Electrotransport Properties of Carbon Nanotubes Irradiated with Ultraviolet Radiation

T.A. Len[1], I.V. Ovsiienko[1], L.Yu. Matzui[1], O.A. Brusilovetz[2], Yu.A. Kunitskyi[1]

[1] *Taras Shevchenko National University of Kyiv, Physical faculty, 4, Glushkov Av., 01601 Kyiv, Ukraine*
[2] *Taras Shevchenko National University of Kyiv, Chemical faculty, 62, Volodymyrska St., 01601 Kyiv, Ukraine*

The electrical resistance of carbon nanotubes irradiated with ultraviolet was investigated. It is established that ultraviolet irradiation results in insignificant functionalization of carbon nanotubes surface that doesn't substantially affect the nanotubes resistivity. It is shown that carbon nanotubes functionalization with strong oxidizers leads to a significant increase of resistivity by breaking electronic system and localization of electrons by functional groups, and also to increase of contact resistance between the individual tubes by reducing the contact area between them.

Keywords: Carbon nanotubes, Electrical resistance, Ultraviolet irradiation, Functionalization.

1. INTRODUCTION

The expansion of the field of application of nanotechnologies caused by the unique properties of nanomaterials requires an in-depth study of the properties, which are, mainly, determined by the electronic structure. The existence of carbon in new structural states, namely, in the form of nanodiamonds, fullerites, nanotubes, and nanofibers, generates an increased interest in the study of their atomic-structural characteristics and properties of the electronic structure. Composites with carbon nanotubes (CNT) are widely used in recent years due to the huge potential of these materials in different fields of science and technology [1, 2]. One of the open questions in the production of composites based on CNT is to ensure stability of such composites under aggressive environments. The directional control of the CNT properties is an important problem when fabricating composites. This problem can be solved in different ways. The functionalization of the CNT surface, partial substitution of the CNT atoms for other types of atoms, adjoining of alien atoms or molecules to the walls and edges of CNT, introduction of atoms or molecules into the inner cavity of CNT or into the space between CNT in aggregates of CNT [3] are used to change the CNT properties. The physical and chemical properties of functionalized CNT were found to be extremely interesting and multifaceted [4].

The aim of the present work is the establishment of the influence of functionalization and short-term ultraviolet irradiation on the electrical resistance of CNT.

2. DESCRIPTION OF THE OBJECTS AND METHODS OF STUDY

The initial CNT were obtained by the method of high-temperature evaporation of graphite electrodes in the electric arc with subsequent desublimation. Nickel was used as a catalyst in CNT fabrication. The initial tubes are multiwalled with the diameter up to 30 nm. Functionalization of the initial CNT was performed according to the following scheme:

1. boiling of CNT during 3 hours in an aqueous solution of nitric acid;
2. washing of CNT in water;
3. boiling of CNT in concentrated nitric acid;
4. washing of CNT up to neutral pH;
5. drying of CNT.

The authors of [5] presented the investigation results of the initial CNT structure by the X-ray diffraction method which revealed the presence of metal-catalyst Ni in the samples. According to the X-ray studies, the crystallite size in the initial CNT is equal to $L_c = 24$ nm. As the investigations of the functionalized CNT structure showed, decrease in the crystallite sizes during functionalization of CNT is not observed.

The initial CNT were exposed to ultraviolet irradiation (UVI) with the electrical power of 400 W that corresponds to the light power of 54 W during $t = 20$ min.

The studies of the initial and irradiated with ultraviolet CNT powders by the infrared (IR) spectroscopy were performed for the determination of the quantitative composition of functional groups on the CNT surface. The studies were carried out using the IR-spectrometer Spectrum BX FT-IR by Perkin Elmer Co. with the operating frequency of 4000-400 cm^{-1}. The samples in the form of tablets of the diameter of 10 mm were manufactured from the mixture of pre-dried CNT and KBr powders.

The bulk samples were fabricated from the CNT powder in the form of rectangular parallelepipeds of the sizes of 2 mm $\times$ 3.5 mm $\times$ 15 mm to measure the electrophysical properties [6, 7]. The investigations of the electrotransport properties were conducted by the 4-probe technique [8, 9]. The samples are marked as follows: initial CNT; CNT-UVI are the CNT exposed to the action of ultraviolet irradiation; CNT-COOH are the CNT, to which the COOH groups are attached, i.e. functionalized CNT; CNT-COOH-UVI are the functionalized CNT exposed to the action of ultraviolet irradiation.

3. EXPERIMENTAL PART AND ANALYSIS OF THE RESULTS

In Fig. 1 and Fig. 2 we illustrate the IR-spectra for the CNT and CNT-UVI samples and also for the CNT-COOH and CNT-COOH-UVI normalized to the –OH line.

