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Surface functionalization of CNTs by a nitro group as a sensor device element: theoretical research

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Abstract: The problem of modifying carbon nanotubes (CNTs) by functional groups is relevant in connection with the intensive development of the nanoindustry, in particular, nano- and microelectronics. For example, a modified nanotube can be used as a sensor device element for detecting microenvironments of various substances, in particular, metals included in salts and alkalis. The paper discusses the possibility of creating a highly efficient sensor using single-walled carbon nanotubes as a sensitive element, the surface of which is modified with the functional nitro group —NO_2. Quantum-chemical research of the process of attaching a nitro group to the outer surface of a single-walled CNTs of the (6, 0) type were carried out, which proved the possibility of modifying CNTs and the formation of a bond between the —NO_2 group and the carbon atom of the nanotube surface. The results of computer simulation of the interaction process of a surface-modified carbon nanotube with alkali metal atoms (lithium, sodium, potassium) are presented. The sensory interaction of a modified carbon nanosystem with selected metal atoms was investigated, which proved the possibility of identifying these atoms using a nanotubular system that can act as a sensor device element. When interacting with alkali metal atoms in the "CNT – NO_2" complex, the number of major carriers increases due to the transfer of electron density from metal atoms to the modified CNTs. The results presented in this paper were obtained using the molecular cluster model and the DFT calculation method with the exchange-correlation functional B3LYP (valence split basis set 6-31G).

Keywords: carbon nanotube; sensory properties; functional nitro group; molecular cluster model; alkali metals; density functional theory; quantum-chemical research.

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Поверхностно-модифицированные нитрогруппой углеродные нанотрубки как элемент сенсорного устройства: теоретические исследования

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Аннотация: Проблема модификации углеродных нанотрубок (УНТ) функциональными группами актуальна в связи с интенсивным развитием наноиндустрии, в частности, нано- и микроэлектроники. Так, например, модифицированная нанотрубка может быть использована в качестве элемента сенсорного устройства для обнаружения микроколичеств различных веществ, в частности металлов, входящих в состав солей и щелочей. В работе обсуждается возможность создания высокоэффективного сенсора, использующего в качестве чувствительного элемента однослойные углеродные нанотрубки, поверхностность которых модифицирована функциональной нитрогруппой —NO_2. Выполнены квантово-химические исследования процесса присоединения нитрогруппы к внешней поверхности однослойной УНТ типа (6, 0), доказавшие возможность модифицирования УНТ и образование связи между группой —NO_2 и атомом углерода поверхности нанотрубки. Представлены

результаты компьютерного моделирования процесса взаимодействия поверхностно-модифицированной углеродной нанотрубки с атомами щелочных металлов (литий, натрий, калий). Исследовано сенсорное взаимодействие модифицированной углеродной наносистемы с выбранными атомами металлов, доказавшее возможность проведения идентификации этих атомов с использованием нанотубулярной системы, которая может выступать в качестве элемента сенсорного устройства. При взаимодействии с атомами щелочных металлов в комплексе «УНТ – NO_2» увеличивается число основных носителей, обусловленное переносом электронной плотности от атомов металла к модифицированной УНТ. Результаты, излагаемые в данной статье, получены с использованием модели молекулярного кластера и расчетного метода DFT с обменно-корреляционным функционалом B3LYP (валентно-расщепленный базисный набор 6-31G).

Ключевые слова: углеродная нанотрубка; сенсорные свойства; функциональная нитрогруппа; модель молекулярного кластера; щелочные металлы; теория функционала плотности; квантово-химические исследования.

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1. Introduction

One of the most promising and actively developing areas of physics in recent years is the research field of low-dimensional electronic systems. Consideration of quantum-size effects leads to a qualitative restructuring of the energy spectrum of systems and significantly affects their properties. Advances in technology are driving the in-depth study of new phenomena in nanomaterials. This is necessary to create new generation devices based on them, including devices in a new field of electronics – the so-called nanoelectronics operating on nanometer-scale objects. Among such objects, the most interesting and attractive materials in terms of their properties are carbon nanotubes (CNTs) and structures based on them [1–4]. Unique sorption, mechanical and conductive characteristics, high carrier mobility in CNT-based structures lead to unique physical properties that are used in various fields, including nanotechnology, nano-, optoelectronic and plasmonic devices, micro- and nanoelectronics.

