

The Structure and Transport Properties of Single-walled Carbon Nanotubes Modified by Cobalt-containing Complexes

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The paper presents the results of investigation of structural and morphological peculiarities and transport properties of single-walled carbon nanotubes modified by cobalt-containing complexes. A scheme that allows simultaneously to clean the source nanocarbon material from the catalyst impurities and particles of disordered carbon, to separate single-walled tubes bunches into individual tubes, to cut the tubes along to defects and to modify tubes surface by cobalt-containing complexes is proposed. Using the thermomagnetometric method, it was found that attached to the surface of the carbon nanotubes cobalt is in the form of cations in the complicated complexes. When heating modified carbon nanotubes the complicated complexes are destroyed, and cobalt nanoparticles are formed. It is revealed that for bulk specimens of source single-walled carbon nanotubes the main mechanism of conductivity is the hopping conductivity with the variable hopping length for 3D system. Such conduction mechanism is typical of disordered graphite materials, as well as of mats and binders of single-walled carbon nanotubes. It is shown that modification of single-walled carbon nanotubes by cobalt-containing complexes results in a change in the character of the conductivity for bulk specimens of single-walled carbon nanotubes. For bulk specimens of modified single-walled carbon nanotubes, conductivity is described in terms of power temperature law that is typical of individual single-walled carbon nanotubes. It is shown that such a change in the conduction mechanism during surface modification is associated with the creation of a small negative charge on the surface of nanotubes during the modification.

Keywords: Single-walled carbon nanotubes, Cobalt-containing complexes, Magnetic susceptibility, Hopping conductivity with the variable hopping length.

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1. INTRODUCTION

One of the many aspects of investigation of the single-walled carbon nanotubes (SWCNTs) is the study of the possibilities of their surface functionalization and modification. Surface functionalization, which is usually carried out using strong oxidants, leads to the formation on the SWCNTs surface of functional groups [1-5]. These functional groups, on the one hand, provide the formation of homogeneous dispersion of SWCNTs in solvents including polymer matrix, and, on the other hand, cause a significant number of defects in SWCNTs structure. Another promising direction is chemical functionalization of SWCNTs with metal-containing molecular complexes. A number of works are devoted to the issues of covalent and non-covalent functionalization of CNTs by metal-containing complexes [6-8]. In these papers, methods for obtaining such complexes on the surface of CNTs and their properties are considered. In this case, the main attention is paid to the chemical properties of the obtained modified CNTs, in particular, their catalytic activity and the possibility of using them as catalysts in chemical synthesis [9]. However, the questions of changing the physical properties of SWCNTs modified on the surface with metal-containing complexes, especially the properties associated with charge transfer, are discussed in these works much less.

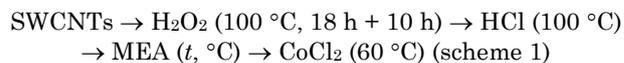
The objectives of the present work are to establish the possibility of surface modification of SWCNTs by cobalt-containing complexes, to identify the structural

and morphological state of cobalt on the surface of SWCNTs, as well as to study the electrical conductivity of modified SWCNTs and determine the mechanisms of charge transfer in them.

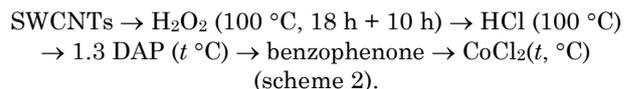
2. OBJECTS AND METHODS

SWCNTs produced by catalytic decomposition of acetylene using yttrium and nickel as catalysts have been chosen as a source for modification. According to the logbook, the mean diameter of CNTs $\langle d \rangle = 1.4$ nm and the packed density is equal to 15 mg/cm³.

