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Functionalization of carbon nanotubes in nitrogen plasma for electrochemical applications

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The paper investigates the functionalization of carbon nanotube layers in nitrogen plasma. Scanning electron microscopy studies have shown changes in the morphology of the nanotube layer after plasma treatments. X-ray photoelectron spectroscopy and infrared spectroscopy revealed that nitrogen is embedded in the structure of graphene nanotube layers in pyridine, pyrrole, and graphite-like configurations as a result of plasma treatments. The result of plasma treatment is an increase in the electrical conductivity of the nanotube layer.

Keywords: Carbon nanotubes, Scanning electron microscopy, X-ray photoelectron spectroscopy, IR-spectroscopy, Nitrogen plasma.

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The development of microelectronics, electric transport, and portable electronics necessitates the development of energy storage, storage, and conversion devices such as electrochemical batteries, supercapacitors, and fuel cells [1]. The electrode materials for these devices must have high electrical conductivity, a well-developed surface and electrochemical activity. Carbon nanotubes (CNTs) are a very promising for electrodes of electrochemical devices. It is known that nitrogen in the composition of carbon nanotubes in an electroactive state in the form of defects in pyridine and pyrrole configurations increases the catalytic activity of platinum group metals and significantly increases the electrical conductivity of CNT layers [2,3]. The most common method of post-synthesis doping of carbon nanotubes with nitrogen is chemical treatment, however, it can be accompanied by the formation of undesirable nitride compounds on the surface of nanotubes. Promising methods for doping CNTs include ion plasma treatments, since they allow controlling the degree of alloying and the composition of functional groups on the surface of carbon materials [4]. The morphology, elemental and chemical composition of carbon nanotube layers treated in nitrogen plasma is studied in this paper.

This paper studies thin layers of commercial CNTs of the MUNT-1 brand produced by Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. CNTs were dispersed in isopropyl alcohol by ultrasound and aerosolized onto monocrystalline silicon as a substrate. Doping of carbon nanotubes with nitrogen was carried out in nitrogen plasma using a gas-metal ion beam accelerator (OSC of SB RAS). The plasma discharge power was 50 W, and the treatment duration was 20 min. The morphology of CNT layers was studied using a Jeol JSM6610-LV scanning electron microscope with an IncaX-Act energy dispersion analyzer. The chemical state of the samples was studied using an X-ray photoelectron spectrometer LAS-3000 and a BRUKER Vertex 70 Fourier infrared spectrometer. A CNT suspension in isopropyl alcohol was applied to the CaF substrate for the study by IR spectroscopy, followed by drying for 3 hours at a temperature of $\sim 80\,^\circ$C.

The conductivity of nanotube layers was studied by the Van der Pau method using an Agilent E4980A LCR meter. For this purpose, polycrystalline glass plates with nickel contacts applied to the surface were made. A layer of CNT was applied over the plates by aerosol spraying, which was subsequently subjected to plasma treatments. The resistivity of the sample layer was calculated using the formula:

$$\rho = \frac{d\pi}{2\ln 2} k(R_{\mathrm{AD,CB}} + R_{\mathrm{DC,BA}}), \tag{1}$$

where ρ is the layer resistivity, d is the layer thickness, k is the correction factor, $\mathrm{R_{AD,CB}}$ and $R_{\mathrm{DC,BA}}$ is the resistance between the electrodes.

