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Fluorination of Carbon Nanostructures and Their Comparative Investigation by XPS and XAES Spectroscopy

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Abstract: X-ray photoelectron (XPS) and Auger electron (XAES) spectroscopies have been used to investigate fluorine interaction with surfaces of nanocarbons. MWCNT, SWCNT and Fiber were fluorinated in F\textsubscript{2} and HOPG in ClF\textsubscript{3} atmosphere at room temperature. The performed measurements imply that the surface of the samples is inert to the environmental before and after fluorination. The XPS spectra show that MWCNT and Fiber after fluorination have similar composition, which includes CF, CF\textsubscript{2} and CF\textsubscript{3} states, but MWCNT includes CF\textsubscript{4} state as well. During defluorination of the fluorinated HOPG sample with initial C-F bonds the formation of CF\textsubscript{2} and CF\textsubscript{3} states has been observed. XAES spectra show the absence of C-F bonding in the outer layers of fluorinated HOPG, MWCNT and Fiber, while C-F bonding exists in SWCNT.

Keywords: Nanocarbon, HOPG, fluorination, XPS, Auger

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INTRODUCTION

Fluorination of carbon nanotubes is one of the ways for deep functionalization and opens both great possibilities to replace the fluorine atoms with various functional groups and develop nanotube chemistry (1–3) for practical applications (4–6). Understanding the chemistry of carbon nanostructural materials is a crucial step towards their ultimate practical use. X-ray photoelectron spectroscopy (XPS) has been widely used to investigate the surface chemical states of carbon atoms after fluorination of carbon black, highly oriented pyrolytic graphite (HOPG), single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotubes (MWCNT) and carbon nanofiber (CNF) (7–17). It has been found that CF, CF, CF₂, CF₃ groups may form during fluorination of the above-mentioned materials. Both the number and relative intensities of the functional groups depend on the method of fluorination. Unfortunately, to our knowledge, there are no data on depth distribution in multilayered structures. A partial interest is the chemical state of the carbon atoms in the top layer of any carbon nanostructure. It is supposed that the only top layer of graphite is involved in the fluorination reaction at low temperatures, and that the outer fluorinated surface hinders further migration of fluorine to deeper layers (16).

The information depth (ID) of C 1s XPS spectroscopy with Al Kα excitation is about 10–12 monolayers (18). So the chemical states of carbon atoms in the top layer can be hardly identified using these excitation sources. Another problem concerns the possibility for detecting contaminations of the surface with adventitious carbon (AC). This problem is related to the question: Are the surfaces of the fluorinated carbon nanostructures inert to the environmental? Since ID of C KVV Auger spectroscopy in graphite is about two monolayers (18), these problems can be resolved using a combination of XPS and X-ray Auger electron spectroscopy (XAES). The present paper describes an approach to resolve the above-mentioned problems and presents some experimental data.

EXPERIMENTAL

CNF used in this study were prepared by pyrolysis of methane using Ni-containing catalyst (5). CNF have metal (Ni, Fe, Co) particles on the tips, which are washed out with weak hydrochloric acid solution. MWCNT were synthesized by pyrolysis of methane at an elevated temperature with the presence of a metal catalyst. SWCNT of 1.2–1.5 nm in diameter bound into bundles of about 10 nm in diameter were produced by the standard electrical arc method with the presence of Ni/Cr catalyst (6). Both carbon nanotubes and CNF were fluorinated with 1 atm F₂ gas at room temperature for 48 hours. The HOPG sample with dimensions 10 × 10 × 1 mm³ was fluorinated with 1 atm CIF₃ gas at room temperature for 60 hours. It was
found that the thickness of the sample increased from 1 mm up to 15 mm as a result of fluorination. The central part of the fluorinated sample remained hard after fluorination. We analyzed the top layer (region I), the middle of expanded part (region II) and the central hard part (region III) of the HOPG sample. The fluorinated HOPG sample was defluorinated at 270°C in the preparation chamber of the spectrometer without contact with environment before XPS study.

The experimental data were obtained using a MK II VG Scientific spectrometer. The C 1s and F 1s photoemission and C KVV Auger emission were excited using an Al Kα source with photon energy of 1486.6 eV. The pressure in both the analytical and preparation chamber was kept at $5 \times 10^{-10}$ mbar. Spectra were collected in the constant analyzer energy mode, with a pass energy of 20 eV and 0.1 eV step size. The energy resolution determined as full width at half-maximum of the Au 4f7/2 photoelectron line is 1.1 eV. We used an energy of 284.4 eV for charge reference of HOPG (19). The value of 285.0 eV was used for charge referencing of non-fluorinated nanotubes and CNF C 1s spectra.