As seen from Fig. 1 and Fig. 2, a number of lines, which correspond to vibrations of both functional groups and carbon atoms in CNT, is observed in the spectra of the initial and irradiated CNT. Two lines corresponding to valence vibrations of the –OH group are observed in
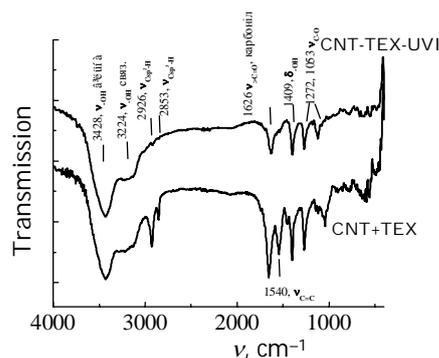
Fig. 1 – IR spectra of CNT and CNT-UVI samples
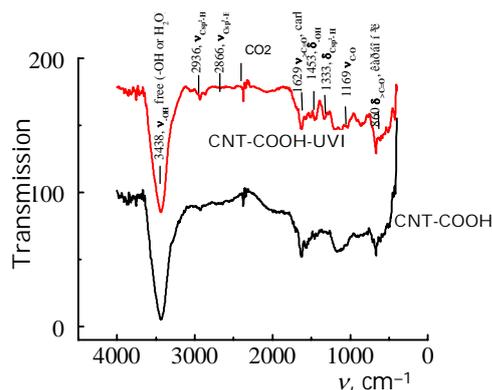
Fig. 2 – IR spectra of CNT-COOH and CNT-COOH-UVI samples

the short-wave spectral region of the samples. The first (3428 cm^{-1}), more intense line corresponds to valence vibrations of the free –OH group, i.e. those which enter the composition of functional groups (for example, COOH carboxyl groups). The next two lines (2926 cm^{-1} and 2853 cm^{-1}) are associated, respectively, with vibrations of sp^2 and rehybridized sp^3 carbon atoms located on the boundaries of crystallites and connected to the hydrogen: Csp^2-H and Csp^3-H. One more line associated with vibrations of the graphite core is the C=C line (1540 cm^{-1}). This line is observed in both the graphite materials and CNT. As seen from the figure, intensity of this line in the initial CNT sample is approximately equal to the intensity of Csp^2-H and Csp^3 lines as well as to the intensities of lines which correspond to different functional groups. Intensity of this line for the irradiated samples can be neglected. The line, which corresponds to vibrations of the carbonyl group > C=O (1626 cm^{-1}), is observed in the spectra of both samples. Comparing the relative intensity of this line with the relative intensity of the line corresponding to Csp^2-H, Csp^3-H, and C=C vibrations and taking into account that the number of Csp^2-H, Csp^3-H, and C=C bonds does not decrease in irradiation, one can suggest that intensity of this line significantly increases after irradiation. The next one is the line (1409 cm^{-1}), which is associated with deformation vibrations (δ OH) of the –OH group. We note that intensity of this line in both spectra correlates with the intensity of the line of valence vibration ν-OH. The next two lines (1272 cm^{-1} and 1053 cm^{-1}) are associated with vibrations of the C-O functional group involved to the composition, in particular, of the lactone group or esters (R-O-C-O-R).

Analysis of the CNT spectra allows to assume that relative concentration of functional groups in the initial

CNT samples is very small. Short-term irradiation of CNT by ultraviolet led to the significant increase in the relative concentration of functional groups, in particular, hydroxyl and carbonyl groups and C-O groups. This process can be explained by the fact that UVI leads to a partial ozonation of air. Ozone is a strong oxidizer. During its interaction with the CNT surface, the oxygen-containing groups are formed. This process substantially depends on the irradiation time. There is a certain optimal time interval, during which there occurs ozonation of air under the UVI action and interaction of ozone with the CNT surface. Amount of zone for small irradiation times is insufficient for functionalization, while for large times the structure destruction of the CNT surface begins.

As seen from Fig. 2, unlike the CNT and CNT-UVI samples, the differences in the IR spectra of the CNT-COOH and CNT-COOH-UVI samples are minimal. For both samples, it is possible to observe the intense lines associated with vibrations of functional groups: hydroxyl group (valence and deformation), carbonyl group (valence and deformation), and C-O group (valence). At that, the relative intensities of the lines corresponding to the C-H vibrations are significantly smaller than the relative intensities of the lines corresponding to the vibrations of functional groups, and also UVI weakly affects the ratio of these intensities. Thus, relative intensity of the line, which corresponds to the Csp^2-H vibrations, after irradiation slightly increases in comparison with the relative intensity of the –OH line, and a wide line corresponding to vibrations of the C-O group in the spectrum of the initial CNT-COOH sample after irradiation splits into several individual less intense lines. We note that line, which corresponds to the C=C vibrations, is not observed in the spectra of both the initial sample and irradiated one. Thus, the UVI effect on the pre-functionalized CNT leads, obviously, to an insignificant decrease in the concentration of functional groups on their surface.

In Fig. 3 we illustrate the temperature dependences of the electrical resistivity of bulk CNT samples.

As seen from Fig. 3, a similar form of the temperature dependences of the electrical resistivity is observed for all CNT samples: an abrupt decay of the electrical resistance at low temperatures and a weak temperature dependence of the electrical resistance with increasing temperature. Parameters of the electrical resistivity of the samples are presented in Table 1.

