Computer simulation of the sensory interaction of carbon nanotubes with various modifications in relation to alkali metal atoms

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Abstract. The performed theoretical studies obtained by computer modeling and calculations performed by the semi-empirical method using the MNDO calculation scheme showed the possibility of creating sensitive chemically active probes, which are semiconductor sensor systems with boundary modification, which can act as the tip of the cantilever of the atomic force microscope. These studies allow us to predict that such a sensor based on a modified boro-carbon nanotube will react to the presence of ultra-small amounts of substances, which opens up prospects for its use in the field of chemistry, biology, medicine, etc. The use of chemically modified nanotubes, including in atomic force microscopy, is the way to create probes with distinct chemical characteristics.

1. Introduction

In recent decades, such a direction as nanotechnology – the science that allows manipulating materials with dimensions of one billionth of a meter-has become widely known and widespread. It has revolutionized the field of materials science by providing access to materials with extremely small scales and unprecedented properties. It should be said that the latest nanotechnologies, along with information and biotechnology, are the basis of the scientific and technical revolution of the 21st century, comparable and even superior in scale to the progress in technology caused by scientific discoveries of the 20th century. In addition to stimulating the development of new systems of methods, technical skills and means of all production activities based on the movement from individual atoms and molecules to the product, nanotechnology is also a source of new approaches to solving many social problems.

As is known, each property of a substance has a characteristic length associated with it. When the size of solids is reduced to a size comparable to this length, which lies within nanometer limits, the properties of the bodies change. An example of this is the change in the behavior of semiconductor particles of the order of the wavelength of an electron or hole in the conduction band, which is the basis of the so-called quantum dots, which have nanometer dimensions in three dimensions.

Carbon-based nanomaterials occupy a special niche, they have many applications due to their unique optical, thermal, mechanical, chemical and electronic properties [1]. Carbon nanomaterials, and especially carbon nanotubes, are widely used as base matrices or as functional additives in various applications due to their versatile structure.
Carbon nanotubes were experimentally obtained, one of the boundaries of which was modified by a carboxyl group [2], sensitive to ethanol vapors, gases NO, CO and NO2 [3, 4]. It can be assumed that such sensor devices using carboxylated carbon nanotubes as sensors can be used to identify other elements, such as metals, which are included in the composition of salts and alkalis. In recent years, research has been actively conducted to study the possibilities of modifying carbon nanotubes, leading to a predicted change in their properties. Various methods of such modification of the surface and boundaries of nanotubes can affect, among other things, and sorption activity, making nanotubes more sensitive to the presence of various substances. That is, the possibilities of using nanotubes as elements of sensor nanodevices are expanding.

Based on studies of the functionalization of carbon nanotubes, namely, that carbon nanotubes can be chemically functionalized using different atoms, such as boron, nitrogen or fluorine, functional groups (hydroxyl, carboxyl and similar), etc. [5,6] it is possible to predict the control of sorption characteristics of nanomaterials to create new generation devices.

It is proved that one of the ways of modifying carbon nanotubes is a method of replacing carbon atoms with other elements. Among them, nanotubes obtained in 2004 by replacing carbon atoms on the top of carbon nanotubes with boron atoms in the BCl3 gas stream look particularly attractive [7]. Thus, it is possible to create so-called borocarbon nanotubes VSP, n = 1, 3, 5, where part of the carbon atoms are replaced within the hexagon by one or more boron atoms. Thus, borocarbon layers and borocarbon nanotubes of different configurations can be constructed: BC nanotubes, BC3 nanotubes or BC5 nanotubes. Substitution of a part of carbon atoms by boron atoms changes the type of conductivity of such structurally modified nanotubes, which can be referred to the class of semiconductors, regardless of their types, diameters and chirality [8, 9 - 17], in contrast to pure carbon nanotubes. Obviously, the surface change will lead to a change in the sorption activity of such structurally modified tubular systems [18, 19]. Therefore, the study of the effect of such modification on the sorption properties of nanotubes presented in this article is an interesting task that was solved in the course of our research.

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2. Materials and methods

This paper presents the results of computer simulation of boundary functionalization processes by chemical groups of carbon nanotubes modified by boron atoms to form a BC3 structure and mechanisms of their sorption activity against alkali metal atoms (potassium, lithium and sodium). The semiempirical method of investigation of solid-state and molecular systems MNDO was used as calculation methods.

One of the computational methods used in this paper in the calculation of nanotubular systems is the semi-empirical quantum chemical method MNDO. Despite the fact that there are more modern, including non-empirical methods of calculation, the MNDO scheme is still in demand due to the proven high accuracy of calculations for many high-molecular systems.
The MNDO (Modified Neglecting of Diatomic Overlap) method is a semi-empirical calculation method in which the condition of zero differential overlap proposed by Pariser, Parr, Pople in the 60s is true for all atomic orbitals belonging to different atoms. All three- and four-center integrals are assumed to be zero, and two-center integrals of different types remain.