Figure 1, *a* shows images of scanning electron microscopy (SEM) of a layer of initial CNTs deposited by aerosol spraying. The carbon nanotubes in the layer are randomly oriented and form $1-3\,\mu$m clusters. There are many pores and voids in it, which is due to the method of applying a layer of nanotubes. The outer diameter of the CNT in the layer, according to the SEM data, is $20-35$ nm. N-plasma treatment leads to the formation of defects on the outer surface of nanotubes under the action of nitrogen ions,

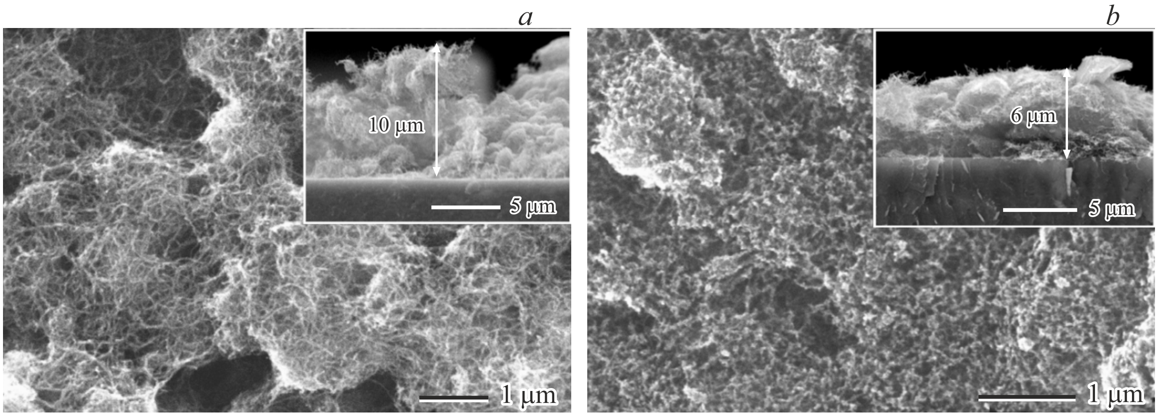

Figure 1. SEM images of the CNT layer: *a* — initial layer, *b* — layer after N-plasma treatment. Cross-sectional images of the CNT layer are shown in the inserts.

Table 1. Elemental composition of CNT layers before and after treatment in N-plasma

Sample	Concentration, at.%			
	C	O	N	Si
CNT (original)	95.7	3.4	–	0.9
CNT N-plasma 20 min	73.2	17.6	7.8	1.4

which is reflected in a change in the morphology of the layer as a whole (Figure 1, *b*). Irregularly shaped particles are visible on the surface of the CNT, presumably formed as a result of the destruction of the CNT. Also, after plasma treatment, there is a slight decrease in the thickness of the nanotube layer (Figure 1, *b*, insert).

Figure 2, *a* shows the overview spectra of X-ray photoelectron spectroscopy (XPS) of CNT samples before and after ion irradiation. Quantitative elemental analysis using the method of elemental sensitivity coefficients was performed using the XPS survey spectra (Table 1). The presence of a small amount of silicon in the composition of the initial CNTs is explained by the signal from the substrate. After plasma treatment, an increase in the silicon concentration in the sample is observed, which is associated with a decrease in the thickness of the CNT layer. The spectrum of the initial sample contains photoelectron lines of oxygen (O1s, ~ 529 eV) and carbon (C1s, ~ 285 eV). After treatment in N-plasma, a nitrogen line appears in the overview spectrum of the sample (N1s, ~ 400 eV), and an increase in the intensity of the oxygen line (O1s, ~ 529 eV) is also observed. This is due to the formation of defective areas in graphene layers, on which various functional groups are fixed both during plasma treatment and after contact with the atmosphere [4].

Analysis of C1s XPS CNT spectra indicates a change in the chemical state of the CNT surface after plasma treatment (Figure 2, *b*). The value of the half-width of the C1s XPS spectrum increases significantly after processing from 1.68 to 2.55 eV, which indicates an increase in the defects of the nanotubes after treatment. Analysis of the C1s XPS spectra allows us to identify several main components corresponding to different chemical states of carbon: as part of C=C bonds (~ 284.5 eV, C1); as part of C–H bonds, as well as those located near heteroatoms (C^*–C(O,N,H)) and as part of C–C bonds with sp^3-hybridization of valence electron shells (~ 285.1 eV, C2); as part of single C–O and C–N bonds (~ 286.4 eV, C3); consisting of double C=O and C=N bonds (~ 287.8 eV, C4); COOH groups (~ 288.5 eV, C5). N-plasma treatment leads to a decrease in the relative intensity of component C1 and an increase in the intensity of components C2, C3, and C4, which, together with an increase in the concentration of oxygen and nitrogen in the sample, indicates their incorporation into the structure of graphene layers of nanotubes [4,5].