**RESULTS AND DISCUSSION**

It is well known that metal and oxide surfaces adsorb carbon-containing molecules or in other words adventitious carbon (AC). It is quite easy to recognize them at metal or oxide surfaces, while in the case of carbon nanomaterials this may be a serious problem. To determine the degree of contamination of pure and fluorinated carbon surface by environmental AC we used XAES, which is highly sensitive to the state of the outer surface layer. We studied the C KVV spectra for AC at surfaces of different metals and their oxides and found that the C KVV line shape is independent of substrate, with carbon atoms having sp3–bonds (20). Comparison between the C KVV spectra of “reference AC” and studied samples (Figure 1) allows us to conclude that their surfaces are free of AC.

The survey XPS spectra of SWCNT, MWCNT and Fiber before and after fluorination show the presence of oxygen and metal impurities (about 1%). Figure 2 shows the C 1s XPS spectra for fluorinated SWCNT, MWCNT and Fiber. The C 1s spectra of the MWCNT and Fiber have similar line shapes excluding for the high-energy region. Fluorine content in MWCNT and Fiber is practically the same. The C 1s XPS spectra of SWCNT, MWCNT and Fiber were deconvoluted. The results are submitted in Table 1. The carbon states were identified in accordance with the relevant data for fluorinated polymers and fluorocarbons (17, 21). However, it was difficult to find correlation between the chemical states of fluorinated carbons and fluorine because of approximately equal intensities of CF, CF2, and CF3 states in the C 1s spectrum while the F 1s spectrum has only one state with an enhanced intensity. At the same time the peaks with the
largest binding energies in the C 1s and F 1s spectra may be assigned to CF₄
gas-like phase intercalated into MWCNT. The similar states were observed in
fluorographite (17).

Figure 3 shows F 1s XPS spectra for fluorinated SWCNT, MWCNT,
HOPG and Fiber. The widths of SWCNT, MWCNT and Fiber spectra are
considerably differ from that of HOPG. Obviously these effects are caused
by significant differences in a chemical environments of F-atoms.

Figure 1. C KVV spectra for pure HOPG, SWCNT and fluorinated MWCNT
and reference AC. Dissimilarity between the spectra of the samples and that of refer-
ence AC allows one to conclude that the samples do not contain AC.

Figure 2. C 1s XPS spectra for fluorinated Fiber, MWCNT and SWCNT.
In distinction to fluorinated MWCNT, in fluorinated SWCNT only one chemical state of fluorine appeared in the F 1s spectrum, which was identified as the singlet state. A similar spectrum was observed by Pehrsson et al. (7), however the most intense state was assigned to CF state.

Figure 4 shows HOPG C 1s spectra after fluorination. The C 1s spectrum of HOPG has two components as in (11) with a peak separation of about 2.5 eV. These peaks are assigned to $\text{C}-\text{CF}$ and $\text{C}-\text{F}$ bonds. This separation is more than that observed in polymers between peaks corresponding to $\text{C}-\text{CF}$ and $\text{C}-\text{F}$ bonds (21). The low-energy peak was shifted to 285.75 eV in accordance with energy for $\text{C}-\text{CF}$ state in poly(vinyl fluoride) (21). Measurements were carried out on three sections of the extended sample. The relation of $\text{C}-\text{CF}/\text{C}-\text{F}$ for those sections has changed insignificantly. It testifies that fluorination of the top layer did not retard penetration of F-atoms from a surface into deeper layers.

