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Hydrogenated carbon nanotubes: x-ray absorption spectroscopy and *ab initio* simulation analysis

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Abstract. The paper presents the results of investigation of the chemical bond formation in hydrogenated single-walled carbon nanotubes using X-ray absorption spectroscopy. All measurements were performed with the use of synchrotron radiation at BESSY II. The C1s absorption spectra point to formation of covalent chemical bonding between the hydrogen and carbon atoms in H-SWNTs. The investigation of the H-SWNT local structure has been carried out on the basis of the semi-empirical PM6 method (MOPAC 2009) and Finite Difference method. The possibility of H-SWNTs dehydrogenation was also investigated.

1. Introduction

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. Therefore, during recent decades researchers continue seeking for techniques for hydrogen storage and transportation. 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 carbon nanotubes (CNTs) may be used as hydrogen reservoirs [1]. 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 spectroscopy (NEXAFS) technique was 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 possibility of H-SWNTs dehydrogenation was also investigated.

2. Methods

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 (SWNT paper). The SWNTs were hydrogenated at $P \sim 5.0$ GPa and $T \sim 500^\circ\text{C}$ and contained 5.335 wt.% of hydrogen [2]. Measurements were performed at the Russian-German beamline BESSY II (Berlin, Germany) by using experimental station Mustang. NEXAFS spectra of all the samples were recorded at the C 1s absorption edge in the total electron yield mode with the photon energy resolution of 75 meV. In all the dehydrogenation experiments, temperature was controlled by a thermocouple and pyrometer. Variations in the sample electron structure were monitored by NEXAFS.

Investigation of the local structure of hydrogenated single-walled carbon nanotubes was performed based on advanced theoretical analysis of experimental NEXAFS data. In order to get detailed understanding of the origin of the chemical bond between C and H atoms in H-SWNTs, semiempirical calculations were carried out using the MOPAC2009 code with PM6 parameterization.

Models of C-H chemical bonds where H atoms are connected to the SWNT outer surface were investigated. Fig. 1 shows the model structure of C-H chemical bonds that is a result of geometry optimization. In the case when hydrogen was located on the nanotube surface, formation of a tetrahedral structure with C-H bonds was observed.

Theoretical C K-edge XANES was analyzed using the non-muffin-tin approach, the finite difference method (FDMNES 2012) [3]. The C1s absorption spectra of H-SWNTs were calculated for two cases of absorbing atoms. In the first case, the atom unbound with hydrogen was assumed to be absorbing; in the other case, that bound with hydrogen was chosen.

3. Results and discussion

In the C1s absorption spectra of carbon nanotubes, 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 $2p$ electron states of carbon atoms and have π and σ symmetry, respectively [4]. Significant differences in the structure of C1s spectra of the pristine SWNTs and H-SWNTs are observed. There is a drastic decrease in the A peak intensity, emergence of new features B_1^* (288.8 eV), B_2^* (287.3 eV), B^* , C^* , D^* instead of B – D structures, and formation of isolated band E^* – F^* (Fig. 2). Note that, in addition to new absorption bands in H-SWNT spectra, A band observed in the pristine nanotube spectrum still persists thus proving incompleteness of nanotube hydrogenation.

It would be natural to associate the changes observed in the H-SWNT C1s spectra with chemical interaction between the H atoms and nanotube wall. What is significant is that the SWNT C1s spectrum variations taking place after SWNT hydrogenation are similar to those after SWNT fluorination (F-SWNTs). The F-SWNT C1s spectra that we have measured under the same conditions exhibit similar main features. Among them, the most considerable ones were reduction of π - and σ -resonances (peaks A and B , respectively), rise of new spectral features in the 286 to 292 eV range, and band E^* – F^* at the energies of 303 to 310 eV. Similarity of H-SWNT and F-SWNT C1s spectra allows us to assume that the chemical binding of fluorine and hydrogen atoms with carbon ones occurs in both cases mainly by binding the fluorine and hydrogen atoms to carbon atoms on nanotube sidewalls with forming $\sigma(\text{C}-\text{F})$ and $\sigma(\text{C}-\text{H})$ bonds due to covalent mixing of $\text{F}2p$ - and $\text{C}2p_z$ -, and $\text{H}1s$ - and $\text{C}2p_z$ - valence electron states, respectively [5]. Obviously, this binding of fluorine and hydrogen atoms modifies the coordination of carbon atoms from triangular in original nanotubes to nearly tetrahedral in fluorinated and hydrogenated nanotubes; this is possible only when sp^2 valence state hybridization of carbon atoms changes for sp^3 hybridization in F-SWNTs and H-SWNTs. At the same time, the H-

SWNT spectrum has one more new peak at 287.3 eV as compared with the F-SWNT spectrum. This peak is commonly attributed to C-H bonds in the C1s NEXAFS of hydrocarbons [4]. The two new peaks in the C1s 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 $\sigma(\text{C-H})$ bonds with different value of charge transfer between C and H atoms.