To assess the chemical state of nitrogen in the CNT structure after plasma treatment, an analysis of the N1s XPS spectrum was performed, which made it possible to identify several components (Figure 2, *c*). The N1 component on energy ~ 398.5 eV corresponds to nitrogen in a chemical bond with carbon to form a pyridine configuration of atoms. The N2 component on energy ~ 399.8 eV corresponds to nitrogen embedded in the graphene plane in a pyrrole configuration. The N3 component on energy ~ 401 eV corresponds to nitrogen replacing a carbon atom in a graphite-like configuration in the graphene layer structure. The N4 component on energy ~ 403 eV corresponds to nitrogen oxide in the pyridine configuration [4,6].

The conducted IR spectroscopy studies also showed a change in the chemical composition of the samples after plasma treatment. The following absorption bands are distinguished in the spectrum of the sample of the initial nanotubes (Figure 2, *d*): stretching of C–H bonds in the region of $\sim 2890\,\mathrm{cm}^{-1}$; stretching of C=O carboxyl groups in the region of $\sim 1736\,\mathrm{cm}^{-1}$; vibrations of the C=C bond of the carbon skeleton of nanotubes $\sim 1586\,\mathrm{cm}^{-1}$; deformation vibrations of C–H bonds in the region of $\sim 1426\,\mathrm{cm}^{-1}$ and $\sim 1386\,\mathrm{cm}^{-1}$; vibrations of C–O