### Table 1. Deconvolution parameters of C 1s spectra for MWCNT, Fiber and SWCNT after fluorination

<table>
<thead>
<tr>
<th>Component</th>
<th>$E_b$(C 1s), eV</th>
<th>FWHM, eV</th>
<th>Relative intensity</th>
<th>Functional group</th>
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<tbody>
<tr>
<td>MWCNT + F</td>
<td>C1 285.6</td>
<td>1.2</td>
<td>4.4</td>
<td>C-CF</td>
</tr>
<tr>
<td></td>
<td>C2 286.9</td>
<td>1.5</td>
<td>1.5</td>
<td>C-CF$_2$</td>
</tr>
<tr>
<td></td>
<td>C3 288.2</td>
<td>1.5</td>
<td>1.8</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>C4 289.6</td>
<td>1.5</td>
<td>4.2</td>
<td>CF$_2$-CF$_n$</td>
</tr>
<tr>
<td></td>
<td>C5 291.4</td>
<td>1.6</td>
<td>2.2</td>
<td>CF$_2$</td>
</tr>
<tr>
<td></td>
<td>C6 293.3</td>
<td>1.2</td>
<td>1.7</td>
<td>CF$_3$</td>
</tr>
<tr>
<td></td>
<td>C7 295.9</td>
<td>2.6</td>
<td>2.0</td>
<td>CF$_4$</td>
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<tr>
<td>Fiber + F</td>
<td>C1 285.0</td>
<td>1.2</td>
<td>14.1</td>
<td>C-C</td>
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<tr>
<td></td>
<td>C2 285.6</td>
<td>1.4</td>
<td>3.2</td>
<td>C-CF</td>
</tr>
<tr>
<td></td>
<td>C3 286.9</td>
<td>1.4</td>
<td>3.7</td>
<td>C-CF$_2$</td>
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<tr>
<td></td>
<td>C4 288.3</td>
<td>1.4</td>
<td>2.9</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>C5 289.6</td>
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<td>5.2</td>
<td>CF$_2$-CF$_n$</td>
</tr>
<tr>
<td></td>
<td>C6 291.4</td>
<td>1.6</td>
<td>2.9</td>
<td>CF$_2$</td>
</tr>
<tr>
<td></td>
<td>C7 293.2</td>
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<td>1.2</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>SWCNT + F</td>
<td>C1 284.8</td>
<td>1.7</td>
<td>0.72</td>
<td>C-C</td>
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<tr>
<td></td>
<td>C2 285.6</td>
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<td>1.1</td>
<td>C-CF</td>
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<td></td>
<td>C3 286.9</td>
<td>1.6</td>
<td>2.5</td>
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<td>C4 288.2</td>
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<td>C8 295.9</td>
<td>1.3</td>
<td>0.25</td>
<td>CF$_4$</td>
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The C 1s spectra for HOPG after defluorination are presented in Figures 5 and 6. As a consequence of defluorination, one can observe the presence of C=C-C state as well as CF$_2$ and CF$_3$ states of carbon atoms.

The C KVV Auger spectra in Figure 7 allow us to obtain information about modification of chemical state of C-atoms on the HOPG surface after defluorination. After heating for 4 minutes, the C KVV spectrum was not changed and after 10 minutes it was transformed to HOPG-like. Such spectrum we observed on surface of HOPG after ion sputtering. Apparently the process of defluorination results in amorphous carbon layer on the surface.

![Figure 3. F 1s XPS spectra for fluorinated Fiber, MWCNT, SWCNT and HOPG.](image)

![Figure 4. C 1s XPS spectra for 3 sections of fluorinated HOPG as shown in framing.](image)
The carbon atoms in HOPG, SWCNT, MWCNT are in an sp²-configuration. Their C KVV Auger spectra have similar line shape excluding for the high energy part, which reflects, on our opinion, the interlayer interaction which is present in HOPG and MWCNT and absent in SWCNT and C_{60} (22). The observed distinction of C KVV spectra for HOPG and MWCNT may be due to the curvature of graphene sheets in nanotubes.

**Figure 5.** C 1s XPS spectra for HOPG after in situ defluorination at 270°C during 4 min.

**Figure 6.** C 1s XPS spectra for HOPG after in situ defluorination at 270°C during 10 min.
In view of these data it is probably that coincidence of fluorinated MWCNT spectrum with that for non-fluorinated SWCNT (Figure 1) and HOPG spectrum after fluorination (Figure 8) is caused by disappearance of interlayer interaction.

The absence of strong shift for fluorinated HOPG and MWCNT spectra (Figure 8) in comparison with the shift for SWCNT spectrum allows

**Figure 7.** Modification of C KVV Auger spectra for HOPG during fluorination and defluorination.

**Figure 8.** C KVV Auger spectra for fluorinated MWCNT, SWCNT and HOPG, and pure HOPG and MWCNT. The spectra of Fiber (not shown) before and after fluorination coincide with that of MWCNT. The spectrum of MWCNT after fluorination coincides with that of SWCNT.
speculation that the top layer of HOPG and MWCNT do not interact with F-atoms. Obviously the F-atoms are in deeper layers and only change the interaction between the uppermost layers.

CONCLUSIONS

The performed measurements imply that the HOPG, SWCNT, MWCNT and Fiber samples before and after fluorination are inert to the environmental. The XPS spectra show that MWCNT and Fiber after fluorination have similar composition, which includes CF, CF$_2$ and CF$_3$ states, but MWCNT also include CF$_4$. Fluorine atoms have four chemical states in fluorinated MWCNT and one state in HOPG, SWCNT and Fiber. It was observed that the degree of fluorination in HOPG changes in depth. During defluorination of the fluorinated HOPG sample with initial C-F states the formation of CF$_2$ and CF$_3$ states has been observed. XAES spectra show the absence of C-F bonding in the outer layers of fluorinated HOPG, MWCNT and Fiber while C-F bonding exists in the outer layer SWCNT.

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