Specific Features of the Electronic Structure of Fluorinated Multiwalled Carbon Nanotubes in the Near-Surface Region

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Abstract — The C 1s and F 1s X-ray photoelectron spectra of fluorinated multiwalled carbon nanotubes with different fluorine contents have been measured using the equipment of the Russian–German beamline at the BESSY storage ring by varying the energy of exciting photons. It has been established that two fluorocarbon phases in which the chemical bonding is characterized by a different electron transfer from carbon atoms to fluorine atoms are formed in the near-surface region of nanotubes with fluorine concentrations of 10–39 wt %. The content of the dominant first phase with a large electron transfer in nanotubes remains unchanged with an increase in the probing depth. This phase is identified as a bulk phase formed as a result of the covalent attachment of fluorine atoms to graphene layers of the graphite skeleton without its destruction. The second phase with a small electron transfer is a near-surface phase, because it is predominantly located within two or three upper graphene monolayers and its contribution considerably decreases with an increase in the probing depth of fluorinated multiwalled carbon nanotubes.

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1. INTRODUCTION

Carbon nanotubes have been considered among the most promising materials for nanotechnologies in electronics, sensorics, hydrogen power engineering, bioengineering, and medicine [1, 2]. It should be noted that the chemical inertness of carbon nanotubes is a considerable obstacle to their practical application. The chemical inertness can be decreased only by changing the atomic and electronic structures of carbon nanotubes, for example, through their fluorination. This technological process has been characterized by investigating fluorination products with the use of various experimental methods [3–11] and theoretical calculations [12–16]. However, the results of these investigations do not provide deep insight into the influence of fluorination on the atomic and electronic structures of carbon nanotubes. As a consequence, up to now, it has not been possible to formulate optimum conditions for the fluorination technology (such as the type, temperature, and duration of the chemical reaction).

In our previous work [17], we demonstrated the possibility of using C and F K (1s) absorption spectra in order to obtain information on the atomic and electronic structures of products of fluorination of multiwalled carbon nanotubes and to characterize the process of nanotube fluorination with the use of this information. Fluorinated multiwalled carbon nanotubes 10–30 nm in diameter with different fluorine contents (5–55 wt %) were studied in detail by X-ray absorption spectroscopy with the use of synchrotron radiation. A comparative analysis of the fine structure of the absorption spectra obtained for the fluorinated multiwalled carbon nanotubes by the method of the total electron yield demonstrated that, within the probing depth (~15 nm), only one fluorocarbon phase clearly manifests itself and the process of fluorination occurs uniformly in the probed layer and does not depend on the fluorine content in the nanotubes. The interaction of fluorine atoms with the multiwalled carbon nanotubes proceeds through the covalent attachment of fluorine atoms to graphene layers of the graphite skeleton without its destruction and is accompanied by a change in the hybridization of the 2s and 2p valence electron states of the carbon atoms from the trigonal ($sp^2$) to tetrahedral ($sp^3$) hybridization due to the formation of the additional $\sigma$ (F 2p–C 2s, 2p) bond.

It is quite obvious that the method of the total electron yield with a probing depth of the order of the average diameter of the multiwalled carbon nanotubes
(several tens of graphene layers) does not allow one to obtain information on the characteristics of the fluorinated tubes under investigation in their near-surface regions, in which the fluorination process can occur in a different manner as compared to large depths. This information for the near-surface region only several graphene layers in thickness can be provided, in particular, with the use of X-ray photoelectron spectroscopy used for obtaining the C 1s and F 1s core level X-ray spectra of fluorinated multwall nanotubes. X-ray photoelectron spectroscopy is well known as a surface-sensitive method for studying the electronic structure of materials [18]. In this method, the probing depth is determined by the photoelectron escape depth, which depends on the kinetic energy of photoelectrons and can vary from several tenths of a nanometer (two or three atomic monolayers) to several nanometers with a variation in the energy of exciting photons. Several works in which X-ray photoelectron spectroscopy has been used to characterize fluorinated single-walled carbon nanotubes [6, 10, 11], fluorinated multiwalled nanoparticles [19], and fluorinated multiwalled carbon nanotubes [20] have been known to date. In [20], the core photoemission spectra of fluorinated nanotubes were investigated using only one energy of exciting photons, i.e., Al Kα X rays with an energy of 1486.6 eV, which ensured a probing depth of slightly larger than 2 nm (of the order of six or seven graphene monolayers). By analyzing the spectral parameters of the C 1s and F 1s X-ray photoelectron lines, the authors in [20] made the inference that only one fluorocarbon phase is formed in the probed layer, which, in principle, is in agreement with the conclusions of the aforementioned X-ray absorption study, even though the probing depths of the fluorinated multiwalled carbon nanotubes in the methods under consideration differed significantly.