The chemical modification of SWCNTs by cobalt-containing complexes has been performed according to two schemes:



and



As it follows from the schemes, the processes of SWCNTs surface activation, "caps opening" at the ends of each tube and cutting of tubes along defects occurred simultaneously during CNTs treatment by hydrogen peroxide. The refuses of metal catalyst and the particles of disordered carbon were removed from the source nanomaterial at the second stage of treatment through boiling in hydrochloric acid. At the next stage,

SWCNTs were treated by an organic compound, which is a surface-active material, in order to form complicated complexes at CNTs surface. At the ending stage, SWCNTs were heated in cobalt chloride solution, while the cobalt cations were attached through complicated complexes to the surface of the SWCNTs.

The structure of modified SWCNTs has been investigated by methods of X-ray diffraction and tunnel electron microscopy. For investigation of electric resistivity, the bulk specimens from source and modified SWCNTs powders were prepared by cold compacting without binder. In the obtained bulk specimens, there is a prevailing orientation of CNTs so that the axes of CNTs lie in a plane perpendicular to the pressure direction. Electric resistivity of bulk specimens has been studied in the temperature range 4.2-293 K using standard four-probe technique. Also, the temperature dependence of magnetic susceptibility of modified SWCNTs has been measured within the temperature range 300-850 K using standard Faraday technique [10] upon heating and cooling of specimens. The heating and cooling rates did not exceed 10 K/min.

3. EXPERIMENT AND DISCUSSION

3.1 The Structure and Phase Composition of Modified SWCNTs

X-ray studies of modified SWCNTs have been performed to analyze their structure and phase composition. Fig. 1 presents the fragments of the X-ray diffraction patterns for two specimens of SWCNTs modified according to the schemes 1 and 2. A fragment of the X-ray diffraction pattern for the source SWCNTs is also presented for the comparison.

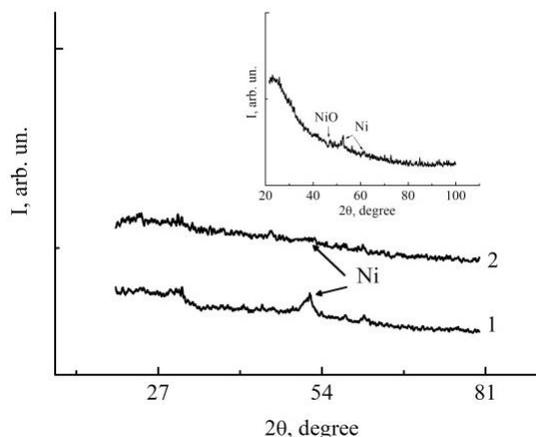


Fig. 1 – Fragments of the X-ray diffraction patterns for source SWCNTs (inset) and SWCNTs modified by cobalt-containing complexes according to the schemes 1 (1) and 2 (2)

As it follows from Fig. 1, no graphite reflections are observed at the pattern for source SWCNTs, hence, this material does not contain the ordered multilayered carbon structures or SWCNTs splices. Meanwhile, weak reflections of nickel catalyst are observed. The X-ray diffraction patterns obtained for SWCNTs modified according to schemes 1 and 2 contain weak reflections, which correspond to nickel catalyst. It evidences that the methods of SWCNTs cleaning involved in schemes

1 and 2 of chemical modification do not lead to the total removal of the metal catalysts particles. No reflections corresponding to cobalt were detected at the X-ray diffraction patterns. So, modified SWCNTs specimens do not contain cobalt coherent scattering regions larger than 0.3 nm. No graphite reflections were observed at the X-ray diffraction pattern for SWCNTs specimens modified according to the scheme 2. Meanwhile, in the case of the scheme 1 being used a broad peak at $2\theta = 30^\circ$ is observed, which could be interpreted as 002 reflection formed by a nanoscaled graphite structure.

Fig. 2 presents the fragments of TEM images of source (a) and modified according to scheme 2 (b) SWCNTs.

