



Electronic structure of hydrogenated carbon nanotubes studied by core level spectroscopy



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ABSTRACT

The high-resolution near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy were used to elucidate the nature of chemical bonding between carbon and hydrogen atoms on the surface and inside hydrogenated single-walled carbon nanotubes (H-SWNTs). The measured spectra showed formation of chemical bonding between the hydrogen and carbon atoms in H-SWNTs. In order to obtain a detailed understanding origin of the chemical bond between C and H atoms, density functional calculations and theoretical analysis of experimental NEXAFS spectra were carried out.

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1. Introduction

At present, it was accepted that chemical functionalization of carbon nanotubes (CNTs), i.e., attachment of individual atoms/molecules or their aggregates to CNTs, can extend the field of application of these nanosystems in nanoelectronics, sensors, hydrogen power engineering, bioengineering, medicine, etc. [1–3]. Since oil resources are impermanent, hydrogen is gaining more and more importance as highly efficient and ecological energy carrier that is very promising for wide use in the power industry, especially as vehicle fuel. However, none of the current methods for hydrogen storage (at high pressure, in the absorbed state at low temperatures, in the liquid state, in the form of metal hydrides or intermetallics) ensures safe reversible storage and compact transportation of gaseous hydrogen. It was found out that CNTs may be used as hydrogen reservoirs [4]. Therefore, a lot of investigations are now aimed at studying peculiar features of hydrogen sorption by carbon nanotubes that exhibit extremely high porosity.

In this work, high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS) as well as density functional calculations and theoretical analysis of experimental NEXAFS spectra were used

to elucidate the nature of chemical bonding between carbon and hydrogen atoms on the surface and inside hydrogenated single-walled carbon nanotubes (H-SWNTs).

2. Experimental and theoretical details

SWNTs were synthesized by the electroarc method using nickel-yttrium catalyst. The purified nanotubes had a narrow diameter distribution with the average value of ~1.5 nm. High-purity SWNTs (~98 wt.%) were prepared in the form of paper. The SWNTs were hydrogenated at $P \sim 5.0$ GPa and $T \sim 500$ °C and contained 5.335 wt.% of hydrogen [5].

The X-ray and photoelectron spectra were measured at the Russian–German beamline of BESSY II (Berlin) by using experimental station Mustang equipped with the Phoibos 150 spherical analyzer from Specs [6]. The samples for X-ray absorption and photoelectron measurements were prepared in air. The powders of the SWNTs and H-SWNTs were rubbed into a scratched surface of a pure substrate (metallic copper plate 7 mm × 7 mm in size) in order to ensure the substrate uniform surface coating without any noticeable gaps.

The NEXAFS spectra were obtained by recording the total electron yield (TEY) of the X-ray photoemission [7] in the mode of measurement of the drain current of the sample by varying the energy of incident photons. The energy resolutions ΔE of the monochromator in the range of the C 1s X-ray absorption edge ($h\nu \sim 285$ eV) was equal to 70 meV. The X-ray absorption and

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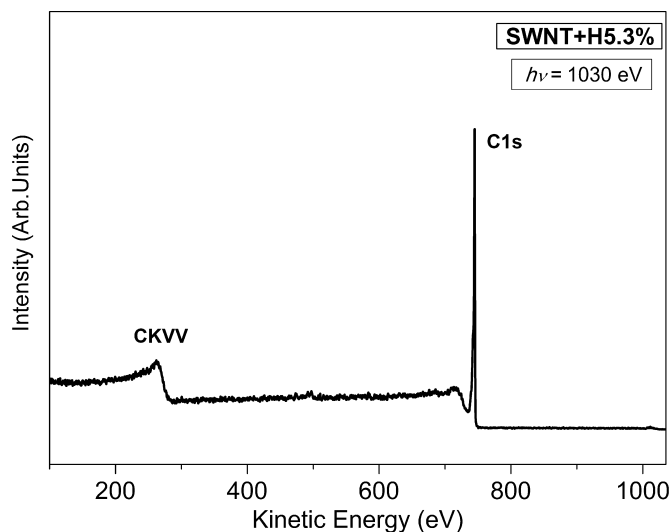


Fig. 1. C 1s X-ray photoelectron spectrum of SWNT + H3.5%, measured at the photon energy of 1030 eV.

photoelectron spectra were measured under ultrahigh vacuum ($\sim 2 \times 10^{-10}$ Torr). The samples were located at an angle of $\sim 45^\circ$ with respect to the incident beam of monochromatic radiation. The size of the focused spot on the sample was $\sim 0.2 \text{ mm} \times 0.1 \text{ mm}$.