We investigated the mechanism of attachment of amino (-NH$_2$) group to the open boundary of a semi-infinite borocarbon BC$_3$ nanotube. Computer modeling of the joining process consisted in stepwise approximation of the functional group with a step of 0.1 Å perpendicular to the axis of the borocarbon nanotube to the selected carbon atom at the open boundary of the nanotube. During the simulation of this process and optimization of the accession process were the peculiarities of the spatial orientation of the amine group on bioperegnoy nanotubes, its geometrical parameters and charge distribution on the atoms of functional groups on the carbon atom, joined by an amine group.

Calculations showed that the functional group joined the nanotube at an angle of 109°. The n-H bond lengths were 1.23 Å and 1.36 Å. The charges on the atoms of the functional group were: on the nitrogen atom $q_N = + 0.9$ and on the hydrogen atoms $q_H = 0.2$. The charge on the nitrogen atom of the functional group indicates that when the selected functional groups are attached to the nanotube boundary, the electron density is transferred from the nitrogen atom of the group to the surface of the nanotube. Thus, this system can be characterized as a sensor probe model, which will be based on a boundary-modified borocarbon nanotube. In such a system, the mechanism of action of a sensor based on a field-effect transistor on a single nanotube, described in [20], can be implemented, as a result of which an additional charge carrier appears in the resulting system acting as a sensor sensor, providing the appearance of conductivity in the system.

Boundary-modified carbon nanotubes can serve as probes in sensor devices. For example, such a sensor can be an atomic force microscope, on the tip of which is a boundary-modified nanotube with a specially selected functional group. In [5] it is reported that carbon nanotubes have been experimentally obtained, one of the boundaries of which is modified by a carboxyl group attached to it. In the experiments, a multilayer nanotube was used, which was fixed to the Golden pyramid of the silicon cantilever microscope. The tip of the nanotube was shortened in an oxygen-holding atmosphere, applying a voltage between the tube and the mica surface with a layer of niobium sprayed on it. At the same time, a carboxyl group was formed at the open end of the nanotube. If desired, methods of organic chemistry carboxyl group can be replaced by other functional groups. The tip with the modifying group interacts differently with the surfaces of samples of different chemical composition, i.e. the tip of an atomic force microscope equipped with a nanotube with a specially selected chemical group becomes chemically sensitive (Figure 1).

Figure 1. A nanotube with a functional chemical group as the tip of a cantilever scanning atomic force microscope; the motion of the tip is shown in determining the interaction energy of the functional group with the sample surface.
It is logical to assume that the use of modified carbon nanotubes as sensors is not limited to gases. Other chemical elements, such as metals, can also be identified. Moreover, it is possible to establish the presence of both metal atoms themselves and their ions, which are part of salts and alkalis.

Also, the calculations showed that when a functional group is attached to a borocarbon nanotube, a chemical interaction is realized, which indicates the stability of the resulting complex.

3. Results and discussion

Further, the mechanism of interaction of some atoms of alkali metals, namely potassium, lithium and sodium, with the edge hydrogen atoms of the amine group of the resulting system was modeled (Figure 2). The simulation of the process was also a step-by-step approximation of metal atoms along the perpendicular to the hydrogen atom of the functional group with a step of 0.1 Å. As a result of the performed calculations, the profiles of the potential interaction energy of the systems were constructed: "nanotube + 2– alkali metal atom", which are presented in Figure 3. Analysis of the obtained curves, taking into account the distance between the metal atoms and boundary atoms of the functional group, and the values of the interaction energy suggests that there is a weak vanderwaals interaction, which confirms the reusability, the thus obtained probe without its destruction, what could make the formation of chemical bonds between elements. The main characteristics of the joining process of alkali metal atoms are presented in table 1.

![Figure 2](image1.png)

**Figure 2.** Model of interaction of Na atom with edge hydrogen atom of amide group attached to borocarbon nanotube.

![Figure 3](image2.png)

**Figure 3.** Profiles of potential energy surface of the interaction processes between divisional functional groups at the nanotube has been and atoms of alkali metals (Na, Li, K).
Table 1. The main characteristics of the addition of Na, K, Li to the edge hydrogen atoms of the amine nitro group modifying the borocarbon nanotube (6, 0): \( g_{in} \) - the interaction distance between the metal atom and the hydrogen atom of the functional group, \( E_{in} \) - the corresponding interaction energy.

