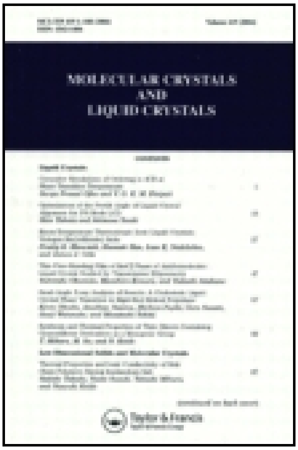

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Fluorine-Introduced sp^3-Carbon Sites in a Nano-Sized π-Electron System and their Effects on the Electronic Properties

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Activated carbon fibers (ACFs) are microporous systems comprised of a random network of nano-sized graphites. We investigated the structure and electronic properties of fluorinated ACFs in order to clarify the effects of fluorine-introduced sp^3-carbon sites on the electronic state of the nano-sized π-electron system. The orbital diamagnetism is monotonically reduced with increasing *F/C*, suggesting that introduced sp^3 carbon sites make the extended π-conjugated system reduced. In the intermediate fluorine concentration region, the localized spin concentration is enhanced by fluorination, reaching a maximum at $F/C \sim 0.8$, whereas it tends to be lowered in the high concentration region. The enhancement in the spin concentration is explained in terms of the local destruction of the π-conjugated system at interior carbon sites by fluorine-inherited sp^3-carbon sites.

Keywords: activated carbon fibers; nano-sized graphite; π-electron conjugated systems; sp^2/sp^3 mixed carbon; fluorination; orbital diamagnetism

INTRODUCTION

Activated carbon fibers (ACFs), which unusually have large specific surface areas (*SSA*) ranging from 1000 to 3000 m^2g^{-1}, are disordered carbon systems consisting of a three-dimensional random network of nano-sized graphitic domains, where each nano-sized graphite has three to four graphene sheets with the typical dimension of 2 × 2 to 3 × 3 nm.[1, 2] Nanographites, which attract great interests as a mesoscopic system intermediate between aromatic molecules and bulk graphite, are characterized with a combination of nano-sized π-electron conjugated systems and localized spins of edge origin.[3] Meanwhile, it is well known that bulk graphite generally forms charge-transfer compounds with various guest species.[4] But with fluorine, graphite generates another kinds of compounds, where fluorine is covalently bonded to an sp^3-hybridized carbon.[5] Fluorination of ACFs provides an interesting aspect related to the introduction of sp^3-carbons into nano-graphites that are featured as finite-sized sp^2-carbon systems. In this paper, we clarify the effects of fluorine-introduced sp^3-carbon sites on the structure and the electronic state of the nano-graphites in ACFs by means of magnetic susceptibility, magnetization, thermogravimetry (TG), mass spectrometry (MS), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Pristine ACFs used in this study are commercially available samples (Kurare Chemicals, FR-20, $SSA \sim 2000$ m^{2}g^{-1}) prepared from phenol-based precursor materials. Before fluorination, pristine ACFs were heat-treated above each fluorination temperature under 1×10^{-3}Torr, in order to eliminate the absorbed gases in ACFs and to prevent unexpected reaction in the synthesis. In the case of well fluorinated samples, fluorination of ACFs was carried out by the direct reaction between fluorine gas and ACFs under various conditions of temperatures, fluorine pressures, and reaction times. On the other hand, slightly fluorinated samples were prepared by defluorination of low fluorinated samples at high temperatures because of the difficulty in preparation by the direct reaction. ACFs heat-treated at 200 °C in vacuum were prepared as nonfluorinated samples. In order to avoid the effects of water and so on, all measurements and handling of the samples were carried out in vacuum or in the Ar atmosphere. Magnetic measurements were carried out in the field up to 5 T between 1.6 K and 380 K for typically 20 mg of the samples vacuum-sealed in quartz tubes. Thermogravimetry and mass spectra were investigated in the temperature range up to 600 °C. XPS spectra were measured by using a Ulvac Phi Model 5600 spectrometer with Mg Kα (1253.6 eV) X-rays for the ionizing radiaton.

RESULTS AND DISCUSSION

The conditions for sample preparation are summarized in TABLE I. By the direct reaction with fluorine gas and ACFs, samples with the range from $F/C \sim 0.5$ up to $F/C = 1.2$ are obtained, where F/C represents the atomic composition ratio determined by the ratio of C_{1s} peak-area to F_{1s} peak-area in XPS. In bulk graphite, fluorination is completed at $F/C = 1$, because each carbon atom grabs one fluorine atom for the formation of sp^3 bonds. However in the case of ACFs, some samples have the value $F/C > 1$. This suggests a contribution of carbon atoms at the edge sites, which generates CF_2 bonds. The sample with $F/C = 1.2$ is fully fluorinated because of the absence of graphite peak in the X-ray diffraction pattern.[6] Sup-

TABLE I F/C of F-ACFs in the various preparation conditions. Temperature and time in the column denote defluorination temperature and time for $F/C \leq 0.48$, fluorination temperature and time for $F/C \geq 0.49$, respectively. Sample with $F/C = 0$ represents non-fluorinated ACFs heat-treated at 200 °C for 1 hour.