Models of C–H chemical bonds where H atoms are connected to the SWNT outer surface were investigated. The optimization of the H-SWNTs structures in order to get detailed understanding of the origin of the chemical bond between C and H atoms was carried out by using ADF2009 [8]. The density functional theory (DFT) method employed the GGA-B3LYP type exchange correlation potential and doubly polarized (TZ2P) basis set was used. Semiempirical calculations were carried out using the PM6 parameterization [9]. Theoretical C K-edge NEXAFS spectra were simulated using the non-muffin-tin approach, the finite difference method (FDMNES 2012) to solve the Schrödinger equation [10].

To control compositions of the samples, general photoelectron spectra at $h\nu = 1030 \text{ eV}$ within the binding energy range of $BE = 0\text{--}900 \text{ eV}$ were measured in the normal photoemission registration mode. They did not show the presence of oxygen in the H-SWNT samples (see Fig. 1).

3. Results and discussion

In the C 1s absorption spectra of pristine carbon nanotubes (Fig. 2), the main structures A–a and B–F reflect transitions of the carbon atom 1s electrons into the conductivity band free states that are formed from the $2p_z$ and $2p_{x,y}$ electron states of carbon atoms and have π^* and σ^* symmetry, respectively [11].

A comparison of the X-ray absorption spectra of the hydrogenated/fluorinated and pristine single-walled carbon nanotubes demonstrates that their fine structures differ substantially. The most significant differences involve a drastic decrease in the intensity of the resonance A associated with the free π states and the appearance of the high-energy σ band $E^* \text{--} F^*$. It is evident that the observed changes are governed by the hydrogenation of the SWNTs as we demonstrated earlier for fluorinated SWNTs (F-SWNTs) [12]. The resonance A is retained in the spectra of the hydrogenated/fluorinated samples but has a considerably lower intensity with respect to the other spectral portion associated with the transitions of the 1s electrons to the free σ states of the conduction band. The other specific features in the spectra of the pristine SWNTs have no clear analogs in the spectra of the hydrogenated/fluorinated samples.

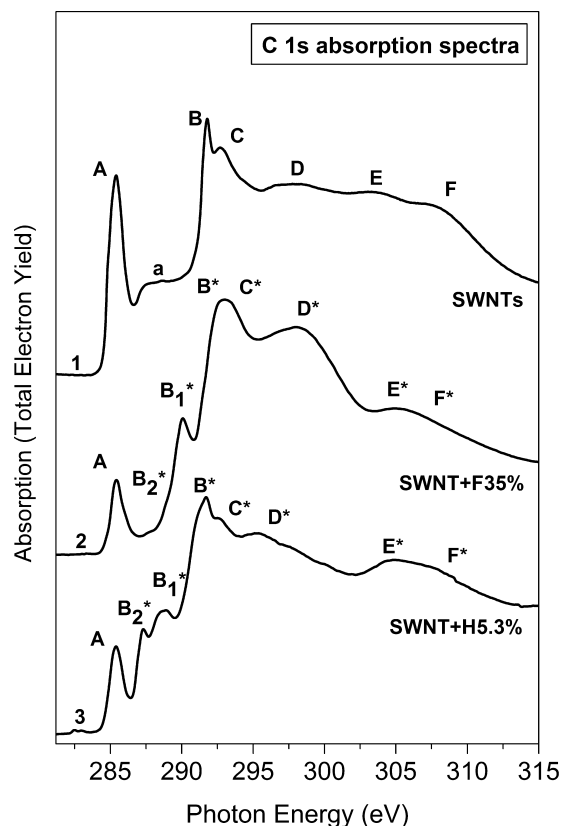


Fig. 2. Experimental C K-edge spectra of SWNTs (1), SWNTs+F35% (2) and SWNTs+H5.3% (3).

