Local and electronic structure of fluorinated single-walled carbon nanotubes: X-ray absorption and DFT Analysis

Maria Brzhezinskaya¹,², Galina Yalovega³, Valentina A. Shmatko², Anatoliy Krestinin⁴, Alexander Vinogradov²
(¹) ALBA Synchrotron Light Source, 08290 Barcelona, Spain
(²) V.A. Fock Institute of Physics, St. Petersburg State University, 198504 St. Petersburg, Russia
(³) Department of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia
(⁴) Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, Russia
E-mail: yalovega1968@mail.ru

Abstract. The paper presents the results of investigation of the chemical bond formation in fluorinated single-walled carbon nanotubes using X-ray absorption spectroscopy. All measurements were performed with the use of synchrotron radiation at the BESSY II. The C1s and F1s absorption spectra point to formation of covalent chemical bonding between the fluorine and carbon atoms in F-SWCNTs. The investigation of the local structure of the F-SWCNTs has been done on the basis of calculations by the Density Function Theory and Finite Difference methods.

Introduction
The graphene layer forming the wall of a single-wall carbon nanotubes (SWCNTs) is a structure that is extremely stable against chemical treatment. Several problems exist, the solution to which urgently demands techniques to chemically modify the nanotube surface to be designated. First, chemical functionalization is required for the use of SWCNTs as the additive in a polymer matrix for the improvement of polymer binder in mechanical properties. Second, for the effective use of SWCNTs in many applications, it is necessary to achieve the best nanotube disintegration in the various media possible, down to the isolated tubes. Fluorination only can potentially become basis for the industrial technology of the chemically modified SWCNT production [1]. In this work, the high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy is used to elucidate the nature of chemical bonding between carbon and fluorine atoms on the surface and inside fluorinated SWCNTs.

1. Methods
SWCNTs were synthesized by an electroarc method using nickel-yttrium catalyst. The purified nanotubes had a narrow diameter distribution with an average value of ~1.5 nm. High-purity SWCNTs (~ 98 wt.%) are obtained in the form of paper (SWCNT paper). The direct fluorination was carried...
out at a temperature 222 °C for 5 hours. The fluorinated SWCNTs had ~ 35 wt.% fluorine (SWCNTs+F35%). Measurements were performed at the Russian-German beamline at the BESSY II (Berlin, Germany). NEXAFS spectra of all samples were recorded at the C 1s and F 1s absorption edges in the total electron yield mode with photon energy resolution of 75 and 150 meV, respectively. The investigation of the local structure fluorinated single-walled carbon nanotubes has been done on the basis of advanced theoretical analysis of experimental NEXAFS data. In order to determine the possible geometry of F-SWCNT, DFT (Density Functional Theory) calculations (ADF2008 code) [2] were performed using unfrozen all core orbitals and valence triple zeta, doubly polarized (TZ2P) basis sets in the GGA Becke88 Perdew86 framework.

Theoretical analysis of the C K-edge NEXAFS was performed using the Finite Difference Method (FDMNES code) to solve the Schrödinger equation [3]. For the pristine nanotube and for fluorinated SWCNTs, the XANES has been calculated for clusters containing 19 atoms and 13 atoms accordingly (radius about 4.2 Å and 4.0 Å).

2. Results and discussion
The NEXAFS spectrum of the pristine SWCNTs (figure 1) corresponds well to the spectra of HOPG and MWCNTs (multi-wall carbon nanotubes). Small distinctions in these spectra usually appear as consistent changes in the relative intensities of the most typical features of the A-B-C structure and inefficient broadening. First, the agreement in the spectra of HOPG and SWCNTs indicates the high structural perfection of nanotubes. Next, this agreement proves the key role of a single graphene layer in the formation of the C1s absorption spectra in HOPG, MWCNTs and SWCNTs. Therewith, in both the C1s absorption spectra of nanotubes and in the HOPG spectrum, the main structures A–A' and B–F reflect transitions of 1s electron of carbon atoms into the free states of the conductivity band, which are formed from the 2p electron state of carbon atoms and have π and σ symmetry, respectively [4].

