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The effect of He : O plasma treatment on the structure of multi-walled carbon nanotubes

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The functionalization of multi-walled carbon nanotubes in He : O plasma is investigated. It is shown that plasma treatment leads to the removal of defective outer graphene layers and their fragments due to oxidation. It is established that the surface of functionalized multi-walled carbon nanotubes contains numerous uncoordinated carbon atoms and oxygen-containing functional groups. The preservation of the structure of the internal graphene layers of nanotubes and the formation of broken chemical bonds ensure a decrease in electrical resistance. At the same time, there is a narrowing of the distribution of electrical resistance values of nanotube ensembles.

Keywords: multi-walled carbon nanotubes, plasma treating, functionalization, transmission electron microscopy, X-ray photoelectron spectroscopy

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Multi-walled carbon nanotubes (MWCNTs) are promising for developing new materials to be used in producing electrodes of lithium−ion batteries and supercapacitors [1,2]. High mechanical characteristics of MWCNTs offer great opportunities for fabricating based on them porous materials for electrodes of variable−geometry power supplies. When MWCNTs are used as an electrode material, of great importance is the nanotube layer resistance that depends on both the inherent resistance of individual nanotubes and resistance of the inter-tube contact. The total nanotube layer resistance may be reduced by attaching functional oxygen−containing groups to the MWCNT surface [3]. Besides, fixation of the functional groups and complexes on the nanotube surface promotes an increase in the carbon material specific capacity due to oxidation−reduction reactions occurring during interaction with electrolyte [4,5]. Because of low energy of charged particles, the plasma treatment modifies only outer graphene layers of the carbon nanotube and does not change the structure of inner layers [6]. Introduction of reaction gases (O_2, N_2, NH_3 , etc.) during the plasma treatment enables controlled chemical functionalization of the MWCNT surface [7,8]. In this work, the MWCNT structure after treatment with the He : O plasma was studied by transmission electron microscopy (TEM) and X−ray photoelectron spectroscopy (XPS). The effect of plasma treatment on electrophysical properties of nanotube ensembles has been investigated.

MWCNTs were synthesized by the CVD (chemical vapor deposition) method according to the procedure described in [1]. Functionalization of the MWCNT layer was performed in He : O plasma 250 W in power. The gas mixture flowrate was 40 sccm, the mixture composition was $He : O_2 = 1 : 3$. The treatment time was 20 s.

XPS−analysis of elemental composition of the initial and plasma treated MWCNTs

Sample	Concentration, at.%			
	[C]	[O]	[N]	[Fe]
Initial MWCNTs	92.4	2.9	3.4	1.3
Plasma−treated MWCNTs	77.2	19.8	2.0	1.0

The MWCNT structure was studied with electron microscope JEOL JEM-2100. The structural−chemical state of carbon in the nanotube walls was studied by the XPS method at the Surface Science Center (Riber) unit. The spectra were excited by nonmonochromatic AlK_α radiation. The probing depth did not exceed 2 nm. The quantitative elemental analysis was accomplished based on survey XPS spectra using the technique of elemental sensitivity factors.

Conductivity of the MWCNT ensembles was studied with LCR−meter Agilent E4980. The resistance of limited ensembles was determined via JV characteristics of rarefied MWCNT ensembles located between golden interdigital contacts.

As per the TEM data, initial MWCNTs are of the bamboo−like structure characteristic of nanotubes doped with nitrogen (Fig. 1, *a*) [1,3]. The carbon nanotube outer diameter varies from 20 to 60 nm. The interplane distance between graphene layers in the initial MWCNT walls, which was obtained based on the results of fast Fourier transform of images, is $\sim 0.34-0.35$ nm. Graphene layers of the MWCNT walls are free of disruptions and significant bends. Wall width of the initial nanotubes varies insignificantly.

After exposure in plasma, craters ~ 30 nm in size are observed on the MWCNT outer surface; the craters arise