As we proved earlier for F-SWNTs, all new details in the spectra of the hydrogenated single-walled carbon nanotubes should be associated with the transitions of the C 1s electrons to the free electron states for at least one hydrocarbon phase, which is formed as a result of the chemical bonding between the carbon and hydrogen atoms during the hydrogenation of the single-walled nanotubes. A significant similarity of the shape of the C 1s X-ray absorption spectra of the hydrogenated single-walled and fluorinated single-walled carbon nanotubes allows us to assume that the hydrogenation as well as fluorination of the single-walled leads to the formation of similar fluorocarbon and hydrocarbon phases [12]. In other words, this means that the hydrogenation of the single-walled carbon nanotubes, as in the case of fluorination of SWNTs, predominantly occurs through the attachment of hydrogen atoms to carbon atoms on the lateral surface of nanotubes with the formation of the $\sigma(\text{C}\text{--}\text{H})$ bonds due to the covalent mixing of the H 1s and C $2p_z$ π electron states without destruction of the tubular structure of carbon layers [13,14]. This attachment of the hydrogen atoms leads to a change in the trigonal coordination of the carbon atoms in the pristine nanotubes to a close to tetrahedral coordination in the hydrogenated nanotubes and is possible only with a change in the sp^2 hybridization of the valence states of the carbon atoms in the pristine nanotubes to the sp^3 hybridization in the hydrogenated single-walled carbon nanotubes. It is evident that this transformation of the atomic structure of the nanotubes should be accompanied by the corrugation of their lateral surfaces. This inference is confirmed by the fact that, in the spectra of the hydrogenated nanotubes, a single band $E^* \text{--} F^*$ (at the energies of 303–310 eV) appears, which is characteristic of the C 1s absorption spectrum of diamond with the tetrahedral coordination of carbon atoms [15].

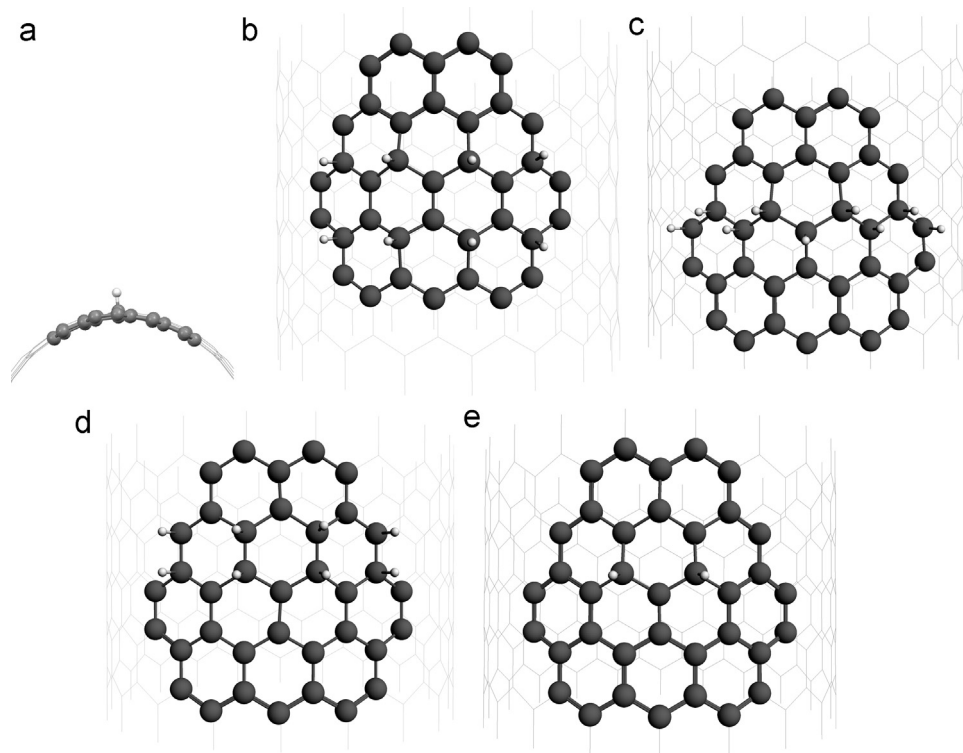


Fig. 3. The model structures of H-SWNTs. View of H-SWNT fragments with marked clusters used in calculation.

At the same time, the H-SWNT spectrum has one more new peak B_2^* at 287.3 eV as compared with the F-SWNT spectrum. This peak is commonly attributed to C–H bonds in the C 1s NEXAFS spectra of hydrocarbons [11]. The two new peaks B_1^* and B_2^* in the C 1s spectrum of H-SWNTs could arise due to existence of two different manners in which H atoms are connected to the SWNT graphene surface with forming σ (C–H) bonds with different value of charge transfer between C and H atoms.

It is clear that the observation of the band A characteristic of the spectra of the pristine nanotubes in addition to the new absorption bands in the spectra of the hydrogenated single-walled carbon nanotubes indicates an incomplete hydrogenation of the bundles of the single-walled nanotubes in the probed region of the sample with a depth of 15–20 nm. Possibly, this is associated with the fact that the depth of hydrogenation of the bundles of single-walled carbon nanotubes under the above mentioned conditions is considerably smaller than the probing depth for the X-ray absorption spectra under consideration.

