Characterization of CuHal-intercalated carbon nanotubes with x-ray absorption spectroscopy combined with x-ray photoelectron and resonant photoemission spectroscopies

M Brzhezinskaya¹, A Generalov²,³, A Vinogradov³ and A Eliseev⁴

¹Institut für Nanometeroptik und Technologie, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany
²St. Petersburg State University, Ulyanovskaya Str. 1, 198504 St. Petersburg, Russia
³Technical University Dresden, Mommsenstrasse 9, 01062 Dresden, Germany
⁴Moscow State University, Leninskii Gori 1, 119991 Moscow, Russia

E-mail: maria.brzhezinskaya@helmholtz-berlin.de

Abstract. Encapsulated single-walled carbon nanotubes (SWCNTs) with inner channels filled by different compounds present the new class of composite materials. Such CNTs give opportunity to form 1D nanocrystals as well as quantum nanowires with new physical and chemical properties inside the tubes. The present study is aimed to characterize the possible chemical interaction between CuHal (Hal=I, Cl, Br) and SWCNTs in CuHal@SWCNTs and electronic structure of the latter using high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy combined with high-resolution X-ray photoelectron spectroscopy and resonant photoemission spectroscopy. The present study has shown that there is a chemical interaction between the filler and π-electron subsystem of CNTs which is accompanied by changes of the atomic and electronic structure of the filler during the encapsulating it inside CNTs.

1. Introduction
Owing to unique structural and electronic properties, single-walled carbon nanotubes (SWCNTs) could cover the full range of properties important for technology [1]. These potential applications of SWCNTs essentially depend upon the ability to modify their intrinsic properties by manipulating their structure and electronic properties. A promising route for modification of SWCNTs is a chemical modification via substitution of carbon atoms or the addition of atoms or polyatomic groups (so-called functionalization) [2]. An alternative procedure is to add electron acceptors or donors in a controlled manner (intercalation) by encapsulating corresponding atoms (compounds) inside SWCNTs. It generates unique one-dimensional (1D) nanostructures that have a large potential [3].

The present study is aimed to characterize the possible chemical interaction between CuHal (Hal=I, Cl, Br) and SWCNTs in CuHal@SWCNTs and electronic structure of the latter using high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy combined with high-resolution X-ray photoelectron spectroscopy and resonant photoemission spectroscopy.
2. Methods

SWNTs were obtained by catalytic arc-discharge method. The pristine SWCNTs have diameters 1.4-1.6 nm. Pre-opened SWNTs (0.025 g) were grinded in agate mortar with CuCl, CuBr or CuI (Aldrich, 99 wt.%) in molar ratio 1:2, 1:1.5 or 1:1, accordingly, then evacuated in quartz ampoules at 1 Pa for 1 hour and sealed. The ampoules were heated at a rate of 1K/min up to the temperature 100 K above the melting point of CuHal. This temperature was maintained for 6 hours, whereupon the samples were slowly cooled at a rate around 0.02 K/min. The CuHal@SWNT were directly observed using TEM. Microphotographs confirm continuous intercalation of CuHal into SWNT channels. The loading factors amount to 20% for CuCl@SWNT, 50% for CuBr@SWNT and ~90% for CuI@SWNT [4].

The x-ray absorption, x-ray photoelectron and photoemission spectra of SWCNTs, CuHal@SWCNTs, CuI and CuO were measured at the RG beamline at BESSY II (Berlin).

The NEXAFS spectra were obtained by recording total electron yield (TEY) of x-ray photoemission in the mode of measurement of the drain current of the sample. The samples were positioned at an angle of ~45° with respect to the incident beam. The energy resolutions \( \Delta E \) of the monochromator in the range of the Cu 2p x-ray absorption edge (\( h\nu \approx 935 \text{ eV} \)) and C 1s x-ray absorption edge (\( h\nu \approx 285 \text{ eV} \)) were equal to ~250 and 70 meV, respectively.