| Interatomic communication | \( r_{in}, \text{ Å} \) | \( E_{in}, \text{ eV (MNDO)} \) | The charge on the metal atoms |
|--------------------------|--------------------------|-----------------------------|-----------------------------|
| Na - H                   | 2.3                      | -1.6                        | +0.9                        |
| K - H                    | 1.3                      | -1.7                        | +0.9                        |
| Li - H                   | 2.0                      | -1.4                        | +0.6                        |

At the final stage of the study of the sensory properties of carbon nanotubes with different types of modifications, the scanning process of an arbitrary surface containing an atom to be initialized was simulated and the activity of a boron-carbon nanotube with a boundary functional group with respect to the selected element was determined. The process was modeled by the motion of the metal atom perpendicular to the system "activity of the borocarbon nanotube-amine group" at the interaction distance determined by the earlier calculations, so that the motion passed strictly under the hydrogen atom of the functional group. The analysis of the constructed interaction curves obtained as a result of energy calculation is presented in figure 4. As a result of the analysis of the obtained data, it can be judged that the nanotube with the selected functional group becomes sensitive to alkali metal atoms: there is a characteristic minimum on the curves, indicating the formation of physical interaction of the atom with the amine group. The minimum on all curves is under the hydrogen atom of the group-NH\(_2\). The main characteristics of the scanning process are presented in table 2.

Figure 4. Surface profiles of the potential energy of the scanning process of the system "borocarbon nanotube-amine group" of an arbitrary surface containing potassium, lithium and sodium atoms.
Table 2. The main characteristics of the scanning process of an arbitrary surface containing alkali metal atoms modified by an amine group nanotube, $r_{s, in}$ - distance of sensory interaction, $E_{s, in}$ - interaction energy.

| Atom | $R_{s, in}$ Å | $E_{s, in}$ eV |
|------|---------------|---------------|
| Na   | 2.6           | -2.36         |
| K    | 2.89          | -3.97         |
| Li   | 2.3           | -3.83         |

Thus, the theoretical studies performed by us, obtained by computer modeling and calculations performed by the semi-empirical method using the MNDO calculation scheme, showed the possibility of creating sensitive chemically active probes, which are semiconductor sensor systems with boundary modification, which can act as the tip of the atomic force microscope cantilever. The charge carrier in such a nanotubular system is the electron supplied by the attached functional groups. Such systems are sensorially active against the alkali metals lithium, sodium, potassium, and modified nanosystems and metals interact with each other through small Van der Waals forces. Due to this type of interaction between the probe tubular system and the identifiable metals, such a probe can be reused, while the presence of a chemical bond would lead to the destruction of the sensor during its operation. This fact proves the possibility of creating a sensor sensor based on a boundary-modified borocarbon nanotube of multiple use, in which the change in its electrical properties, which can be fixed, is provided by a change in the number of carriers when interacting with identifiable atoms. Such a sensor will have selectivity: the interaction energies of the sensor semiconductor nanostructure with different atoms are not the same, so the response of the system to the presence of atoms or their ions will be different.

This method makes it possible to create sensitive sensor devices with appropriate signal amplification systems based on a borocarbon nanotube bordered by a modified amine group. The presence of metals will be determined by a change in the potential, the value of which can be determined by the value of the interaction energy of the nano-system and the metal.

4. Conclusion
The mechanism of interaction of boron-modified carbon nanotubes with metal atoms has been studied. The process of joining atoms of alkali metals potassium, lithium and sodium to the outer surface of borocarbon nanotubes is investigated. It is proved that the surface saturation of structurally modified borocarbon nanotubes with alkali metal atoms leads to the external "metallization" of the tube and the appearance of "semiconductor-metal" transitions in the semiconductor borocarbon nanotube. Similar results were obtained in the study of carbon nanotubes, the surface of which was modified by regularly arranged alkali metal atoms.

Therefore, the presence of boron atoms in the structure of the nanotube does not affect the process of creating a metal superlattice with regular saturation of the outer surface of the structurally modified borocarbon nanotube. However, due to the fact that such modified structures have stable semiconducting properties (in contrast to carbon nanotubes, which have both semiconducting and metallic properties depending on the diameter and chirality), their use may be more preferable to create nanosystems with certain predetermined properties such as semiconductor-metal transitions. For example, by inserting metal atoms between layers of multilayer borocarbon tubulens, hollow alternating metal superlattices, nanotube conductors in a semiconducting shell, and other tubulene-based composite structures with novel conductive, magnetic, and electrical properties can be created.

These studies allow us to predict that such a sensor based on a modified borocarbon nanotube will react to the presence of ultra-small amounts of substances, which opens up prospects for its use in the field of chemistry, biology, medicine, etc. The use of chemically modified nanotubes, including in atomic force microscopy, is the way to create probes with distinct chemical characteristics.
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