Due to the abnormally high specific surface, where the entire mass is concentrated, nanotubes display extremely high sorption properties and characteristics [5, 6]. With a high sensitivity of electronic characteristics to molecules adsorbed on the surface and to the specific surface area providing such sorption, carbon nanotubes are a promising material for creating supersensitive and miniature sensors (chemical and biological) [7, 8]. The operation principle of such devices is based on the change in the current-voltage characteristics of a nanotube during the sorption of certain type molecules on the tube surface. Nanotube sensors have high selectivity, fast response and high recovery rates.

In recent years, there have been a lot of studies carried out to investigate the possibilities of modifying carbon nanotubes leading to a predictable change in their properties. Various methods of such modification, functionalization of the surface and boundaries of tubulenes can affect, among other things, the sorption activity of nanotubes making them more sensitive to the presence of various substances. In other words, the possibilities of using tubulenes as elements of sensor nanodevices are expanding. At present, quite a lot of experimental and theoretical works have been published, where the results of studying various aspects related to the manufacture and usage of such sensors are presented. Using the possibilities of modifying nanotubes, including various functional groups, it is possible to create systems with new characteristics. This fact leads to the expansion of their application areas, for example, in microelectronics [9, 10], computer technology [11, 12], drug therapy [13], electrochemical biosensors [14], and chemical sensors [15, 16].

The article [17] provides a detailed review of works devoted to the study of a wide range of gas sensors, the main principle of which is the adsorption of gaseous molecules; the molecule gives or takes an electron from the nanotube, which leads to changes in the electrical properties of the CNT that can be recorded. The paper discusses gas sensors based on pure CNTs, including single-walled and multi-walled carbon nanotubes, as well as CNTs modified with functional groups, metals, polymers, and metal oxides. In 2000, Kong et al. [18] demonstrated a phenomenon where a single-walled carbon nanotube (SWCNT) increases or decreases its conductivity when interacting with NO_2 or NH_3 gases, respectively. The sensor shows a fast response, which can be due to the large surface area of the CNT. However, the most remarkable feature is that this system operates at room temperature. In 2005, Huang et al. showed [19] that a three-component device

based on multi-walled carbon nanotubes can detect molecular nitrogen.

Devices based on field transistors with one semiconducting carbon nanotube or on the basis of ultrathin CNT films are often considered as active sensors.

Devices using boundary modified carbon nanotubes can also act as sensors, for example, an atomic force microscope, on the tip of which there is a nanotube with a specially selected functional group.

In addition to gas sensors, there are a number of sensor devices for identifying various substances. They include: (i) biosensors with a configuration of field transistors based on a carbon nanotube modified with bioreceptors [20] which are used to determine biological compounds; (ii) photosensors based on CNTs [21–23] and photodetectors based on films consisting of many carbon nanotubes [24], including those modified with other nanostructures, which leads to an increase in the photoresponse [25–29].

However, one of the main limitations in using sensors is the lack of selectivity which is the main point that delays the further propagation of these devices. This problem can be reduced by selecting CNT compounds with other materials, i.e. by modifying nanotubes. Nanotubes can be easily functionalized due to their high specific surface area. Such improvements make CNT-based sensors very competitive and also quite miniaturized.

We assume that modified carbon nanotubes can act not only as gas sensors, but also determine other chemical elements, for example, metals. Thus, the tip of an atomic force microscope equipped with a nanotube with a specially selected chemical group at its end interacts differently with the surfaces of samples of different chemical composition, i.e. it is chemically sensitive [30]. In addition, we assume that the surface activity of carbon nanotubes can also ensure their use as sensors for determining microenvironments of various substances.

Despite the available experiments on modifying CNTs and studies on the sorption activity of CNTs with respect to certain gases, the addition mechanism of a number of functional groups, including nitro groups, to the surface of carbon tubulene has not been studied yet. Besides, the activity of such a modified nanotubular system in relation to other chemical elements, for example, metals, has not been studied, which allows to assert the possibility of CNT surface sensory activity. All of the above determines the relevance of this work.

It can be assumed that the use of modified CNTs as a supersensitive element will make it possible to create sensors that are significantly superior to other devices of a similar size [20, 31, 32].

In [33, 34], the results of quantum-chemical research on the possibility of creating sensor devices based on boundary-modified functional carboxyl, amine and nitro groups (—COOH, —NH_2, —NO_2) of carbon nanotubes and nanotubes surface-modified with an amino group are presented. However, the search for new versions of modified nanotube systems that can be used as sensors for sensor devices is still relevant, since they allow expanding the class of materials used and determining the most effective of them in terms of the degree of sensory response.