The model of zigzag SWNT (20, 0) with 1.6 nm diameter was generated for further interpretation of our experimental results. The possible reaction pathways of hydrogen molecules reacting with CNTs were investigated. After geometry optimization, five model structures were chosen for calculation of C 1s NEXAFS spectra (Fig. 3).

The concept of a finite cluster of atoms was used for theoretical analysis [16]. During the geometry optimization, the carbon and hydrogen atoms were not frozen that allows observing the phenomena of changing C–C bond length in the CNT sidewall caused by hydrogen bonding. The carbon atoms bonded with H atoms were picked out from the CNT sidewall for all calculated models (Fig. 3). Formation of tetrahedron with C–H and C–C bonds took place, as a result of a local rehybridization from sp^2 to sp^3 that is in agreement with recent investigations [17–19].

Model “1” represents a cluster with one hydrogen atom bound to the SWNT wall was selected as a model for the absorption spectra

calculation. Models “2” and “3” has been chosen by association with two isomeric structures, resulting from fluorine addition to either 1,2 or 1,4 positions within a hexagonal ring on the graphene-like side wall of the nanotube [20]. From molecular mechanics [21], semiempirical calculations [22], and density functional theory [23] it was found that the 1,2 and 1,4-isomers are stable for fluorinated SWNTs. From other side, as was shown in [17] the adsorption of hydrogen atoms onto the sidewall of CNTs are energetically favorable and the most stable state correspond to hydrogen addition to either 2,3 position within a hexagonal ring (model 4). As was shown in [24], the 1,3 configuration is less stable than the 1,2 and 1,4. The selection of model “5” is not random in our simulations. First, we assume that the hydrogenation of the nanotube surface can have a combined mechanism, as suggested in fluorinated CNTs with fluorine atoms in positions 1,2 and 1,4 [20]. At the same time, model “5” is part of the models 2 and 4. Second, contents of hydrogen atoms in the model 5 is equal to the content of hydrogen atoms in the SWNT + H5.335 wt.% used in experiments. Therefore, we used this model to demonstrate the influence of the partial contributions from absorbing carbon atoms bound and unbound to hydrogen atoms on the shape of the NEXAFS spectrum.

The C 1s NEXAFS spectra were calculated for all mentioned above models (Fig. 4). As one can see from Fig. 4 (spectrum 1), the C K-edge spectrum of model 1 does not reproduce all main features presented in the measured spectrum. This means that experimental spectrum is not a signal contribution from only carbon atoms chemically bounding to hydrogen atoms but more complicated processes take place. Therefore, the C 1s NEXAFS spectra of models 2–5 were calculated as a sum of relative contributions from carbon atoms bounded to hydrogen atoms and not bounded to them. The contribution for each type of carbon atoms was multiplied by atomic weight.

The calculated C 1s NEXAFS spectra of models 2–5 differs significantly. The calculated spectrum of H-SWNT model 4 (Fig. 4, spectrum 4) reproduces all the main details of the experimental

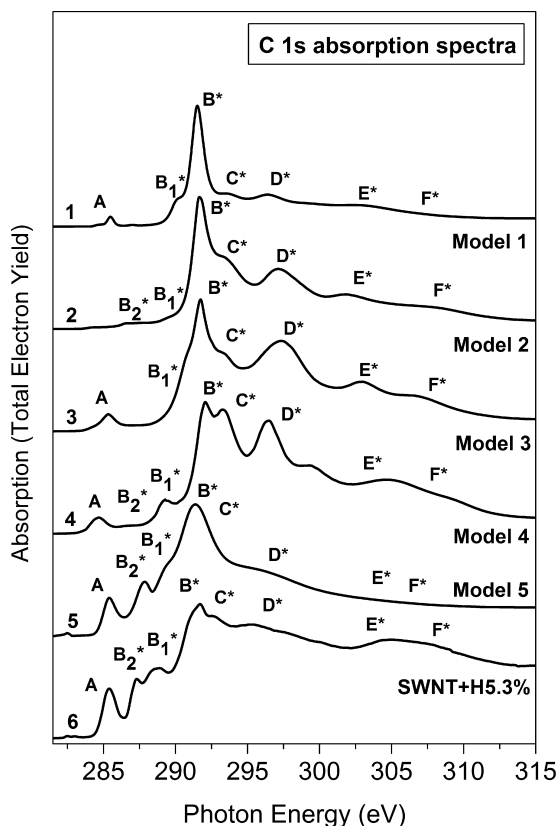


Fig. 4. Measured and calculated C K-edge spectra of H-SWNTs.

spectrum except feature B_2 which has much lower intensity compare to experimental one. However, peaks A and B in calculated spectrum are shifted a little compare to experimental ones. On the other hand, the calculated C 1s NEXAFS spectrum of model 5 (Fig. 4, spectrum 5) does not have pronounced featured B_2 .

