fluorine gas at room temperature or elevated temperatures.

On the FTIR spectra (Supporting Information Figure S4), CF-1 shows an absorption band at 1106 cm⁻¹ related to the “semi-ionic” C–F bonds, whereas CF-2 and CF-3 exhibit a strong band at 1212 cm⁻¹ that can be attributed to the covalent C–F bonding.²³ These observations are in good agreement with the previous XPS study, in that the C–F bond changes from “ionic” to “semi-ionic” to covalent with increasing fluorination.²⁴ Compared to graphite,²¹ pitch-based ordered mesoporous carbons exhibit higher degrees of fluorination at much lower temperatures. The sample fluorinated at 150 °C shows FTIR characteristics that were observed on graphite fluorinated at ~600 °C. This can be attributed to the unique mesoporous structure and the higher content of sp³ carbon in our starting carbon material with the ordered pore structure.

The effects of fluorination on the structural changes for CF-1, CF-2, and CF-2 are also reflected on the nitrogen adsorption isotherms and the corresponding pore size distributions (Supporting Information Figure S5). The moderately fluorinated sample (CF-1) showed an adsorption step in the relative pressure range of 0.05–0.25 that corresponds to the capillary condensation of nitrogen in uniform mesopores, which is analogous to the unmodified ordered carbons. The peak maximum of pore size distributions for ordered carbon, CF-1, and CF-2 gradually changed from 1.9 to 2.0 to 2.4 nm, respectively. These results are consistent with the XRD results shown in Figure 1. However, the sample fluorinated at 250 °C (CF-3) did not show ordered pore structure, because in this case the severe fluorination reaction damaged the ordered primary arrangement of pores in the starting carbon. Even for this sample, the adsorption characteristics for mesoporous solids were observed with a surface area as high as 332 m²/g. The changes of the surface area and pore volume for C-48, CF-1, CF-2, and CF-3 were

insignificant if the change of mass was taken into consideration (Supporting Information Table S1).

In summary, a new fluorinated carbon with an ordered mesoporous structure was synthesized by reacting ordered carbon with fluorine at room temperature or moderately elevated temperature. The structure was confirmed with XRD, microscopy, FTIR, and nitrogen adsorption. Compared to fluorinated carbon nanotubes, the pore structure of the fluorinated ordered carbons can be well controlled by selecting proper silica templates or precursors. Furthermore, these fluorinated carbons can be synthesized on a much larger scale than the fluorinated carbon nanotubes. These fluorinated carbons with ordered pore structure could have great potential applications in electrochemistry or batteries.

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Supporting Information Available: Synthetic procedures for the ordered silica MCM-48; TEM images for the fluorinated samples CF-1 and CF-2; energy-dispersive X-ray (EDX) and FTIR spectra for fluorinated carbons CF-1, CF-2, and CF-3; nitrogen adsorption/desorption isotherms, pore size distributions, BET surface area, and total pore volume for carbon C-48 and fluorinated sample CF-1, CF-2, and CF-3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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