Throughout the history of physics, along with experimental work, theoretical studies were widely conducted, allowing both interpreting and explaining the results obtained from the experiment and predicting new properties of substances, new effects in them and new applications. Therefore, at present, to obtain new deep ideas about the structure and properties of solid bodies (including nanotubes), consistent theoretical approaches and effective models that complement physical research methods must be used for a detailed description of the electron-energy structure and various processes.

The presented paper shows the results of theoretical studies on the interaction between the CNT, the surface-modified nitro-group and atoms of alkali metals (lithium, sodium, potassium) subject to initialization, which can be part of salts and alkalis. The mechanism of sensory interaction of modified carbon nanosystems with metals atoms was investigated. To perform quantum-chemical calculations, a molecular cluster model and the calculated method, i.e. the Density Functional Theory (DFT) with B3LYP-correlation functional (valence-split basic set 6-31G) was used [35–37].

2. Materials and methods

Recently, the methods of *ab initio* calculations based on the Density Functional Theory are becoming common in solid body physics [35, 36]. According to this theory, all electronic properties of the system, including energy, can be obtained from electronic density (without knowledge of wave functions). The system is described by no wave function (WF), but an electron density ρ (R) defined as:

$$\rho(r) = \int ... \int |\Phi_e|^2 d\sigma_1 d\sigma_2 ... d\sigma_N ,$$

where Φ_e is a multielectronic WF system, σ_i is a set of spin and spatial coordinates of electrons, and N is the number of electrons. Thus, $\rho(r)$ is the function of only three spatial coordinates of r point, where $\rho(r)$ allows detecting any of the molecule electrons. It can

be considered as the density of "electron gas" forming the "electronic cloud" of the molecule [35, 36].

If the property of the molecule main state can be expressed in ρ, then the electron energy is expressed as follows:

$$E[\rho] = T[\rho] + V_{en}[\rho] + V_{ee}[\rho],$$

where $T[\rho]$ is the kinetic energy, $V_{en}[\rho]$ is the potential energy of electron-nuclear interactions, $V_{ee}[\rho]$ is the energy of interelectronic interactions which can be written in the form:

$$V_{ee}[\rho] = V_{\text{Coul}}[\rho] + V_{xc}[\rho],$$

where $V_{\text{Coul}}[\rho]$ is the energy of the Coulomb interaction of electrons, while $V_{xc}[\rho]$ is the so-called exchange-correlation energy, i.e. the part of the potential energy of the electron interaction among themselves which takes into account the exchange member in the Hartree–Fock method and correlation energy.

The functionals $T[\rho]$, $V_{en}[\rho]$ and $V_{\text{Coul}}[\rho]$ can be found accurately. The easiest way is the so-called Kohn–Sham method. In this method, ρ is represented as the amount of contributions of individual electrons described by certain auxiliary self-consistent orbitals (Kohn–Sham orbital):

$$\rho[r] = \sum_{i=1}^{N_{orb}} |\psi_i(r_i)|^2 .$$

The energy components are:

$$T[\rho] = 2\sum_{i=1}^{N_{orb}} \left(\int \psi_i \left(-\frac{1}{2}\nabla^2 \psi_i \right) dr \right);$$

$$V_{en}[\rho] = \sum_{i=1}^{N_{orb}} \left(\int \psi_i \left(-\sum_A \frac{Z_A}{r_{iA}} \psi_i \right) dr \right);$$

$$V_{\text{Coul}}[\rho] =$$

$$= \sum_{i=1}^{N_{orb}} \sum_{j>1}^{N_{orb}} \int\!\!\int \psi_i(r_1)\psi_i(r_2)\frac{Z_A}{r_{iA}}\psi_i(r_1)\psi_i(r_2)\, dr_1 dr_2 .$$

$V_{xc}[\rho]$ exchange-correlation potential is not represented accurately, and the introduction of additional approximations is required. There are many models for their description. It is discussed that TFP is used with different functionals. The most famous and widely used among them are Becke–Perdew (BP), Perdew–Wang (PW91), Becke–Lee–Yang–Parr (BLYP) and Perdew–Burke–Ernzerhof (PBE) functionals.

One of the most popular is B3LY-hybrid functional which includes three components of the exchange function (the exact Hartree–Fock exchange operator, the Becke functional and the Slater functional), while the correlation part is a combination of Lee–Yang Parr (LYP) and Vosko–Wilk–Nusair (VWN) functionals. A feature of this approach is that the three exchange components are accepted with weight coefficients selected according to comparison with experimental data. It turns out that in most cases its accuracy is much higher than that of methodologically "clean" functions. Apparently, this is due to the fact that the exchange energy is nonlocal and any attempts to reduce it to local functions lead to errors. The inclusion of Hartree–Fock exchange allows considering this nonlocality. In the present theoretical study, the B3LYP functional was used.