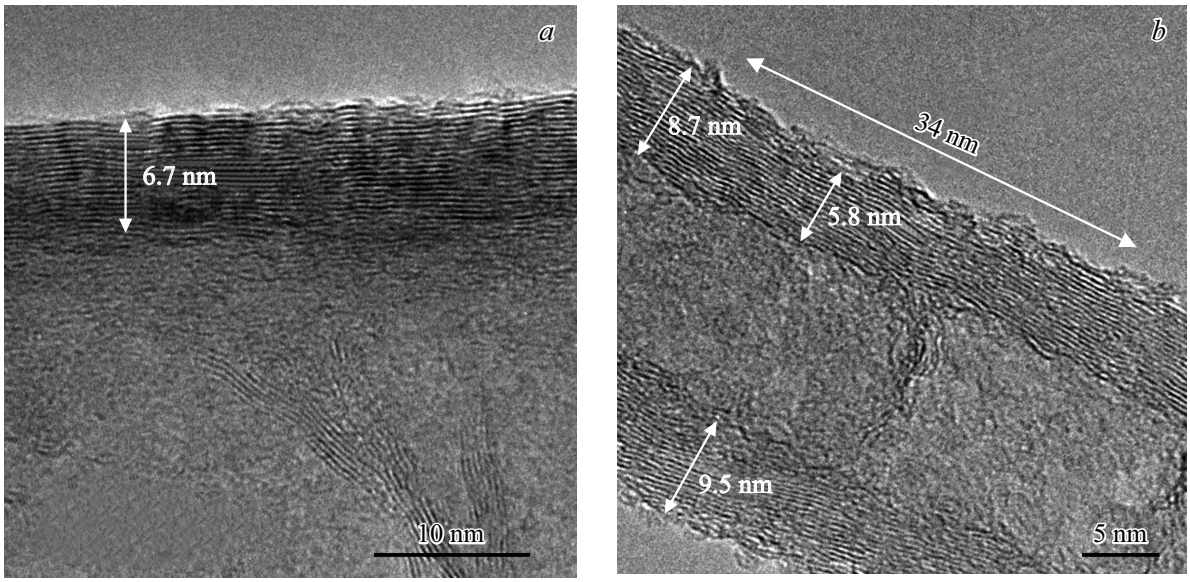

Figure 1. TEM image of the MWCNT wall prior to plasma treating (*a*) and of MWCNT after plasma treating (*b*).

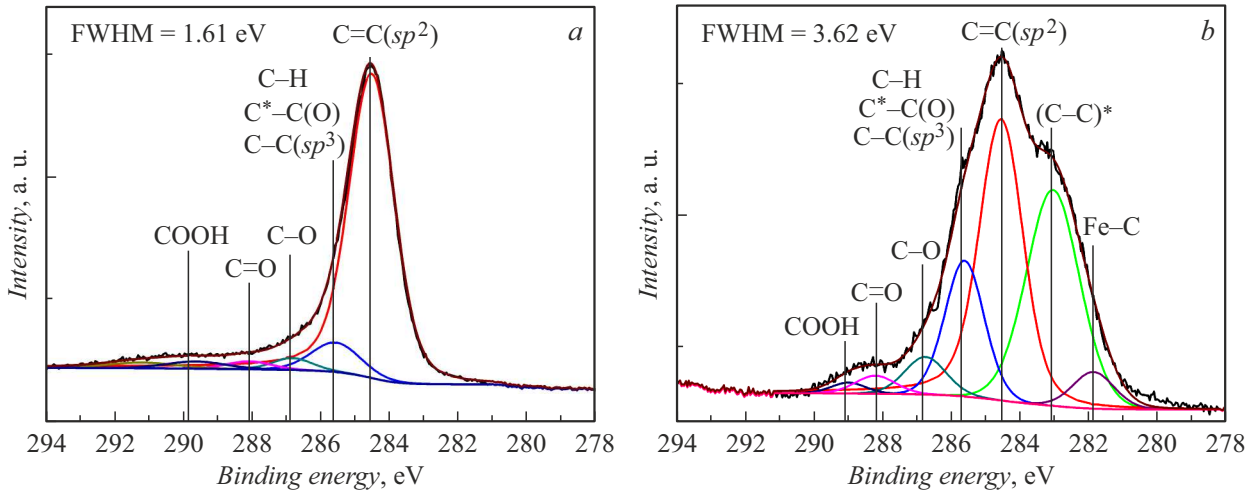

Figure 2. XPS C 1*s* spectra. *a* — initial MWCNTs, *b* — plasma treated MWCNTs.

due to removal of large fragments of graphene layers (Fig. 1, *b*). The crater depth is nonuniform; in local MWCNT regions it reaches 3 nm ($\sim 8-10$ graphene layers). Formation of such defects is probably connected with the removal of carbon atoms from the MWCNT surface because of oxidation. Regardless of the presence of large structural defects in the outer graphene layers of MWCNT walls, inner layers exhibited no essential changes upon treatment.