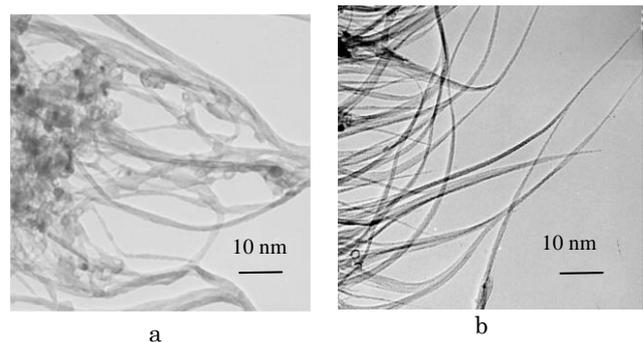


Fig. 2 – Fragments of TEM images of source (a) and modified with scheme 2 (b) SWCNTs

As it is seen from Fig. 2, the source specimen contains the nanotube bunches up to ~ 3 nm in diameter and particles of disordered carbon ~ 5.5 nm in size. The chemical treatment of source SWCNTs leads to a substantial shortening of CNTs and separation of bunches of tubes into individual tubes. CNTs walls in TEM images are seen more distinctly as compared to those in the source SWCNTs. The absence of "waviness" indirectly indicates an increase in nanotubes stiffness, presumably due to adjoining of the large-scale cobalt-containing complexes.

3.2 Magnetic Susceptibility of Modified SWCNTs

One of the most efficient methods to control the metal content in the carbon materials is the proposed in [10] thermo-magnetic method that allows to detect the presence of magnetic metal in nanocarbon material by the data on the temperature dependence of magnetic susceptibility. To determine the presence of cobalt and nickel particles in the fabricated specimens of modified SWCNTs, the investigations of the temperature dependence of magnetic susceptibility have been performed in the temperature range 300-850 K using the Faraday technique.

Fig. 3 presents the temperature dependence of magnetic susceptibility $\chi(T)$ for the source SWCNTs specimen.

As it is seen from Fig. 3, the character of the temperature dependence of magnetic susceptibility $\chi(T)$ for source SWCNTs is typical for carbon materials containing ferromagnetic constituent with the Curie temperature $T_c \sim 580$ K. Carbon materials including

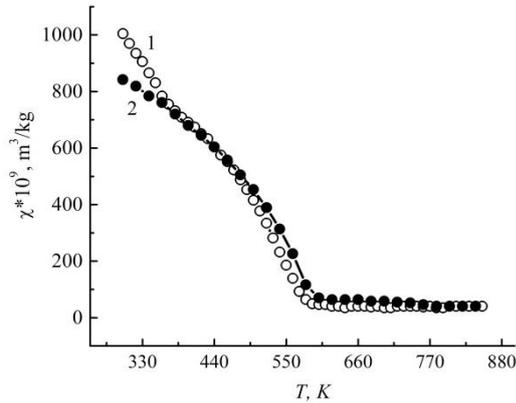


Fig. 3 – Temperature dependence of magnetic susceptibility $\chi(T)$ for source SWCNTs: 1 – heat, 2 – cool

CNTs are known to be diamagnetic with $\chi < 0$. That is why, the character of the $\chi(T)$ curve presented in Fig. 3 could only be associated with the presence of metal catalyst particles in the source material. According to the data of the X-ray phase analysis, the refuses of nickel catalyst, for which the Curie temperature T_{cNI} is equal to 631 K, are observed in this specimen. Nevertheless, the observed value of the Curie temperature is $T_c \sim 580$ K. This reduction is caused by the nanoscaled structure of nickel particles used as catalyst for SWCNTs synthesis [10].

Fig. 4 presents the temperature dependences of magnetic susceptibility for SWCNTs specimen chemically modified by cobalt-containing complexes (scheme 2) for the alternating heating/cooling cycles.