F/C	0	0.13	0.30	0.38	0.48	0.49	0.59	0.85	1.1	1.2
Temperature [°C]	200	600	500	400	200	R.T.	R.T.	100	150	200
Time [hour]	1	1	1	1	1	0.5	120	168	168	168
Pressure [atm]	-	-	-	-	-	0.1	0.1	1	1	1

posing condensed polycyclic aromatic molecule $C_{216}H_{36}$ with an in-plane size of about 25 Å as a representative of a graphene sheet constituting the nanographite of ACFs, each nano-sized graphene has 150 interior carbon sites and 66 edge carbon sites. In the edge sites, 36 carbon atoms generate CF_2 bonds and the others generate CF bonds, while each carbon atom grabs one fluorine atom at the interior carbon sites. Then, the composition ratio of the fully fluorinated samples is calculated to be $F/C = 1.17$. Good agreement of the experimental value with the calculation at the fully fluorinated sample supports the structural assumption of nanographites based on the structural investigations for ACFs by X-ray diffraction and Raman spectroscopy.[2] Heat treatment of slightly fluorinated ACFs gives samples with $0 < F/C \lessapprox 0.5$. In this case, the F/C is calculated from a weight reduction estimated by TG with the assumption that defluorination mainly proceeds with the formation of CF_4, based on the mass spectrum during the defluorination process.

FIGURE I shows the typical results of the temperature dependence of magnetic susceptibility for fluorinated ACFs. In all the samples, the magnetic susceptibility appears to be a combination of a Curie-Weiss like term and a temperature-independent term χ_0, represented by the following equations;

$$\chi = \frac{C}{T - \Theta} + \chi_0 , \qquad (1)$$

where C and Θ are the Curie constant and the Weiss Temperature, respectively. From the comparison of the magnetization behavior shown later with the Brillouin curves corresponding to $S = \frac{1}{2}$, $S = \frac{3}{2}$ *etc.*, the observed spins are considered to have $S = \frac{1}{2}$. The fluorination dependence of the localized spin density N_s and χ_0 obtained from Eq. (1) with $S = \frac{1}{2}$ is shown in FIGURE II. In the range up to $F/C \sim 0.4$, N_s decreases as fluorination proceeds. Above that fluorine concentration, N_s increases with a maximum around $F/C \sim 0.8$, and then decreases toward zero as the fluorine concentration approaches $F/C = 1.2$. According to the calculation for fluorine-doped $C_{24}H_xF_{36-x}$ clusters by Saito *et al.*,[7] fluorine is more stable at the edge sites than in the interior region. Moreover, the fluorine concentration, where the edge carbon sites are fully fluorinated in the

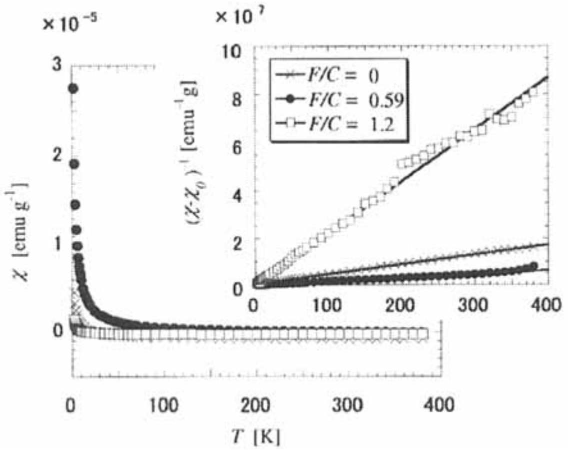

FIGURE 1 Typical temperature dependence of magnetic susceptibility of F-ACFs. The inset shows Curie-Weiss plots of the same data, where solid lines give least square fits.