As soon as the exchange-correlation potential is set, the solution by the DFT method is carried out by solving the so-called Kohn–Sham equation:

$$\hat{E}_{\text{KS}}\psi_i = \varepsilon_i \psi_i ,$$

where the Kohn-Sham operator $\hat{E}_{\text{KS}}$ is defined according to the variation principle as

$$\hat{E}_{\text{KS}} = -\frac{\nabla^2}{2} - \sum_m \frac{Z_m}{|r - r_m|} + \int dr' \frac{\rho(r')}{|r - r'|} + \frac{\delta V_{xc}}{\delta \rho} .$$

Further, the solution procedure is completely analogous to the self-consistency procedure of the Hartree-Fock method. Expanding ψ_i in the orbitals of the atomic basis, one can write equations for the coefficients of molecular orbitals C_{ij}, i.e. equations similar to the Roothaan equations [35, 36].

To perform calculations, we used the Pople Valenz Double–Zeta 6-31G basis set (determined for atoms from H to Zn), where the valence of atomic orbitals consists of two parts – internal, compact and external, diffuse [37]. The abbreviation 6-31G means that six primitive Gaussian functions are used to describe nuclear orbitals (non-valence electrons), and the valence *s*- and *p*-orbitals are divided into a compact part consisting of three Gaussian functions and a diffuse part represented by one Gaussian function. Calculations with such a basic set reproduce various energy parameters with sufficient accuracy. To prove this, experiments were carried out with a large number (298) of energy experimental values for molecules, among which there were 148 heat release values, 85 ionization potentials, 58 similar electron values and seven similar proton values. It was assumed that all these experimental results were

known with an accuracy of 1 kcal·moL^{-1} and more. It was found that the calculations gave a standard deviation of 1.02 kcal·moL^{-1} from these values. Currently, many theoretical studies of carbon nanotubes are carried out with the hybrid functional B3LYP and the basis set 6-31G [38–40].

In this paper, the following problems were solved using theoretical modeling: the possibility of modifying the outer surface of a single-walled carbon nanotube by attaching a functional nitro group to it was investigated; the interaction mechanism of the obtained modified complex with alkali metal atoms was studied, as well as the sensor activity of the nanosystem was investigated by simulating the scanning process of an arbitrary (model) surface containing selected metal atoms created by the CNT + NO_2 sensor nanosystem to determine the energy of the complex's sensory response to the presence of alkali metal atoms.

A molecular cluster of a single-walled carbon nanotube of the "zig-zag" type (6, 0) containing six carbon hexagons along the perimeter and seven layers of carbon hexagons along the longitudinal axis of the nanotube, with boundaries closed by pseudo-hydrogen atoms in order to avoid the influence of edge effects, was chosen as an object of research.

The process of modifying the carbon nanotube was simulated as follows: the nitro group —NO_2 oriented by the nitrogen atom to the CNT surface approached the carbon atom of the surface located approximately in the middle of the tube with a step of 0.1 Å (Fig. 1). The movement of the nitro group was carried out along a perpendicular drawn to the longitudinal axis of the nanotube and passing through the selected C atom. The oxygen atoms of the nitro group were oriented along a straight line parallel to the axis of the nanotube. At each step, the interaction energy between the group and the nanotube was recorded. Based on the data obtained in the course of calculations, the dependence of the complex's interaction energy on the distance between the carbon atom of the CNT surface and the N atom of the nitro group was constructed. The minimum energy value on this energy curve corresponds to the case when a bond is formed between the group and the nanotube.

The simulation of the interaction of an already modified CNT with alkali metal atoms (lithium, sodium, potassium) was carried out according to the same principle as the modification of a tube with a nitro group. The selected atoms of lithium, sodium, or potassium approached one of the oxygen atoms of the functional group with a step of 0.1 Å along a straight line perpendicular to the longitudinal axis of the nanotube and passing through the oxygen atom of the nitro group. At each step, the interaction energy was recorded, and then the energy curve of the process was plotted. The minimum on the curve testified to the interaction between the modified nanotubular system and the metal atom at a certain distance.