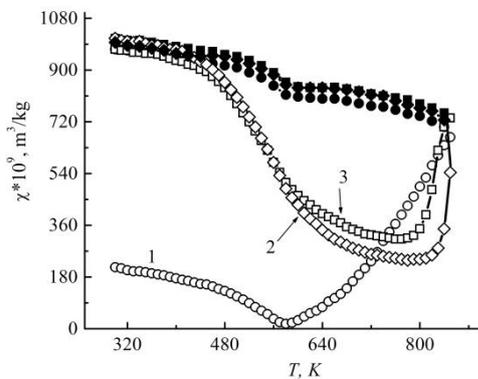


Fig. 4 – Temperature dependences of magnetic susceptibility $\chi(T)$ for SWCNTs modified by cobalt-containing complexes (scheme 1) for the sequenced heating-cooling cycles, the curve number corresponds to the cycle number, the open labels are heating, the closed ones are cooling

As shown from Fig. 4, a peculiar complicated $\chi(T)$ dependence is observed. Its shape changes after each heating/cooling cycle.

Let analyze the obtained results in more details. The character of $\chi(T)$ dependence at the first heating from room temperature coincides with that for the source NCM: magnetic susceptibility decreases, and a kink was observed at $T \sim 580$ K. Meanwhile, χ value at 300 K is 5 times lower than that of the source SWCNTs. This indicates the presence of the only magnetic constituent, namely, the refuses of nickel catalyst, the particle sizes of which are sufficient to exhibit ferromagnetic

behavior. Since SWCNTs have been modified by cobalt-containing complexes, in which cobalt is in an atomic form, these atoms could not promote ferromagnetic behavior of the material. At further heating of the modified SWCNTs, the character of $\chi(T)$ dependence becomes essentially different from that for the source CNTs. Magnetic susceptibility begins to rise and at 850 K reaches the value four times higher than the initial value. Upon cooling of specimen from 850 K to 300 K, a weak $\chi(T)$ dependence with a kink at 580 K is observed. During the second heating cycle, χ also slightly decreases with a kink at 580 K, remaining, however, ferromagnetic in contrast to the first cycle of heating. At further heating, χ values slightly decrease, and then a sharp increase to the values characteristic of the previous cycle is observed. The cooling branch of $\chi(T)$ dependence during the second cycle almost totally coincides with that for the first cycle. $\chi(T)$ curves for all subsequent heating cycles are the same as in the second cycle. Some general regularities may be emphasized: initially χ decreases exhibiting a kink at 580 K and then sharply increases at further heating, χ value is lower as compared to the previous cycle. The character of $\chi(T)$ curve is almost the same for all cooling cycles. Just such character of $\chi(T)$ curve is known to be observed for nanocarbon material containing cobalt particles, the Curie temperature for which is equal to 1121 K. Let analyze the processes occurring in modified SWCNTs upon heating higher than 580 K. Evidently, in this case the destruction of chemical complexes containing cobalt cations on the CNTs surface takes place. Due to the surface diffusion, cobalt agglomerates and, as a result, cobalt metal nanoparticles are formed. The total value of magnetic susceptibility consists of contribution due to nickel refuses, which determines the presence of a kink at 580 K, and magnetic susceptibility of cobalt nanoparticles that are formed as a result of destruction of cobalt-containing complexes.

Thus, thermo-magnetic method directly indicates the presence of cobalt-containing complexes in the chemically modified SWCNTs.

3.3 Resistivity of Modified SWCNTs

Fig. 5 presents the temperature dependence of resistivity for bulk specimens of source and functionalized SWCNTs.

As it follows from Fig. 5, for all specimens the character of resistivity temperature dependence is similar.

A sharp decrease in resistivity at low temperatures is observed and then resistivity is weakly dependent on temperature. However, despite the similar kind of the resistivity temperature dependence for source and functionalized SWCNTs in general, in the low-temperature interval for functionalized SWCNTs there are some peculiarities in the dependence $\rho(T)$. So, for the bulk specimen (modified SWCNTs according to scheme 2), the values of resistivity at low temperatures are significantly reduced. That leads to a significant decrease in the resistivity ratio $\rho_{1.2}/\rho_{293}$ from 26 for source SWCNTs to 6.3 for modified SWCNTs. For modified SWCNTs according to scheme 1, the change in the ratio $\rho_{1.2}/\rho_{293}$ is not so significant ($\rho_{1.2}/\rho_{293} = 24$), but

for this specimen precisely in low-temperature interval the character of the resistivity temperature dependence changes essentially (see inset in Fig. 6).