As seen from Table 1 and Fig. 3, CNT-UVI sample has the least value of the electrical resistivity and CNT-COOH-UVI sample – the greatest value, that is, in one
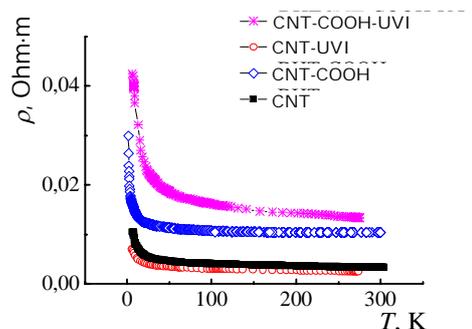
Fig. 3 – Temperature dependences of the electrical resistivity of bulk CNT samples

Table 1 – Parameters of the electrical resistivity of bulk CNT samples

Sample	CNT	CNT-UVI	CNT-COOH	CNT-COOH-UVI
$\rho_{4.2}$, Ohm·m	0.011	0.007	0.030	0.042
ρ_{293}, Ohm·m	0.0033	0.0025	0.010	0.013
$\rho_{4.2}/\rho_{293}$	3.33	2.8	3	3.2

case UVI leads to the decrease in the resistance compared with the initial material, and in another case – to its increase. We should note that $\rho_{4.2}/\rho_{293}$ ratio for all samples is approximately equal to 3, which is more than, for example, for fine crystalline anisotropic graphite, for which this ratio is 1.6, but is significantly less than, for example, for CNT obtained by the method of evaporation and desublimation of graphite in the electric arc (~ 30). Let us consider the mechanisms of formation of the temperature dependence of the electrical resistance for the studied CNT.

Resistance of bulk CNT samples will be determined as a sum of two components [10]

$$\rho = \rho_{CNT} + \rho_{C} , \qquad (1)$$

where ρ_{CNT} is the CNT resistivity and ρ_{C} is the contact resistance between individual CNT, which depends on the pressure on the contacts and contact area of the contacting particles. As a rule, the contact resistance can be neglected for composites with high density, in which concentration of CNT is much higher than the percolation transition (mass concentration is > 10 %), while it is impossible for the functionalized CNT.

Analysis of the electrical resistance of CNT can be performed within the Wallace model [11], which is used for the description of the electrical conductivity of weakly ordered fine crystalline graphites. Within this model, the electrical resistivity can be written as

$$\rho = \frac{\pi\sqrt{3} \cdot \gamma_0 \cdot a_0 \cdot d_{002} \cdot \hbar}{\Delta E_F \cdot e^2 \cdot L_{ef}} , \qquad (2)$$

where γ_0 is the overlap integral of the wave functions of electrons in the graphite layer, a_0 is the lattice constant, d_{002} is the distance between two neighboring graphite layers, $\hbar$ is the Plank constant, E_F is the energy at the Fermi level, e is the electron charge.

The effective free path of charge carriers is determined by the dominant mechanisms of their scattering. For these CNT, scattering on the boundaries of crystallites being the temperature-independent process is the main scattering mechanism of charge carriers [6]. An anoma-

lous increase in the electrical resistance with decreasing temperature is associated with the manifestation of the weak localization effects and electron-electron interaction of charge carriers [6]. Obviously, the change in the electrical resistance of the CNT samples during functionalization and UVI can be associated with both the change in the resistance of the functionalized CNT themselves and change in the contact resistance between individual CNT. The change in the resistance of individual CNT is determined by the change in the mobility of charge carriers (in our case, by the change in the crystallite sizes in CNT) and change in the concentration of charge carriers during functionalization of CNT. As the performed studies of the structure of functionalized CNT showed, the decrease in the crystallite sizes at functionalization of CNT was not observed. Thus, the change in the concentration of charge carriers leading to the shift of the Fermi level is a single factor which influences the value of the electrical resistance of CNT during functionalization. However, the detailed studies of the electronic structure of functionalized CNT, performed in [12], showed that functionalization does not lead to a significant change in the value of the Fermi energy during functionalization.

Thus, as the performed investigations showed, the increase in the electrical resistance of the samples of functionalized CNT is associated with the change in the contact resistance between individual CNT. A significant number of functional groups on the CNT surface causes the increase in the contact resistance between individual CNT. UVI of such CNT leads to an insignificant decrease in the concentration of functional groups on the CNT surface, but it does not substantially change the contact resistance between individual CNT.

4. CONCLUSIONS

1. UVI of CNT leads to an insignificant functionalization of their surface. This, in turn, causes the increase in the concentration of free charge carriers in CNT, but it does not substantially influence the contact resistance between separate tubes.

2. Functionalization of CNT by strong oxidizers results in a considerable increase in the CNT resistance on account of the destruction of the CNT π-system and localization of π-electrons by functional groups as well as the increase in the contact resistance between individual CNT due to the decrease in the contact area between CNT.

3. UVI of functionalized CNT leads to an insignificant decrease in the concentration of functional groups on the CNT surface, but it does not essentially influence the electrical resistance of functionalized CNT.

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