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Formation of nanocomposite structures based on carbon nanotubes and titanium oxide doped with nitrogen

© E.V. Knyazev[1,2], S.N. Nesov[1,2], V.V. Bolotov[1], D.V. Sokolov[1], S.N. Povoroznyuk[1,2], K.E. Ivlev[1], S.A. Matyushenko[1], E.V. Zhizhin[3], A.V. Koroleva[3]

[1] Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, Russia
[2] Omsk State Technical University, Omsk, Russia
[3] St. Petersburg State University, St. Petersburg, Russia

E-mail: knyazevyegor@mail.ru

Received April 30, 2024
Revised October 28, 2024
Accepted October 30, 2024

The morphology and chemical state of carbon nanotube — titanium oxide composite structures modified by ion irradiation are investigated. Scanning electron microscopy methods have shown a change in the morphology of the composite surface after irradiation. X-ray photoelectron spectroscopy data showed the presence of nitrogen in the composite structure after irradiation, and an assessment of the chemical state of the surface indicates the incorporation of nitrogen into the composite structure. Measurement of the conductivity of the nanocomposite layers showed an increase in conductivity after ion treatments.

Keywords: carbon nanotubes, titanium oxide, ion irradiation, scanning electron microscopy, X-ray photoelectron spectroscopy.

DOI: 10.61011/PSS.2024.12.60194.6487PA

Active development of portable electronics and electric vehicles drive the need to search for new technology solutions for chemical sources of current, such as lithium and sodium-ion batteries and supercapacitors (SCs). One of the promising types of devices are SCs, since they allow for accumulation of high densities of energy and have high rate of charge and discharge [1]. The most important characteristic of supercapacitors is capacitance. For supercapacitors, the capacitance is formed from two main components. The first one — capacitance of electric double layer (EDL), which is proportionate to the specific surface area. The second component of the capacitance — pseudocapacitance, which is provided by fast redox reactions at the electrode–electrolyte interface. The materials widely used for SC electrodes are nanocomposites based on carbon nanotubes (CNTs) and nanoparticles of transition metal oxides (MnO_2, TiO_2, FeO etc.) [2]. In this case carbon nanotubes provide for high active surface of the electrode, and metal oxide nanoparticles — pseudocapacitance growth. However, nanocomposites of such type usually have low electroconductivity, which substantially reduces charge/discharge speeds and may negatively impact the capacitance characteristics. Alloying of metal oxide nanoparticles with conducting additives increases their electroconductivity [3]. On the other hand, increased conductivity of electrode material may be achieved by alloying of carbon nanotubes as well [4]. Among alloying methods for nanomaterials, the most effective method is ion-beam action. Radiation of materials directly by alloying elements, for example, nitrogen, makes it possible to functionalize the surface of nanomaterials, but to also form the new chemical compounds within Ti, C and N, providing for improvement of properties of composite materials [5].

The paper studies the structure, chemical state and electrophysical characteristics of composite materials based on carbon nanotubes and titanium oxide (CNT/TiO_2), alloyed by nitrogen using the method of ion implantation.

The composite structures representing the layers of CNT coated with the titanium oxide film are studied. To form the nanocomposite of CNT/TiO_2, the commercial CNTs of grade MUNT-2 made by Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences were used. CNT layer was formed by the method of aerosol sputtering of CNT suspension on a sitall substrate heated to 80°C. To prepare suspension, 20 mg CNT powder was added to 50 ml isopropyl alcohol, after which it was dispersed in the ultrasonic bath for 4 hours. After application, the thickness of CTN layer on the substrate was $1-5\,\mu$m, and nanotubes were located preferentially in the form of horizontally-aligned disordered arrays.

Titanium oxide is applied on the surface of the CNT layer by method of magnetron sputtering of the titanium target on VUP-5M installation. The working volume of the chamber was pumped to the pressure of not more than $5 \cdot 10^{-2}$ Pa, after which the argon was added to the working chamber to the pressure of ~ 1 Pa. The sputtering process was carried out at magnetron voltage of 450 V and current of 250 mA. The thickness of the produced film of titanium oxide made ~ 100 nm.