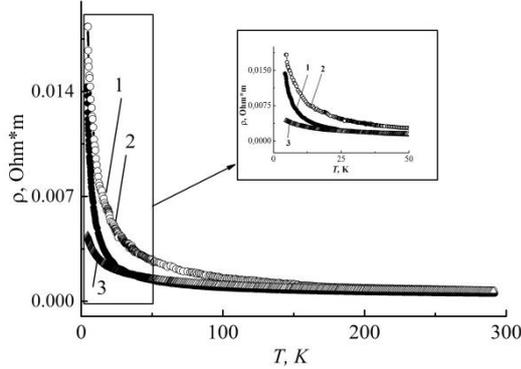


Fig. 5 – Temperature dependences of resistivity $\rho(T)$ for bulk specimens of source SWCNTs (1) and modified SWCNTs according to scheme 1 (2) and scheme 2 (3)

Let us consider the SWCNTs conduction models. As it is known, SWCNTs are considered as the interacting 1D systems and their electronic properties, in particular, electric conductivity, are usually described within the theory of the strongly interacting 1D Luttinger liquid with the power type of the temperature dependence of resistivity [11]:

$$\rho(T) = aT^{-\beta}, \quad \beta = \frac{g + \frac{1}{8} - 2}{g}, \quad (1)$$

where a and β are the constants, Luttinger parameter g characterizes the degree of charge carriers interaction in the system. The parameter g that expresses the extent of electron interaction could acquire different values for different systems. Generally, g values are ranged from 0.2 to 0.3 that is much lower in comparison with the value $g = 1$ for the Fermi liquid. A more complex model is used to describe the resistivity of defective SWCNTs. In this model, in addition to the one responsible for the resistivity of the individual tube, two additions are also considered. The first of these additives is responsible for the resistance of the tube's junctions. This term in the first approximation is linearly dependent on temperature that is characteristic of metallic type of conductivity. The second term describes the barrier conductivity and considers the fluctuation tunneling through a thin barrier created by CNT defects [12-14]. Thus, the expression for resistivity takes the form:

$$\rho(T) = a_1 T^{-\alpha} + a_2 T + a_3 e^{\frac{T_l}{T+T_a}}, \quad (2)$$

where T_l is the temperature below which the barrier tunneling takes place, T_a is the temperature above which the thermo-activated conductivity above the barrier occurs, a_i are the coefficients determined by the geometry of the specimen. In the number of papers [15, 16], for the description of conductivity of SWCNTs mats and plaits the authors use the model of hopping conductivity with the variable hopping length both for

2D and 3D systems:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{d}} \right], \quad (3)$$

where d is the dimensionality of the system, σ_0 and T_0 are the constants. T_0 is related to the localization length ξ and density of states at the Fermi level $N_0(E_F)$ with equation:

$$T_0 = \frac{\eta_d}{n(E_F) \xi^d k_B}, \quad (4)$$

where η_d is the corresponding numerical coefficient. The choice of the system dimensionality is determined by the structural features of the SWCNTs bulk specimens.

As shown by a detailed analysis of the temperature dependence of conductivity for source SWCNTs, for this specimen the hopping conduction mechanism with variable hopping lengths for 3D system is realized.

Indeed, as can be seen from Fig. 6, which presents the temperature dependence of the conductivity $\sigma(T)$ in different coordinates, the experimental dependence $\sigma(T)$ is best described by the equation (3), where $d = 3$.