The XPS data show that after plasma treatment a considerable increase in the oxygen concentration is observed in the sample near–surface region (from ~ 2.9 to 19.8 at.%, see the table). High oxygen concentration indicates the formation of functional oxygen–containing groups on the MWCNT surfaces. Fig. 2 presents the C 1*s* carbon spectra of MWCNT arrays prior to and after treatment. The main component of the initial MWCNT spectrum (Fig. 2, *a*) relates to sp^2-carbon (C = C ~ 284.6 eV) [9]. The component corresponding to the binding energy of ~ 285.5 eV relates to hydrogenated carbon (C–H) and also to carbon positioned close to oxidized carbon (C*–C(O)). The component at ~ 287 eV relates to carbon bound in C–O (epoxide, hydroxide, etheric and other groups). There are also components related to carbon bound in groups C=O and COOH at the energies of ~ 288 and 289 eV, respectively [10].

After the plasma treatment, the MWCNT C 1*s* spectrum shape changes significantly (Fig. 2, *b*), the line half–width increases from 1.61 to 3.62 eV, which evidences an increase in heterogeneity of the carbon chemical environment. The spectrum contains intense components with maxima at the

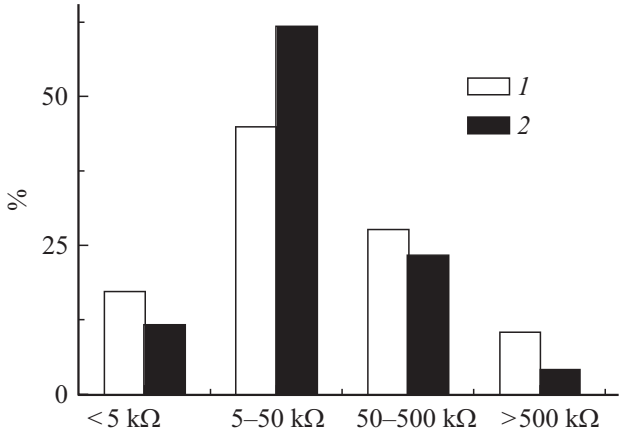

Figure 3. Resistance values distribution for ensembles of initial MWCNTs (*1*) and plasma treated MWCNTs (*2*).

energies of ∼ 283 and ∼ 282 eV. The component at the energy of ∼ 283 eV is associated with the presence of uncoordinated carbon atoms located near the graphene plane ruptures [11], which agrees well with the TEM data that have demonstrated the existence of numerous large−size vacancy−type structural defects in the outer graphene layers. The spectrum component at ∼ 282 eV may be associated with the presence of iron carbides [12]; its emergence in the spectrum may be caused by partial destruction of MWCNT graphene layers and baring of the catalyst particles encapsulated in the nanotube tips. In addition, there is observed a reduction in the relative intensity of the component related to the carbon−carbon chemical bonds (C=C) from ∼ 80% in the initial nanotube spectrum to 40% after treatment, as well as an increase in the intensities of components associated with structural defects and carbon−oxygen groups of various types (hydroxide, epoxide, etheric, etc.).

Fig. 3 presents the distribution diagrams for measured resistances of limited MWCNT ensembles located between golden contacts. The diagram shows that the major part of the distribution of initial nanotube resistances (Fig. 3, distribution *1*) relates to MWCNT ensembles with resistances of 5 to 50 kΩ, which is consistent with literature data [13–15]. A considerable spread of resistances is caused by different numbers of nanotubes in the ensembles and variability of the nanotube outer diameters.

After exposure in plasma, the diagram (Fig. 3, distribution *2*) exhibits an increase in the share of nanotube ensembles with the resistances of 5 to 50 kΩ from ∼ 44 to ∼ 60% of the total number of measured MWCNT ensembles. At the same time, the total share of MWCNT ensembles with the resistance above 50 kΩ decreased from ∼ 37 to ∼ 25%. As a whole, the distribution shape changed insignificantly. Despite the presence of a great number of structural defects on the surface of plasma−functionalized MWCNTs, no increase in the MWCNT ensemble resistances was observed. Preservation of the MWCNT conductivity is caused by retention of the structure of nanotube inner graphene layers ensuring the charge carrier transport [16]. We assume that the presence of uncoordinated carbon atoms, as well as of oxygen−containing groups, can provide formation of bridge bonds in the regions of the individual MWCNTs contact, which can improve the charge carrier transport.

The investigation represented in this paper have shown that short−term He : O plasma treatment promotes removal of fragments of nanotube wall graphene layers and formation of a relief with subsequent fixation of different−type functional groups. Changes in the structural−chemical state of the carbon nanotube surface result in narrowing of the electrical resistance distribution of rarefied MWCNT ensembles. Formation on the nanotube surface of functional groups can positively affect capacitance characteristics of MWCNT−based electrode materials and composites.

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Conflict of interests

The authors declare that they have no conflict of interests.

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