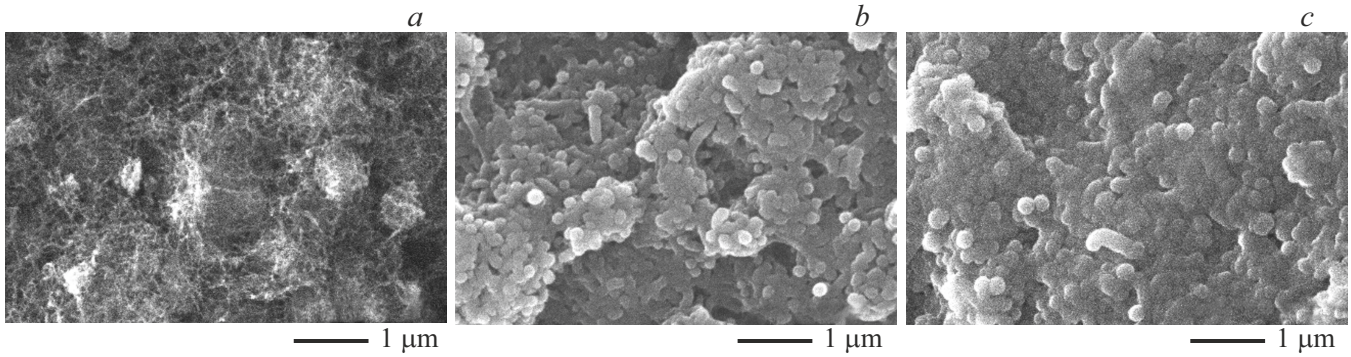

Figure 1. SEM-image: *a* — CNT layer surface; *b* — CNT/TiO_2 composite surface; *c* — CNT/TiO_2 composite surface after irradiation with nitrogen ions.

Alloying of titanium oxide by nitrogen was carried out by the method of ion implantation on „Kompozit" installation. The working chamber of the installation was pumped to the residual pressure of not higher than $5 \cdot 10^{-3}$ Pa, after which working gas — nitrogen — to the pressure of $\sim 5 \cdot 10^{-2}$ Pa was added to the chamber. Working gas ionization was carried out in the crossbred electric and magnetic Penning fields at voltage of 400 V. Then the flux of nitrogen ions was aimed to the target under the action of the accelerating voltage of 20 kV. Duration of the ion irradiation process made 30 min.

Study of the morphology and structure of nanocomposites was carried out at scanning-electron microscope (SEM) Jeol JSM 6610-LV with energy-dispersive analyzer Inca X-Act.

Structural-chemical state of the CNT/TiO_2 composite surface was studied using X-ray photoelectron spectroscopy (XPS) using laboratory electron spectrometer ESCALAB 250 Xi and monochromatized AlK_α-radiation ($h\nu = 1486.6$ eV). The survey and core-level PE-spectra (C1*s*, O1*s* and Ti2*p*) were recorded with the analyzer pass energy of 50 eV and 20 eV, respectively. Quantitative elemental analysis was carried out by survey XPS-spectra using the method of elemental sensitivity coefficients.

Specific conductivity of CNT/TiO_2 was measured by the standard four-probe method at probe station 13 MP-0.5-001 with linearly arranged gold-plated tungsten probes at the distance of 1 mm from each other. Determination of the value of specific conductivity was carried out using formula

$$\sigma = 0.22 \cdot \frac{I}{U \cdot d}, \qquad (1)$$

where d — specimen thickness, U and I — difference of potentials and current between internal and external probes. To determine conductivity of the layer, at least 20 measurements were made in different sections for each specimen.

As a result of aerosol sputtering of the CNT suspension, a dense CNT layer is formed on the substrate, located preferably in parallel to the substrate and having multiple points of crossing with the adjacent tubes (Figure 1, *a*). The external diameter of nanotubes in the layer, according to SEM data, makes 15–20 nm.

Analysis of SEM-images of CNT/TiO_2 composite indicates formation of the solid film of titanium oxide with thickness of ~ 80–100 nm on the surface of the CNT layer. A structure is observed on the surface, which consists of round and lengthy grains with diameter of 90–150 nm with clear boundaries (Figure 1, *b*). Irradiation with nitrogen ions will not substantially change the morphology of the composite surface. Smoothing of titanium oxide grains boundaries is observed after radiation (Figure 1, *c*), which may be related to melting of titanium oxide particles as a result of ion exposure [6].

According to XPS data, the composition of CNT/TiO_2 composite prior to radiation was: C — 31.1 at.%, O — 48.7 at.%, Ti — 20,2 at.%. Figure 2, *a* presents panoramic XPS-spectrum of CNT/TiO_2 sample before and after ion irradiation. The spectrum of the initial specimen includes photoelectron lines of oxygen (O1*s*, ~ 529 eV), titanium (Ti2*p*, ~ 460 eV) and carbon (C1*s*, ~ 285 eV). In the spectrum of radiated composite, the intensity of titanium, oxygen and carbon lines varies, and the nitrogen line appears in the spectrum (N1*s*, ~ 400 eV). Substantial increase of the carbon line intensity (C1*s*, ~ 285 eV) is due to the fact that ion irradiation causes generation of defects in the structure of the specimen (vacancies and interstitial atoms). Such defects help to fix various functional groups on the surface of layer TiO_2, including carbon-containing ones [7].