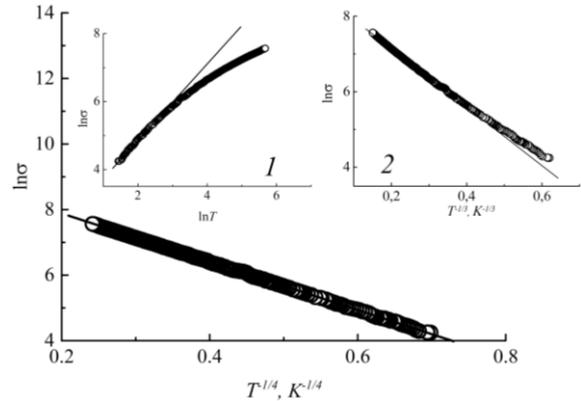


Fig. 6 – Temperature dependences of conductivity for bulk specimen of source SWCNTs in coordinates $\ln\sigma(T^{-1/4})$, $\ln\sigma(\ln T)$ (inset 1), $\ln\sigma(T^{-1/3})$ (inset 2)

Such conductivity mechanism is typical of disordered graphite materials, in particular, so-called amorphous carbon. The same conductivity mechanism is also observed in [17-19] for bundles and mats of SWCNTs.

Let us find out the possible reasons of such a mechanism of conductivity for source SWCNTs. The bulk specimens for investigation of resistivity have been obtained by cold pressure method. For pressed specimens, the total resistance R is determined as a sum of two terms: $R = R_0 + r_c$, where R_0 is the resistance of CNTs and r_c is the contact resistance. For SWCNTs as stated above, resistance is described in terms of the theory of strongly interacting 1D Luttinger liquid, or, if there is a significant number of CNTs junctions, within the theory of conductivity of 2D systems. The contact resistance r_c is dependent on many factors, among them surface condition, size of contact spot, contact pressure. As it is known, the contact resistance between

individual CNTs is big enough. However, the presence in specimen of a significant amount of disordered carbon phase leads to a significant decrease in contact resistance due to the peculiarities of the disordered carbon particle's structure. The disordered carbon phase particles have a sufficiently developed surface that facilitates the adhesion of individual CNTs to each other. It is the presence of a large amount of disordered carbon phase that allows to obtain bulk specimens of SWCNTs without the use of a binder. Thus, a bulk specimen of source SWCNTs can be considered as a 3D system and character of the conductivity temperature dependence indicates this. The calculated parameter T_0 is equal to 2903 K. This value of T_0 is much larger than the corresponding value of T_0 for mats of SWCNTs in [16], but close to the value of T_0 for amorphous carbon in [20].

As shown above, modification of SWCNTs by cobalt-containing complexes did not lead to a major decrease or increase in the resistivity of the CNTs bulk specimens. However, such modification significantly affected the character of the temperature dependence of resistivity of these specimens.

Fig. 7 presents the temperature dependences of conductivity for bulk specimens of modified SWCNTs according to scheme 1 (a) and scheme 2 (b) in the same coordinates as in Fig. 6.

Thus, as it follows from Fig. 7, for modified SWCNTs, the temperature dependence of conductivity is well described in terms of power temperature law, that is typical of individual SWCNTs (equation (1)). Calculated from the dependence $\ln\sigma(\ln T)$ parameters for both modified SWCNTs are presented in Table 1.

Table 1 – Calculated parameters α , g and a for modified SWCNTs

Specimen	α	g	a , Ohm·m
Scheme 1	0.459	0.185	$9.1 \cdot 10^{-3}$
Scheme 2	0.790	0.122	$6.0 \cdot 10^{-2}$

As can be seen from Table 1, for both specimens the values of constants a and g are almost equal to the corresponding values for SWCNTs in [21]. Such change of character of conductivity temperature dependence in our opinion is explained by the following reasons.

As is known, the treatment of SWCNTs with strong oxidizing agents, including hydrogen peroxide, leads to the formation on the surface of CNTs of functional oxygen-containing groups. This is the so-called covalent CNTs' surface functionalization. As a result of covalent functionalization, the surface of the CNTs acquires a small negative charge.