The main objective of the present work was to investigate the specific features of the electronic structure of fluorinated multwall carbon nanotubes in the near-surface layer less than 2 nm in thickness by X-ray photoelectron spectroscopy with a variation in the energy of exciting photons and to obtain additional information on the process of fluorination of multwall nanotubes. For this purpose, the C 1s and F 1s X-ray photoelectron spectra of the pristine and fluorinated multiwalled carbon nanotubes previously characterized by X-ray absorption spectroscopy [17] with different fluorine concentrations (10–55 wt %) were measured over a wide range of photon energies (1130–385 eV), which provided a variation in the probing depth of the sample in the range from ~2.0 to ~0.5 nm. As a result, we revealed that the probed region of the fluorinated multwall carbon nanotubes contains two fluorocarbon phases in which the chemical bonding is characterized by a different electron transfer between carbon and fluorine atoms and analyzed the nature of these phases. Moreover, it was established that one phase is a pure near-surface phase, whereas the other phase represents a bulk phase and is rather uniformly distributed over the entire probing depth.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Multiwalled carbon nanotubes were produced through electric-arc evaporation of graphite rods (spectral purity) in a helium atmosphere (500 Torr) at a current density of 175 A/cm² and a voltage of 23 V [21]. According to the electron microscopic data, the length of the multiwalled carbon nanotubes is more than 1 µm, the outside diameter is equal to 10–30 nm, and the inside diameter amounts to 2–4 nm. The powdered samples of multiwalled carbon nanotubes were fluorinated in a nickel reactor at a temperature of 420°C in a flow of molecular fluorine produced by the electrolysis of acidic potassium trifluoride KF–2HF containing up to 3 wt % HF. The chemical analysis for the fluorine content in the samples was carried out by preliminarily burning the fluorinated material with Na₂O₂ in order to transform fluorine into a water-soluble form, followed by the titration of F⁻ ions with thorium nitrate.

The highly oriented pyrolytic graphite crystal (degree of perfection, Grade SPI-1) was purchased from SPI Supplies. In this work, the spectra of highly oriented pyrolytic graphite were used as the reference spectra when discussing the structure of the spectra of the carbon nanotubes.

The C and F X-ray photoelectron spectra of the pristine fluorinated multiwalled carbon nanotubes and the highly oriented pyrolytic graphite crystal were measured using monochromatic synchrotron radiation and the equipment of the Russian–German beamline at the BESSY II storage ring (Berlin) [22]. The photon energy was varied from 385 to 1130 eV. In this energy range, the energy resolution ∆E of the monochromator with an exit slit width of 200 µm was equal to 150–750 meV.

The samples for the X-ray photoelectron measurements were prepared in air. The powders of the multiwalled carbon nanotubes and the fluorinated multiwalled carbon nanotubes under investigation were rubbed into a scratched surface of a substrate (in the form of metallic indium plates 7 × 7 mm in size) in such a way as to provide a uniform covering of the substrate surface without noticeable defects. The preparation of the samples was described in detail in our earlier work [17].

The X-ray photoelectron spectra for all samples were obtained by recording the normal photoemission with the use of a Mustang measuring station with a Specs Phoibos 150 hemispherical analyzer. During the recording of the spectra, the resolution of the analyzer was equal to 200 meV. The analyzer was calibrated against the Au 4f⁷/₂ and Au 4f⁵/₂ photoelectron spectra. The monochromator was calibrated by recoding the