![C1s absorption spectra](image)

**Figure 1.** C1s absorption spectra of HOPG (1), the pristine MWCNTs (2) and SWCNTs (3), SWCNTs+F35% (4) and MWCNTs+F39% (5).
Significant differences in the structure of C 1s spectra of the pristine and F-SWCNTs are observed. There is a strong decrease in A peak intensity, the emergence of new features for structures B₁*, B₂*, C*, D* instead of A'–D structures, and isolated band E*-F* formation. We mention that, in addition to new absorption bands in F-SWCNT spectra, A band from the spectrum of the pristine nanotube is retained, proving the fact of incomplete nanotube fluorination.

It is logical to associate the changes observed in C1s spectra of F-SWCNTs with the chemical interaction between F atoms and the nanotube wall. The appreciable similarity of F-SWCNT and F-MWCNT spectra allows supposing that the chemical binding of fluorine with carbon occurs in both cases, for the most part, by fluorine atoms bonding to carbon atoms on a nanotube sidewall, forming σ(C–F) bonds owing to covalent mixing of F2p- and C2p-valence electron states [5]. Obviously, such binding of fluorine atoms modifies the coordination of carbon atoms, from triangular in original nanotubes to nearly tetrahedral in fluorinated nanotubes, and it is possible only when sp² valence state hybridization of carbon atoms changes for sp³ hybridization in F-SWCNTs.

The model of F-SWCNTs with 1.6 nm diameter was generated and pieces of nanotube have been used for providing of calculations. We have applied DFT calculations (ADF2008.1) to obtain the optimized geometry for the F atoms/molecule included in carbon nanotubes. Figure 2 shows three various models of C-F chemical bond as result of geometry optimization.

In the case of fluorine over a nanotube surface (model 1), formation of tetrahedron with C-F length of bonds, the corresponding to 1.4 Å is observed. In contrast with the case of fluorine over a nanotube surface, in case of fluorine inside of nanotube formation of C-F chemical bond has not been observed (model 2). The model like "substitution" of carbon atoms by atoms of fluorine in tops of hexagon (model 3), shows destruction of the nanotube surface.

After structure optimization the C K-edge NEXAFS of SWCNT and F-SWCNTs have been calculated and the comparison of both experimental and theoretical spectra are presented in figure 3.

The resulting theoretical spectra are superposition of theoretical spectra from nonequivalent position of C atoms, summarized with the corresponding weight. Thus in the case of F-SWCNTs theoretical spectra both C and F bonded excited C atoms were used.

Theoretical spectra of SWCNT reproduce the all details of experimental spectra but there is some disagreement between theoretical and experimental spectra in the energy position of double peak C.

In the case of F-SWCNTs, the better agreement with experiment is observed for model 1. Energy position of A peak that can be attributed as π state of carbon atoms and B, C peaks of theoretical spectra are close to experimental data, while peak D is shifted toward high energy. From other hand, model 2 and 3 shows more bad agreement between theoretical and experimental data. That can confirm the high probability for formation of C-F chemical bond at the CNT surface and general direction of following investigations.
**Figure 2.** The models of optimized F-SWCNTs (C - black balls, F- gray balls). (a) - model 1, (b) - model 2, (c) - model 3

**Figure 3.** Comparison of experimental and theoretical C K-edge spectra for SWCNTs and F-SWCNTs.

In conclusion, the combined investigation of the F-SWCNTs by highly chemically sensitive X-ray methods is presented. It was observed that fluorination process of SWCNTs is accompanied by chemical bonding between fluorine and carbon atoms on the tube side walls. We may assume that fluorine atoms do not substitute carbon atoms in graphene layers of SWCNTs but they add to them as a result of covalent mixing between C 2$p_z$ and F 2$p$ states. The coordination of carbon atoms changes from $sp^2$-triangular to $sp^3$-tetrahedral.

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