model nanographene $C_{216}H_{36}$, is calculated to be $F/C = 0.47$. Therefore, the reaction of fluorine atoms mainly with edge carbon atoms takes place in the region $0 \leq F/C \lesssim 0.4$. The edge states peculiar to the π-electron conjugated systems having the so-called zig-zag edge, which Fujita *et al.*[9] recently proposed, is of great interest as the origin of localized spins of disordered carbon comprising nanographite-networks such as ACFs. If the localized spins of unfluorinated ACFs originates from these edge states, the decrease in the spin density in the range of $0 \leq F/C \lesssim 0.4$ is explained by the formation of sp^3-bonds between edge carbon atoms and fluorine atoms, which destroys edge states. In the range of $F/C \gtrsim 0.4$, where edge carbon atoms are completely terminated with fluorine atoms, the reaction of a fluorine atom with an inside carbon atom converts a graphite sp^2 bond into an sp^3 bond at the expense of a π-bond. This results in the generation of a dangling bond having a localized spin around the carbon site attacked by the fluorine atom. The maximum in the spin concentration emerging around $F/C \sim 0.8$ is explained by that about half of the interior carbon atoms are reacted with fluorine resulting in the formation of a maximum number of dangling bond spins. The disappearance of spins around $F/C \sim 1.2$ is caused by the completion of the reaction with all the carbon atoms in nano-graphites. The Weiss temperatures have slightly negative values all over the range of F/C, which suggest the presence of weak antiferromagnetic interaction between spins. The magnetizations of F-ACFs are all less than those expected from the Brillouin curve for $S = \frac{1}{2}$ at low temperatures, which are consistent with the observed negative Weiss temperatures. Moreover, from the magnetization, it is clear that the interaction between

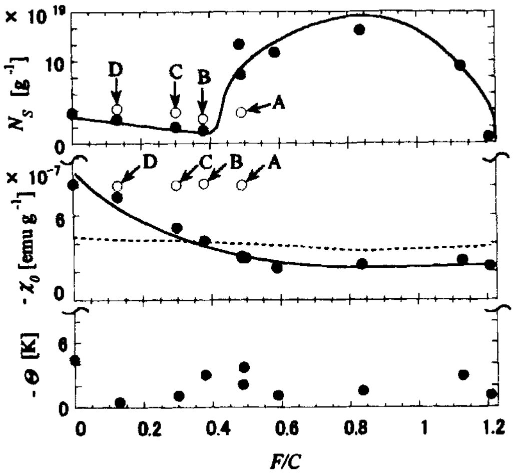

FIGURE II Spin concentration N_s, temperature-independent susceptibility term χ_0, Weiss temperature Θ for F-ACFs with $F/C = 0 - 1.2$ (closed circle). Defluorination of slightly fluorinated ACFs by heat-treatment at 200, 400, 500, and 600 °C gives the samples with $F/C \lesssim 0.48$ (see TABLE I). A, B, C, and D denote non-fluorinated ACFs samples similarly heat-treated at 200, 400, 500, and 600 °C, respectively (open circles). Dotted line represents χ_{core} calculated by the Pascal's law. Solid lines are guides for the eyes.

spins becomes weak as the fluorine concentration increases, and eventually it becomes negligible at the full fluorine concentration. The decrease in the strengths of the interaction with fluorination is explained in terms of the change in the electronic origin of localized spins in F-ACFs. In the range of $0 \leq F/C \lesssim 0.4$, spins of edge-state origin play a major role in the magnetization, where the spins localized near the edge of nano-graphites are interacting with the mediation of conduction π-electrons.[3] On the other hand, the calculation by Saito *et al.* reveals the highly localized features of the F-induced spins on graphite nanoclusters.[7] Therefore, localized spins on the F-ACFs in the high fluorine concentration region behave like isolated spins.

The observed temperature-independent term χ_0 decreases monotonically with fluorination, and it becomes constant above $F/C \sim 0.5$. In the region of $F/C \lesssim 0.5$, the samples were prepared by heat-treatment, which may affect the magnetic feature of the samples. But, we emphasize that non-fluorinated samples similarly heat-treated do not show similar behavior as F-ACFs as revealed in FIGURE II. The decrease is certainly caused by fluorination. The χ_0 consists of the diamagnetism of inner-shell electrons χ_{core}, and the orbital diamagnetism of π-electrons extended on the plane of nano-graphite χ_{orb}. Because χ_{core} calculated by the Pascal's law is almost independent of F/C, the decrease in χ_0 in the range of $F/C \lessapprox 0.5$ is attributed to the dependence of χ_{orb} on the F/C. The decrease in the orbital diamagnetism χ_{orb} at the low fluorine concentration is associated with shrinkage of π-electron conjugated systems by the attack of fluorine to the edge carbon atoms. Above the region of $F/C \sim 0.4$, the π-electron conjugated system begins to be destroyed by the generation of fluorine-induced sp^3 defects at the internal carbon sites. Then, the orbital diamagnetism eventually becomes negligibly small above $F/C \sim 0.5$. The orbital diamagnetism disappears, soon after fluorine becomes to attack the internal carbon sites. This implies that a slight introduction of sp^3-carbon atoms causes a serious damage to the π-electron conjugated systems of nanographites.

SUMMARY

By means of fluorination of ACFs, the effects of the introduction of sp^3-carbons on the finite-sized sp^2-carbon systems is revealed. The F/C ratio of completely fluorinated samples supports the structural model of nanographites of ACFs presented by Kaneko *et al.*[1] The anomalous fluorine concentration dependence of the spin density and the decrease in the strengths of antiferromagnetic interactions induced by F-uptake can be explained by a successive change in the features of spins from edge-state spins to F-induced dangling bond ones.

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