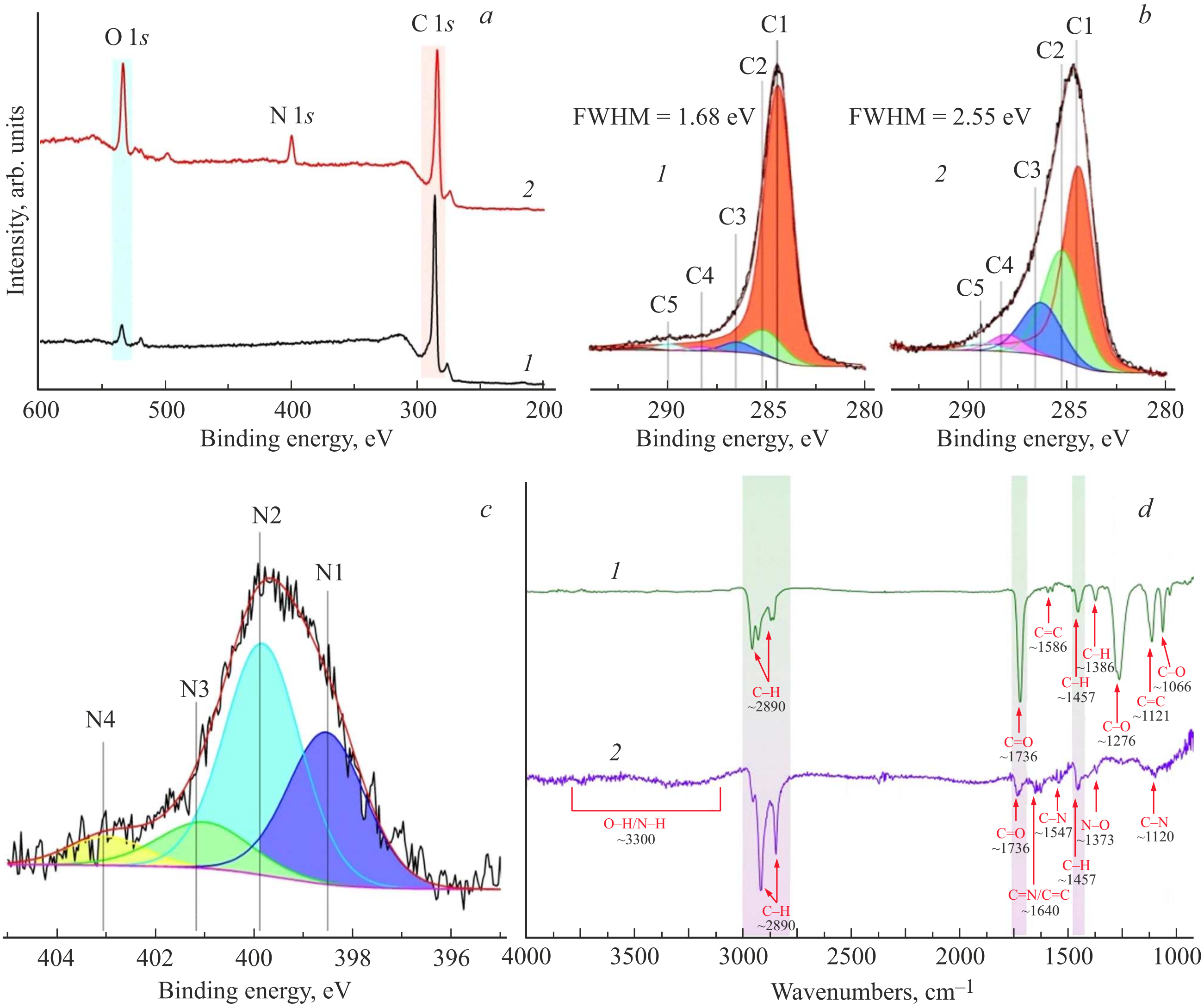

Figure 2. Spectra of CNT layers before (*1*) and after (*2*) N-plasma treatment. *a* — overview XPS spectra of CNT layers, *b* — C1s XPS spectra of CNT layers, *c* — N1s XPS spectrum of CNT layer after N-plasma treatment, *d* — IR spectra of CNT layers.

bonds in the region of $\sim 1276\,\mathrm{cm}^{-1}$ and $\sim 1066\,\mathrm{cm}^{-1}$; stretching of C–C bonds $\sim 1121\,\mathrm{cm}^{-1}$ [7]. N-plasma treatment significantly changes the appearance of the spectrum (Figure 2, *d*). Absorption bands corresponding to stretching of C–O and C–C bonds are not identified on the spectrum, while a wide absorption band with a maximum of $\sim 1120\,\mathrm{cm}^{-1}$ is observed in this region, which It can be attributed to stretching of C–N bonds. The band in the region of $\sim 1547\,\mathrm{cm}^{-1}$ can also be attributed to stretching of C–N bonds. An absorption band corresponding to stretching of N–O bonds is observed in the region of $\sim 1373\,\mathrm{cm}^{-1}$. The absorption band corresponding to vibrations of C=C bonds is not identified after plasma treatments, however, a feature corresponding to a mixed mode of stretching of C=C and C=N bonds is recorded in the region of $\sim 1640\,\mathrm{cm}^{-1}$. Thus, the results obtained indicate the incorporation of nitrogen atoms into the CNT structure after plasma treatments [8,9].

Table 2. Measurement results by the Van der Pau method

Sample	$R_{\mathrm{AD,CB}}$, Ohm	$R_{\mathrm{DC,BA}}$, Ohm	ρ, mOhm · m	G, Sm/m
CNT (source)	64.83	33.26	2.098	476.69
CNT N-plasma 20 min	23.19	85.97	1.295	772.32

The resistivity measurement results are presented in Table 2.

It can be seen from the results obtained that the resistivity of the nanotube layer decreases after plasma treatment, which is probably due to the incorporation of nitrogen into the structure of graphene nanotube layers in an electrically active state [10].