To assess chemical state of nitrogen in titanium oxide structure after irradiation, analysis of XPS-spectrum N1*s* was carried out (Figure 2, *b*), making it possible to separate two components. Component N1 at energy 398.9 eV corresponds to nitrogen within chemical bond with carbon (C-N). The component at energy 399.8 eV corresponds to nitrogen within chemical compound Ti-O-N as nitrogen atoms are introduced into interstitial space in the interstitial space in structure of TiO_2 [5,8].

The results of the studies of the conductivity variation by a four-probe method indicate that the application of the titanium oxide film reduces conductivity of composite compared to the layer of the initial nanotubes (table).

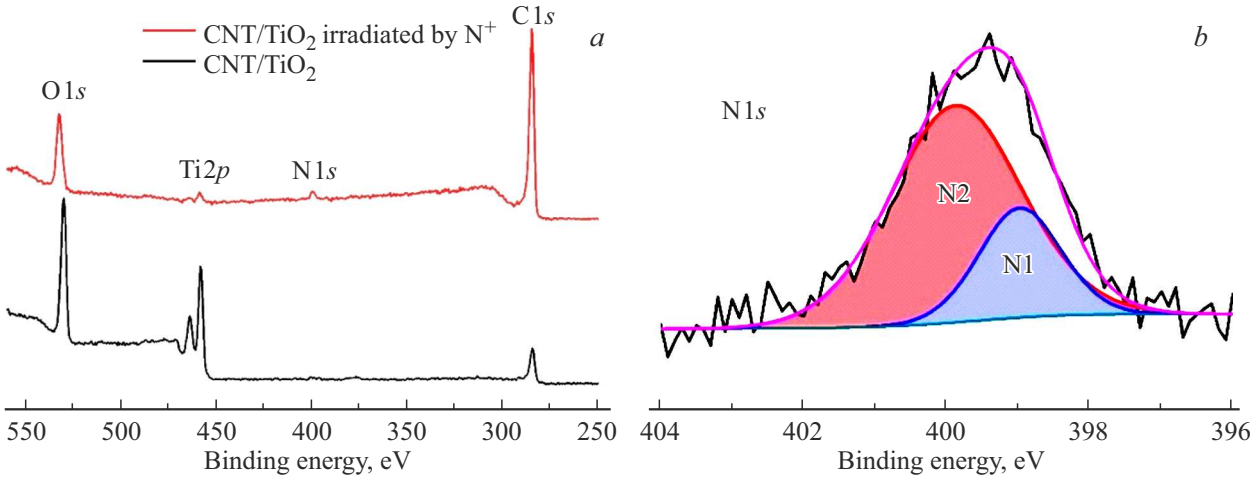

Figure 2. *a* — Survey XPS-spectra of CNT/TiO_2 composite surface before and after radiation with nitrogen ions; *b* — core-level N1*s* XPS spectrum of CNT/TiO_2 composite after radiation with nitrogen ions.

Values of conductivity of CNT/TiO_2 composite layer before and after irradiation with nitrogen ions

Specimen	Conductivity, S/cm
CNT	0.2 ± 0.01
CNT/TiO_2	0.14 ± 0.01
CNT/TiO_2 after radiation	0.39 ± 0.03

Radiation of CNT/TiO_2 composite structure surface with nitrogen ions substantially increases the layer conductivity.

Based on the obtained results, one can conclude on the substantial change of the structure in the near-surface layer of CNT/TiO_2 composite as a result of radiation. This may be related to formation of structural defects upon radiation, and also nitrogen integration into the titanium oxide structure. SEM data specify smoothing of granular boundaries of CNT/TiO_2 composite structure. At the same time XPS data indicate integration of nitrogen atoms into near-surface layers of CNT/TiO_2 composite in the process of radiation. Introduction of nitrogen into the CNT/TiO_2 composite structure is accompanied by substantial increase of layer conductivity. Therefore, alloying of CNT/TiO_2 composite with nitrogen by the method of ion implantation is the effective method to modify the surface layers of titanium oxide.

Funding

This study was carried out as part of the regional grant project No. 24-29-20110 of the Russian Science Foundation.

Acknowledgments

The studies by XPS method are carried out on a grant basis using equipment of the Resource Center „Physical methods of surface investigation“ of the Scientific Park of St. Petersburg University. The authors express gratitude to the Saint-Petersburg State University for the research project AAAA-A19-119082790069-6. The equipment of the Omsk Regional Center for Collective Use of the SB RAS was used in the study.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Verenikina