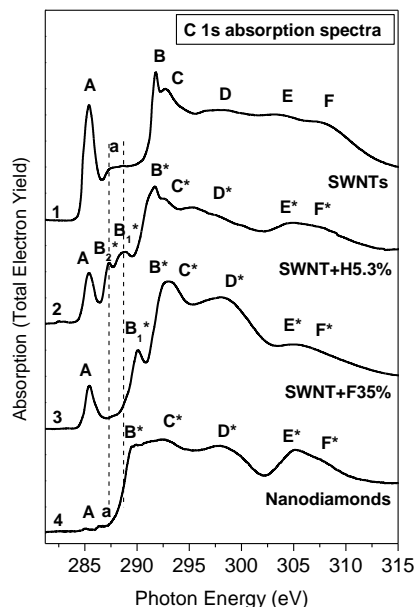
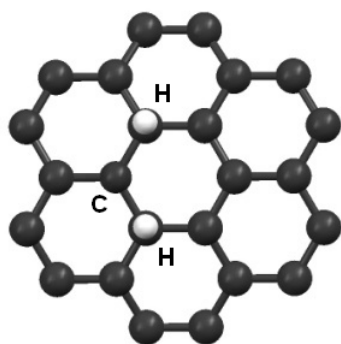


Figure 1. The model structure of H-SWNTs used for calculations. Figure 2. C1s absorption spectra of the SWNTs, SWNTs+H5.3%, SWNTs+F35% and nanodiamonds.

The model of H-SWNTs with 1.6 nm diameter was generated, and nanotube fragments were used in calculations. As a result of geometry optimization, formation of tetrahedron with C-H and C-C bond lengths of 1.2 and 1.5 Å, respectively, took place. The C K-edge spectra of the optimized H-SWNT model were calculated. Results of comparison between the experimental and theoretical spectra are presented in Fig. 3. The H-SWNT theoretical spectra (Fig. 3, curves 3 and 4) reproduce all the main details of the experimental spectrum. This reproducibility confirms our conclusion about formation of C-H chemical bond at the SWNT surface. Fig. 3 shows that, when a carbon atom unbound with hydrogen was chosen to be absorbing, the theoretical spectrum (Fig. 3, curve 3) exhibits both features B_1^* and B_2^* in the 286 to 292 eV energy range. On the other hand, when the carbon atom bound with H was chosen an absorbing (Fig. 3, curve 4), only one feature B_2^* is observed. This can be regarded as an evidence of the fact that the measured C1s absorption spectrum of H-SWNTs is the summed spectrum of carbon atoms of two types with different C-H bond forces and different value of electron transfer between the carbon and hydrogen atoms.

Investigation of CNT dehydrogenation process makes it possible to estimate the type and force of carbon-hydrogen bonds and to find out whether the graphene mesh is distorted. Thermal annealing is one of the possible methods of H-CNT dehydrogenation. Fig. 4 presents the results of H-SWNT dehydrogenation process controlled by NEXAFS. The figure demonstrates that even after annealing at the temperature equal to that of H-SWNT hydrogenation ($T_H \sim 500^\circ\text{C}$) dehydrogenation of H-SWNTs was impossible. This means that the results of hydrogenation are more complicated for H-SWNTs (as well as for F-SWNTs) than for graphene and graphite. It is natural to assume that H-SWNT dehydrogenation temperature is higher than T_H and will be equal to T_H of H-MWNTs. Whereas, our data obtained earlier for F-CNT annealing showed that annealing of F-SWNTs and F-MWNTs started

at the temperatures equal to the fluorination temperature (T_f) of F-MWNTs whose fluorination temperature of $\sim 200^\circ\text{C}$ is higher than F-SWNTs.

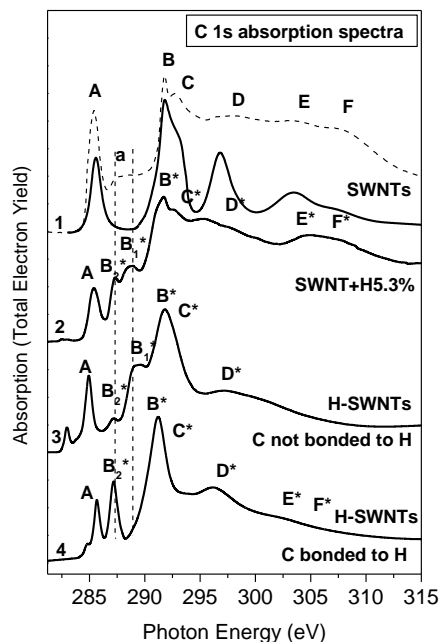


Figure 3. Measured and calculated CK-edge spectra of SWNTs and H-SWNTs.

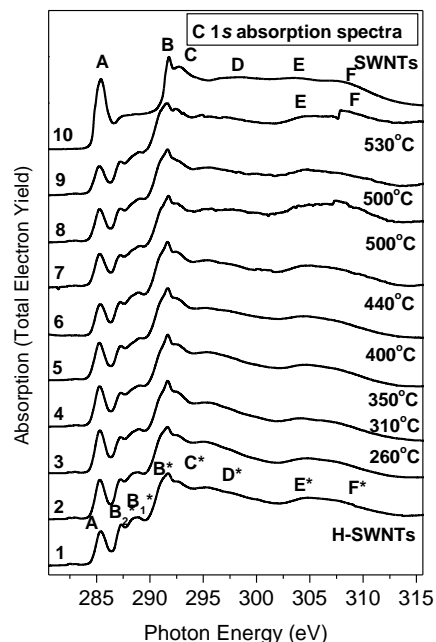


Figure 4. CK-edge spectra of SWNTs+H5.3% before and during annealing.

4. Conclusions

Investigation of chemical bonds formation in hydrogenated single-walled carbon nanotubes by using X-ray absorption spectroscopy has been performed. It was found out that SWNT hydrogenation is accompanied by chemical binding of hydrogen and carbon atoms on the tube side walls. Hydrogen atoms do not substitute carbon atoms in graphene layers of SWNTs but they join perpendicularly to them due to covalent mixing between C $2p_z$ and H $1s$ states. The coordination of carbon atoms changes from sp^2 -triangular to sp^3 -tetrahedral.

Acknowledgements

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