Photoelectron spectra were measured in the normal photoemission registration mode by using the Phoibos 150 spherical analyzer from Specs. The analyzer energy calibration was performed based on photoelectron spectra of Au atom 4f\( _{7/2,5/2} \) electrons. The monochromator was calibrated by recording the main line of C 1s photoelectron spectra exited by radiation reflected from the diffraction grating in the 1st and 2nd diffraction orders.

3. Results and discussion

Fig. 1 presents C K(1s) absorption spectra of initial SWCNTs and CuHal@SWCNTs measured under the same experimental conditions. The A and B-C peaks in the SWCNT spectrum are associated with dipole-allowed electron transitions from 1s carbon states to the unoccupied \( \pi \) and \( \sigma \) symmetry states in the conduction band that are formed from carbon \( \pi^2p_z \) and \( \sigma^2p_{x,y} \) states oriented perpendicular to and parallel to the carbon layer plane (graphene), respectively.

\( \pi \)-resonance \( A \) (285.4 eV) of the pristine SWCNTs contents in its fine structure four shoulders at 284.8, 285.0, 285.4 and 285.8 eV (Fig. 1b). Features \( S_1^*, S_2^* \) and \( S_3^* \) are van Hove singularities (vHs’s) of semiconductor SWNTs, while \( M_1^* \) is vHs of metallic SWNTs [5]. Our pristine SWCNTs contain 70% of semiconductor SWNTs and 30% of metallic ones. These features occur in the CNT x-ray absorption spectrum due to their quasi-1D character [6]. vHs’s are associated with transitions of C1s electrons to unoccupied levels \( S_1^*, S_2^* \) and \( S_3^* \) in semiconductor SWNTs and \( M_1^* \) in metallic SWCNTs.

Fig. 1 also illustrates the changes of the x-ray absorption spectra after incorporation of CuHal into the SWNT channels. It is seen that C 1s absorption spectra for CuHal@SWCNTs (Fig. 1a) are practically identical to the one for pristine SWCNTs except for an additional small shoulder-like peak \( A_1 \) at the low-energy side of the \( \pi \)-resonance \( A \). It is obvious that such a new peak reflects the changes in the spectrum of empty electron states which are take place as a result of chemical interaction.

At the same time, no pronounced variations in the spectra \( \sigma \)-part are observed in the C1s absorption spectra. In the photon energy range of 303 to 310 eV, specific structure that is characteristic of the \( sp^3 \)-hybridized carbon atoms is not observed. This means that filling of the tubes with CuHal does not cause corrugation or deformation of the CNT wall graphene mesh. The mesh may be corrugated or deformed only if the carbon atom hybridization character changes from \( sp^2 \) to \( sp^3 \). Therefore, the absence of corrugation evidences that carbon atoms remain in the state of the \( sp^2 \) hybridization.
Cu 2p spectra for CuHal@SWCNTs, and reference samples CuI and CuO are presented in Fig. 2 (bottom panel). If the dipole rules for 2p electron transitions are taken into account, these spectra reflect local density of empty electron states that have mainly Cu 4s- and Cu 3d-character. It can be seen from the Fig. 2 that the Cu 2p _3/2_ NEXAFS spectra of Cu@SWCNT and CuI show appreciable differences between their absorption structures. The main distinction is an appearance of narrow (full width at half maximum FWHM=1.1 eV) low-energy peak _A_ in the Cu@SWCNT spectrum. With consideration for the valence electron configuration of the Cu^+ ion (3d^{10}4s^0) in CuI, the appearance of narrow low-energy peak _A_ in the Cu 2p _3/2_ spectrum of the composite is reasonable to associate with Cu 2p _3/2_ electron transitions to empty 3d electron states that are lacking in pristine CuI and appear in CuHal@SWCNT as a result of changes in electronic structure of CuI owing to its encapsulation into SWCNTs or to chemical interaction between the filler and the CNT in Cu@SWCNT. This is accompanied by the change in the valence electron configuration of the Cu^+ ion from 3d^{10}4s^0 for Cu to 3d^{10}4s^1 for Cu@SWCNT. The direct comparison of Cu 2p _3/2_ spectra for the composite and CuO confirms this interpretation. The spectrum for CuO with the valence electron configuration of Cu^{2+} ion, 3d^9, has the similar narrow (FWHM=1.0 eV) low-energy peak _A_ as well. It is well known that this peak is due to the Cu 2p _3/2_ - 3d electron transition. Comparison of relative intensities of peaks _A_ from the spectra for CuO and Cu@SWCNT, that were normalized equally, gives the magnitude of \( x = 0.06e \) for the decrease of the Cu 3d charge in the composite. The general resemblance of absorption structures for spectra of CuI and CuHal@SWCNT, except for the peak _A_, is probably evidence for conservation of a tetrahedron coordination of absorbing Cu ion as well as relatively small magnitude of effects under consideration. In this case the broadening and smearing of some absorption structures can be related to a distortion of the tetrahedron environment of Cu ions by iodine atoms.