The results of the studies performed by SEM, XPS, and IR spectroscopy showed significant changes in the morphology and chemical state of the nanotube layers after treatment in nitrogen plasma. Irregularly shaped particles are observed on the surface of the nanotubes, indicating the formation of structural defects. Their presence can have a positive effect on the formation of composite materials and contribute to a more homogeneous distribution of components [2]. The XPS data indicate an increase in oxygen and nitrogen concentrations after treatment. Analysis of the core C1s and N1s spectra indicates the formation of C−N and C−O bonds in the CNT structure with the formation of pyrrole, pyridine, and graphite-like configurations of nitrogen atoms in the graphene layer structure. The IR spectroscopy data correlate with the XPS results and confirm the incorporation of nitrogen into the nanotube structure with the formation of C=N, C−N and N−O bonds in electrically active configurations. The measurements of the resistivity by the Van der Pau method of layers of functionalized CNTs showed that the introduction of nitrogen defects makes it possible to increase the electrical conductivity of the carbon nanotube layer. Thus, CNT treatment in nitrogen plasma is a promising method for the functionalization of nanotubes for their further use as electrode layers of chemical sources and current converters.

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Conflict of interest

The authors declare no conflict of interest.

References

[1] N.V. Glebova, A.A. Nechitailov, A.O. Krasnova, A.A. Tomasov, N.K. Zelenina. Zhurnal tekhnicheskoy fiziki, **89**, 1978 (2019) (in Russian). DOI: 10.21883/JTF.2019.12.48499.451-18

[2] A.S. Pushkarev, I.V. Pushkareva, M.V. Kozlova, M.A. Soloviev, S.I. Butrim, Ts. Ge, V. Sin, V.N. Fateev. Elektrokhimiya **58**, 325 (2022) (in Russian). DOI: 10.31857/S0424857022070118

[3] I.V. Zaporotskova, S.V. Boroznin, N.P. Boroznina, E.S. Dryuchkov, K.Yu. Verevkina, Y.V. Butenko, P.A. Zaporotskov, L.V. Kozhitov, A.V. Popkova, A.D. Grigoriev. Modern Electronic Materials, **10**, *4*, 197–202 (2024). DOI: 10.3897/j.moem.10.4.142799

[4] S.N. Nesov, V.V. Bolotov, E.V. Knyazev, S.N. Povoroznyk. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **525**, 20 (2022). DOI: 10.1016/j.nimb.2022.06.006

[5] A. Skourti, S. Giannoulia, M.K. Daletou, C.A. Aggelopoulos. Nanomaterials, **14**, 1298 (2024). DOI: 10.3390/nano14151298

[6] L.G. Bulusheva, A.V. Okotrub, Yu.V. Fedoseeva, A.G. Kurenya, I.P. Asanov, O.Y. Vilkov, A.A. Koós, N. Grobert. Phys. Chem. Chem. Phys., **17**, 23741–23747 (2015). DOI: 10.1039/C5CP01981H

[7] V. Ţucureanu, A. Matei, A.M. Avram. Critical Reviews in Analytical Chemistry, **46**, *6*, 502–520, (2016). DOI: 10.1080/10408347.2016.1157013

[8] A. Misra, P.K. Tyagi, P.H. Rai, D.S. Misra. Nanoscience and Nanotechnology, **7**, 1820–1823, (2007). DOI: 10.1166/jnn.2007.723

[9] Xianfeng Wu, Jiangning Liu, Xuezhen Liu, Xia An, Xu Wu. Separation and Purification Technology, **361**, 131493 (2025). DOI: 10.1016/j.seppur.2025.131493

[10] H. Lee, B.-J. Kim, S.-J. Kim, Y.-K. Park, S.-Ch. Jung. Int. J. Mol. Sci., **19**, 3830 (2018). DOI: 10.3390/ijms19123830

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