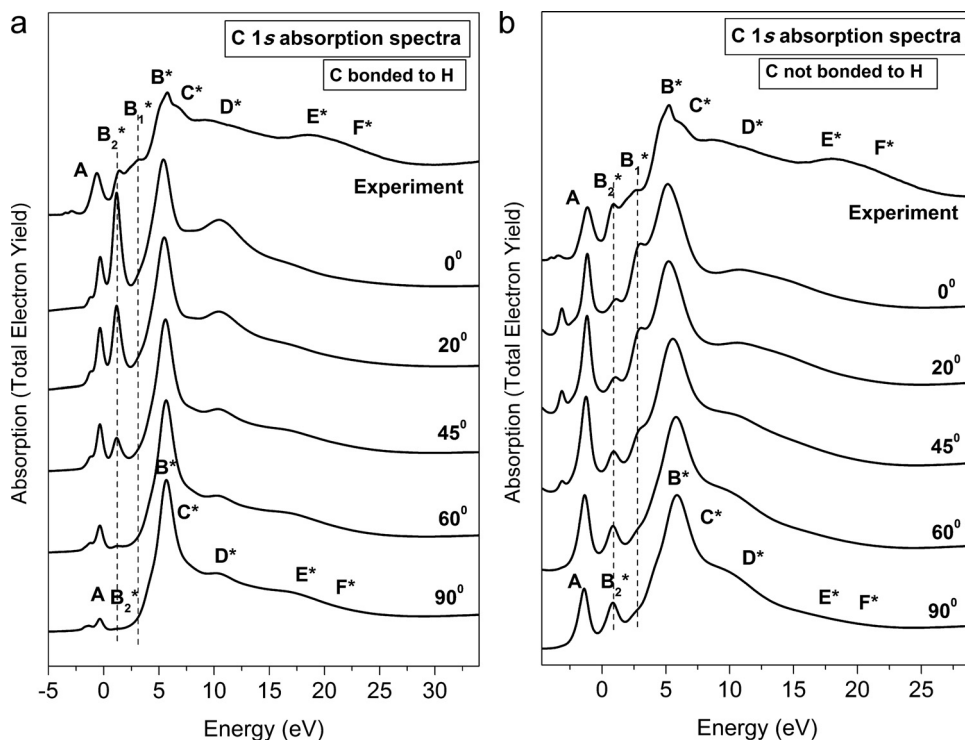


Fig. 5. Comparison of experimental and calculated for various incident angles NEXAFS spectra of H-SWNTs.

It was found out that the shape of calculated C K-edge spectra of H-SWNTs depends on incident angle of X-ray beam (Fig. 5). The C 1s polarized absorption spectra of H-SWNT models were calculated for two cases of absorbing carbon atoms. In the first case, the carbon atom unbounded with hydrogen atom was assumed to be absorbing (Fig. 5b). In the other case, the bounded with hydrogen atom was chosen (Fig. 5a). Polarized NEXAFS spectra proved our interpretation of all main spectral features. The both peaks B_1^* and B_2^* are revealed when a carbon atom unbound with hydrogen atom was chosen to be absorbing. At the same time, polarized spectra showed some variations in B_1^* and B_2^* peak intensities with changing of incident angle of X-ray beam. On the other hand, when the carbon atom bound with H atom was chosen as absorbing one (Fig. 5a), only one peak B_2^* is observed in calculated spectra. In this case, the intensity of B_2^* demonstrates even more strong dependence on orientation of vector polarization of incident beam that can be attributed to addition C–H bond. This observation confirms our assumption about absorption contribution from carbon atoms unbound to hydrogen atoms to experimental C K-edge spectrum of H-SWNTs. Such carbon atoms place between two H-bound carbon atoms which is led to electronic density overlapping between hydrogen atoms as bounded chemically to carbon atoms but and neighboring carbon atoms also.

In the present work, only covalent bounding of hydrogen atoms to carbon ones was only taken into account as the most probable mechanism of hydrogenation. At the same, the interaction between carbon and hydrogen atoms inside SWNTs was not considered.

4. Conclusions

The combined investigation of the hydrogenated single-walled carbon nanotubes by highly chemically sensitive X-ray methods (NEXAFS spectroscopy and XPS) is presented. The formation of the C–H covalent bonds in the H-SWNTs is observed. The interaction of hydrogen atoms with SWNTs proceeds through the covalent

attachment of hydrogen 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 atom from the trigonal (sp^2) to tetrahedral (sp^3) hybridization.

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