The scanning process of an arbitrary imaginary surface containing Li, Na, K atoms to determine the sensory sensitivity of the CNT + NO_2 nanosystem was simulated by the movement of each of the alkali metal atoms along a straight line parallel to the surface of a nanotube with a functional group located at the interaction distance determined in the previous research stage (the process model is shown in Fig. 2). The metal atom sequentially moved from one oxygen atom to another atom of the O group. The presence of sensory sensitivity of the complex in relation to the indicated atoms was fixed by a minimum on the curve, which can be called the curve of sensory interaction.

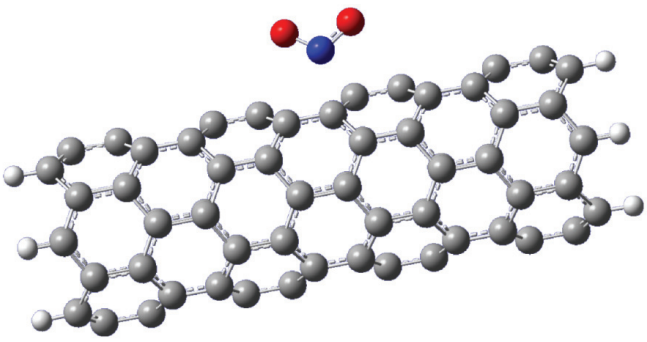

Fig. 1. A cluster model of CNTs with surface modification by a functional nitro group

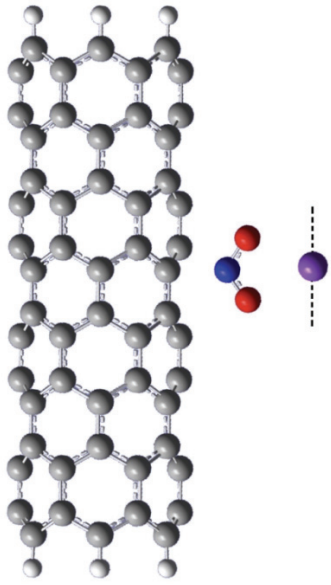

Fig. 2. A model of scanning an arbitrary area of an imaginary surface containing a potassium atom K by a carbon nanotube modified with a nitro group

3. Results and Discussion

After analyzing the energy interaction curve obtained as a result of calculations on modifying a carbon nanotube with a nitro group, it was found that a bond between CNTs and —NO_2 at a distance of 2.2 Å corresponding to an interaction energy of 4.16 eV was formed (Fig. 3). Such a connection proves the possibility of modifying the CNT surface with a functional nitro group with the formation of a stable CNT + NO_2 complex which can be used as a sensor device element.

The performed calculations on the interaction of the CNT + NO_2 complex with alkali metal atoms made it possible to construct surface profiles reflecting the potential energy of the complex "CNT + NO_2 – metal atom" system (Fig. 4). The analysis of energy curves established that the surface-modified nanotube is sensitive to the selected metals: the minimum on the curves illustrates the interaction of an atom with the CNT + NO_2 system. Some interaction characteristics of the studied alkali metal atoms and the modified nanotube, namely, the interaction energies and distances, are shown in Table 1. The analysis of the charge state of the system revealed that, during the interaction, the electron density is transferred from the metal atoms Li, Na, K to the atoms of the modified nanotubular complex. This allows to conclude that an additional Coulomb interaction appears in the system.

The analysis of the scanning process of an imaginary model surface containing potassium, lithium or sodium atoms showed that the modified nanotube becomes chemically sensitive with respect to the selected metals: the curves have a characteristic minimum which indicates the formation of a stable interaction of the element with the CNT + NO_2 system (Fig. 5). The position of the minimum turned out to be approximately in the middle between the oxygen atoms of the nitro group, which indicates the total sensitivity of the entire system with the nitro group with respect to the considered atoms.

The analysis of the distances of the sensor interaction of metal atoms with the modified complex can be very important (Table 2). The obtained distances indicate the absence of a chemical bond between the CNT + NO_2 system and a metal atom at the distance of the sensory response, which ensures the complex integrity after sensory interaction with the metal. This allows reusing a sensor based on surface-modified CNTs.