The consequence of covalent functionalization is, on the one hand, the formation of a large number of broken bonds on the surface of the CNTs, and, on the other hand, a certain destruction of the carbon layer π -system that leads to a deterioration of its conductive properties. Functionalization is used to untangle strands, CNT bundles, to form CNT colloidal solutions, and to strengthen the bond between the filler and the polymer matrix when creating polymer composites.

Let us turn to the studied specimens of SWCNTs. The treatment of the source SWCNTs with hydrogen

peroxide has led to the formation on the surface of the CNTs of a significant number of broken bonds, to which cobalt-containing complexes have joined through functional groups. As a result, there is a splitting of SWCNT's strands into individual CNTs that can be seen, for example, from Fig. 2. Further treatment of CNTs according to the schemes leads to the removal from the CNT's strands of metal catalyst particles and particles of the disordered carbon phase. Bulk specimens of SWCNTs were obtained without a binder polymer, the low concentration of which could provide better bonds between the individual tubes and promote the formation of a 3D conductive system due to the tunneling mechanism. The presence on the SWCNT's surface of a small localized negative charge due to covalent functionalization also creates conditions that prevent the movement of charge carriers between the individual tubes.

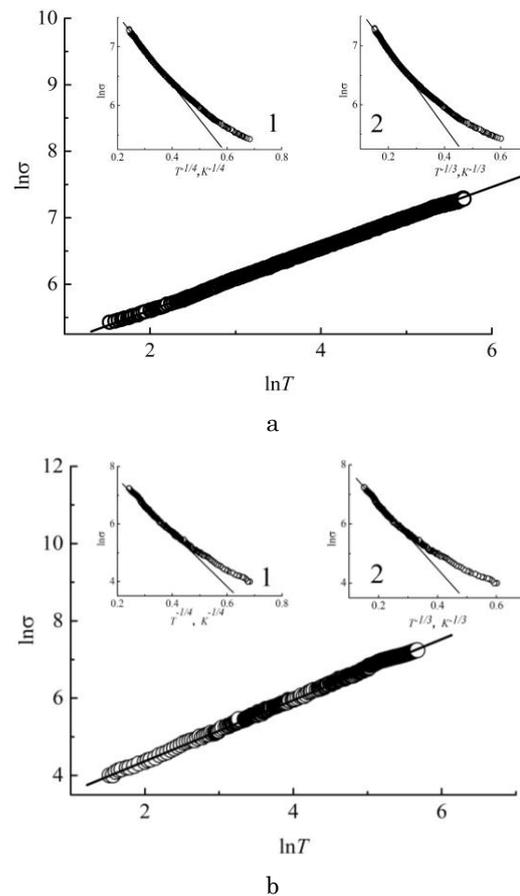


Fig. 7 – Temperature dependences of conductivity for bulk specimens of modified SWCNTs according to the scheme 1 (a) and scheme 2 (b) in coordinates $\ln\sigma(\ln T)$, $\ln\sigma(T^{-1/4})$ (inset 1), $\ln\sigma(T^{-1/3})$ (inset 2)

Thus, all these arguments speak in favor of the fact that as a result of the proposed schemes for treatment the source SWCNTs, the contact resistance between the individual CNTs in the bulk specimens has increased significantly. Particles of the disordered carbon phase, which mainly provided the formation of a 3D conductive system in the bulk specimen, have been removed from the channels through which the charge was transferred between the individual CNTs in the

source SWCNT's bulk specimen. Therefore, the charge carriers in the bulk specimen can move only along each tube, and charge transfer between individual CNTs is unlikely. Thus, in the bulk specimens of SWCNTs, the conductivity mechanism is formed which is characteristic of the 1D systems. This situation in the bulk specimens of SWCNTs is similar to the processes that occur, for example, at the formation of graphite intercalation compounds (GICs). It is known that in the GICs, intercalate layers form an electrostatic barrier associated with a localized charge in the intercalate layers. Due to this, the charge carriers in the GICs can move only along the graphite layers, forming a 2D electronic system. And GICs are considered as 2D conducting systems whose two-dimensionality is caused not by their geometrical sizes, but is connected with the features of their electronic structure.