The peak _A^*_ intensity increases gradually in transitions from Cu@SWCNT to CuBr@SWCNT and then to CuCl@SWCNT thus evidencing sequential decrease in the number of 3d-electrons in copper atoms in this series. This shall result in the increase in the value of electron transfer from Cu atoms. Indeed, the value of effective electron transfer from Cu atoms increases in the Cu@SWCNT-CuBr@SWCNT-CuCl@SWCNT series. It is 0.6e for CuBr@SWCNT and 1.0e for CuCl@SWCNT. There are two ways of charge transfer from copper atoms to CuHal@SWCNTs: either to carbon atoms, or to haloid atom. Thereby, the copper atom configuration is [Ar]3d^{10}4s^0 in Cu@SWCNTs, [Ar]3d^{10}4s^1 in CuBr@SWCNTs, and [Ar]3d^{10}4s^1 in CuI@SWCNTs.
Cu $2p_{3/2}$ and C 1$s$ spectra for CuI@SWCNTs, have been aligned in energy by using the binding energy separation of 648.0 eV between the Cu $2p_{3/2}$ and C 1$s$ core levels (Fig. 2). The positions of the peaks $A_1$ in both spectra are nearly coincide within 1 eV. In the framework of quasimolecular approach, this coincidence of the absorption peaks $A_1$ in both the energetically aligned spectra can be regarded as a result of the transitions of Cu $2p_{3/2}$ and C 1$s$ electrons to the same empty state of CuI@SWCNTs which has hybridized Cu 3$d$-C 2$p_z$ character. In this case, slight difference in positions of peak $A_1$ in C 1$s$ and Cu $2p_{3/2}$ spectra can be associated with a different influence of C 1$s$ and Cu $2p_{3/2}$ holes on the core-excited state under consideration.

4. Conclusions

Electronic structure of single-walled carbon nanotubes intercalated by copper halogenides (CuI@SWCNT, CuBr@SWCNT and CuCl@SWCNT) obtained by capillary technique was study. High-resolution X-ray C 1$s$ and Cu $2p$ absorption and photoelectron spectra of CuHal@SWCNTs were measured for the first time. The present study has shown that encapsulation of CuHal (CuI, CuBr and CuCl) into SWCNTs is accompanied by the changes in electronic structure of CuHal. These changes are caused by the modifications in atomic structure of CuHal in the new nanomaterials CuHal@SWCNT and the chemical interaction between the filler and carbon nanotubes. At the same time, this interaction does not change the hybridization of C atoms from $sp^2$ to $sp^3$. It was found decreasing of electron charge of Cu atoms in the row CuI-CuI@SWCNT-CuBr@SWCNT-CuCl@SWCNT-CuO as a result of electron transfer.

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