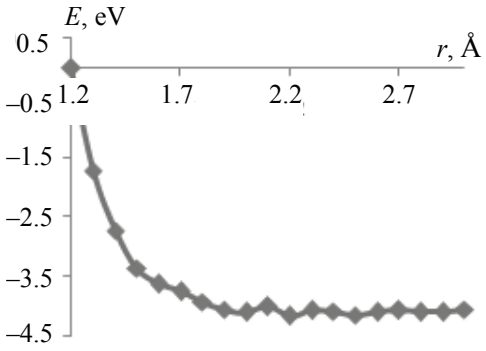

Fig. 3. The CNT and a nitro group interaction energy curve

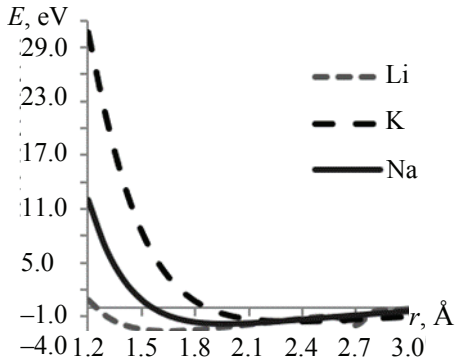

Fig. 4. Surface profiles of potential interaction energy of a carbon single-walled nanotube modified by a nitro group with alkali metal atoms

Table 1. Some interaction characteristics of alkali metal atoms and a carbon nanotube modified with a nitro group

Interatomic bond	Interaction distance, Å	Interaction energy, eV	Charge on metal atoms
Li – O	1.6	–2.60	+0.541
K – O	2.4	–1.52	+0.706
Na – O	2.0	–1.77	+0.605

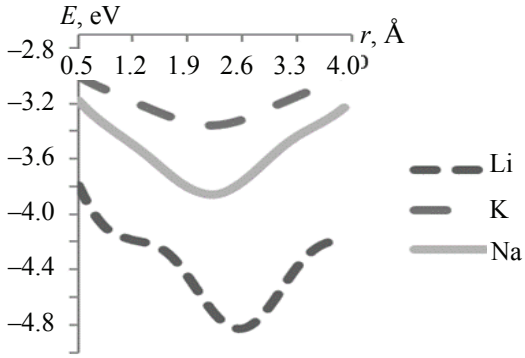

Fig. 5. Sensory interaction of modified CNT with alkali metal atoms when scanning an arbitrary surface of a nanotube

Table 2. Some characteristics of the sensory interaction between the surface-modified nitro group of the nanotubular system and the Li, Na, K atoms

Interatomic bond	Sensor interaction distance, Å	Sensor interaction energy, eV	Charge on metal atoms
Li – O	1.9	–4.82	+0.506
K – O	2.6	–3.36	+0.694
Na – O	2.2	–3.86	+0.576

Thus, a carbon nanotube, the surface of which is modified with a nitro group, displays sensory activity to alkali metal atoms, which can be measured by determining the potential in the sensor system.

4. Conclusions

In conclusion, it should be noted that despite the fact that carbon nanotubes were discovered almost thirty years ago, they still continue to generate great interest in the scientific community. All over the world, at present, the production capacity of CNTs exceeds several thousand tons per year. CNTs are used extensively in the advertising field, including consumer products such as batteries, car parts, sporting goods, and water filters. With regard to CNT-based sensors, some of them are already at the stage where they can be commercialized. In the present paper, we considered one of the effective ways to increase the sorption activity of carbon nanotubes, which is the main operation factor for sensors used in modern devices based on modifying their surface with a functional nitro group.

As a result of the performed study, the interaction mechanism of the nitro group with the outer surface of a single-walled carbon nanotube was studied during the modification made by the addition of the group to the carbon atom of the surface. The possibility of creating a stable complex CNT + NO_2, which can be used as a sensor in sensor devices, has been proved.

The possibility of interaction of alkali metal atoms of potassium, sodium, and lithium with the oxygen atom of the nitro group, which modifies the surface of a carbon nanotube of the type (6, 0), has been investigated. The scanning process of an imaginary model surface containing the mentioned atoms, created by a sensor system based on a carbon nanotube and surface-modified with a nitro group, showed that the system provides a sensory response to the presence of lithium, sodium or potassium. The resulting sensor can be used many times without destroying it and with possible interaction with the identified material (alkali metals in the case considered in the article).

Thus, a carbon nanotube, the surface of which is modified with a nitro group, has sensory activity towards alkali metal atoms, which can be determined by measuring the potential in the sensor system. Surface-modified nanotubular systems can be used to create sensors in the form of active plates, the surface of which is covered with modified carbon nanotubes. In this case, the response of the sensor system is provided by the total response of the entire surface to the presence of atoms or ions of alkali metals which can be present in the form of solutions, salts and alkalis.

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6. Conflict of interests

The authors declare no conflict of interest.

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