4. CONCLUSIONS

Thus, our studies have shown that the proposed modification schemes allow to obtain SWCNTs modified on the surface by cobalt-containing complexes. Moreover, at the modification several processes take place simultaneously, namely, purification of the source nanocarbon material from the catalyst metal impurities and particles of disordered carbon, separation of tubes bunches into individual tubes and cutting of the tubes along to defects.

Investigations of modified SWCNTs by thermo-

magnetometric method have revealed that cobalt attached to the surface of the tubes is in the form of cations in the complicated complexes. When specimens of modified SWCNTs are heated, these complicated complexes are destroyed. Due to the surface thermo-stimulated diffusion, cobalt agglomerates and this leads to the formation of cobalt nanoparticles.

From the investigations of the temperature dependence of electrical resistance it was found that for bulk specimens of source SWCNTs, the main mechanism of conductivity is the hopping conductivity with the variable hopping length, and the source SWCNTs are considered as a 3D system. This conduction mechanism is typical of disordered graphite materials, as well as of mats and binders of SWCNTs.

Modification of SWCNTs by surface with cobalt-containing complexes results in the change in the character of the conductivity of SWCNTs specimens. For modified SWCNTs, the bulk specimens' conductivity is described in terms of power temperature law, that is typical for individual SWCNTs. This is related to a significant increase in contact resistance between the individual tubes due to the modification of their surface. Surface modification of SWCNTs leads to the creation on the surface of CNTs small localized negative charge which acts as an electrostatic screen. The presence of such a charge makes it impossible to transfer charge between individual tubes and promotes the formation of a 1D conductive system of SWCNTs.

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Структура та транспортні властивості одностінних вуглецевих нанотрубок, модифікованих кобальт-вмісними комплексами

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В статті наведені результати досліджень структурно-морфологічних особливостей та транспортних властивостей одностінних вуглецевих нанотрубок, модифікованих кобальт-вмісними комплексами. В роботі запропонована схема, яка дозволяє одночасно проводити очистку вихідного карбонового наноматеріалу від залишок металу-катализатора та частинок непорядкованого нанокарбону, розділяти джгути нанотрубок на окремі нанотрубки, розрізати окремі нанотрубки по дефектам, а також модифікувати вуглецеві нанотрубки кобальт-вмісними комплексами. Проведені термомагнітометричні дослідження встановили, що після модифікації кобальт у вигляді катіонів знаходиться в складі комплексів, приєднаних до поверхні нанотрубок. При нагріванні кобальт-вмісні комплекси руйнуються і на поверхні нанотрубок утворюються наночастинки металічного кобальту. В роботі показано, що для об'ємних зразків одностінних вуглецевих нанотрубок основним механізмом провідності є стрибова провідність із змінною довжиною стрибка для випадку трьохвимірних систем. Такий механізм провідності є характерним для непорядкованих графітових матеріалів, а також для матів та джгутів одностінних вуглецевих нанотрубок. В роботі виявлено, що модифікація одностінних вуглецевих нанотрубок кобальт-вмісними комплексами приводить до зміни механізмів електропровідності об'ємних зразків вуглецевих нанотрубок. Електропровідність об'ємних зразків модифікованих одностінних вуглецевих нанотрубок описується в рамках степеневі температурної залежності, типової для індивідуальних одностінних вуглецевих нанотрубок. В роботі показано, що така зміна механізмів провідності об'ємних зразків одностінних вуглецевих нанотрубок пов'язана із створенням на поверхні нанотрубок невеликого від'ємного заряду внаслідок поверхневої модифікації нанотрубок.

Ключові слова: Одностінні вуглецеві нанотрубки, Кобальт-вмісні комплекси, Магнітна сприйнятливність, Стрибова провідність із змінною довжиною стрибка.