Modified boron-carbon nanotubes as effective sensor devices for environmental pollution control

Evgeniy Dryuchkov*, *Irina* Zaporotskova, and *Daria* Zvonareva

Volgograd State University, Volgograd, Russia

Abstract. In this article, a theoretical study of the sensing properties of a functionalized amino-group boron-carbon nanotube of the zig-zag type (6.0) containing equal amounts of carbon and boron is discussed. Such a nanotube could act as an element of a sensor device for environmental protection. The simulation was performed within a molecular cluster model using the DFT computational method, the B3LYP functional and the 6-31G basis set. The main characteristics of nanotube functionalization, its sorption and sensory activity with respect to the alkali metal atoms Li, Na, and K are obtained. It is concluded that the system can be used to detect the presence of alkali metal atoms.

1 Introduction

Recently, more and more people have become aware of the need to protect the environment and find new ways to protect our planet from various types of pollution. In this regard, science and technology play an important role in finding new solutions to protect the environment. One innovative development is boron-carbon nanotubes, which contain equal amounts of boron and carbon atoms. Modification of such nanotubes with an amine group would allow to use them for creation of highly sensitive sensor devices, which would help to control the levels of lithium, sodium, potassium in the environment and prevent their negative impact on the nature and human health.

Thus, the development of sensor devices based on boron-carbon nanotubes modified with an amine group has great potential for environmental protection. In this article we will consider in detail the properties of these materials, their application as sensor devices for the detection of alkali metals, as well as their possible contribution to solving the problem of environmental pollution.

One advantage of using boron-carbon nanotubes is their low production cost compared to traditional materials such as silicon. In addition, such nanotubes can be used to detect not only the amount of alkali metals [1], but also other types of contaminants, such as toxic gases and harmful chemicals [2].

* Corresponding author: dryuchkov@volsu.ru

There are a number of studies that confirm the effectiveness of boron-carbon nanotubes as sensor materials [3-5]. In addition, it is possible to modify nanotubes, which would improve their sensitivity and selectivity to certain types of contaminants.

However, despite the promise of this technology, its application on an industrial scale is still limited due to insufficient understanding of the properties of boron-carbon nanotubes and the need for additional research.

Nevertheless, the development of boron-carbon nanotubes modified with an amine group has great potential to create highly sensitive sensor devices, which can help to protect the environment from pollution. This could be an important step toward sustainable development and conservation of our planet's natural resources.

2 Materials and methods

In this paper, a semiconductor achiral (6.0) boron-carbon nanotube of zig-zag type containing 50% boron atoms and 50% carbon atoms is considered within the molecular cluster model. Its model is shown in Figure 1. The nanotube was capped at both ends with hydrogen atoms.

The simulation was performed using the DFT computational method [6], the B3LYP functional [7], and the 6-31G basis set [8].

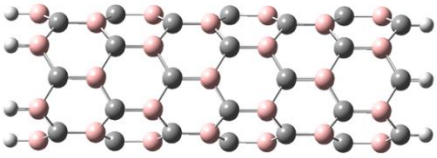

Fig. 1. Model of the anchiral (6.0) boron-carbon nanotube used in this work.

2.1 Molecular cluster method

The molecular cluster model is one of the methods of theoretical chemistry used to describe molecular systems consisting of many molecules or atoms linked together in a particular structure.

In this method, a molecular system is viewed as a cluster, i.e., a set of molecules linked together in a particular structure. Each molecule in the cluster is treated as a separate entity, bound to other molecules in the cluster by weak intermolecular forces, such as van der Waals interactions or hydrogen bonds.

The molecular cluster model allows to describe molecular systems with higher accuracy than the molecular mechanics method, which treats molecules as separate objects without taking into account intermolecular interactions.

The molecular cluster method is widely used in various fields of chemistry, such as catalysis, photochemistry, biophysics, nanomaterials chemistry, and others. It is used to study reaction mechanisms, surface properties, structure and properties of molecules, and to develop new materials and catalysts.

The molecular cluster method has its advantages and disadvantages. One of the main advantages of the method is the possibility to take into account intermolecular interactions, which allows to describe systems with higher accuracy. The method also allows studying large molecular systems, including nanomaterials and biological macromolecules.

However, the molecular cluster method has its disadvantages. It is computationally expensive, which limits its application to the study of very large molecular systems. In addition, the method is not always accurate, especially in cases where interactions between

molecules are strong or where reactions involving the breaking or formation of chemical bonds occur.

Various improvements, such as combining it with other calculation methods, such as the density functional method, or using more accurate functionals and basis sets for calculating interactions between molecules, have been used to address the shortcomings of the molecular cluster method.

2.2 Density functional theory

The density functional method (DFT) is one of the main tools for quantum-chemical calculations. It allows to describe the electronic structure of molecules and solids using the electron density functional.

The basic idea of the DFT method is that the energy of the system can be expressed in terms of its electron density, which is a probability distribution of the arrangement of electrons in space. To calculate the electron density the Cohn-Sham equation is used, which reduces the problem of calculating the energy of the system to the problem of minimizing the electron density functional.

One advantage of the DFT method is its high accuracy and universality. It can be used to calculate a wide range of systems, including molecules, clusters, surfaces, and crystals. In addition, the DFT method provides information about different properties of the system, such as geometric parameters, spectra and thermodynamic characteristics.

There are many different electron density functionalizations that can be used in the DFT method. They vary in their accuracy, versatility, and computational complexity.

One of the important challenges in using the DFT method is choosing the right functional for the particular system. This may require some experience and experimentation, so it is important to have an understanding of the basic principles of the method and its limitations.

2.3 B3LYP functionality

The B3LYP (Becke, 3-parameter, Lee-Yang-Parr) functional is one of the most widely used functional in the density functional method (DFT) for calculations of molecular systems. It was developed in 1993 by R. Becke et al.

The B3LYP functional is a combination of three other functionals: Lee-Yang, Becke, and Parr. Each of these functionals describes a different aspect of the electronic structure of the system and contributes to the energy calculation.

The Lee-Yang functional is used to describe the contribution of the kinetic energy of the electrons, the Becker functional describes the interaction between electrons and nuclei, and the Parr functional describes the correlation energy between electrons.

In addition, the B3LYP functional includes additional parameters that allow it to be tuned for certain types of systems and properties. For example, the parameter alpha determines the fraction of exchange energy in the functional, and the parameter beta determines the fraction of correlation energy.

The B3LYP functional is commonly used to calculate molecular systems, including organic molecules, metal complexes, and biological molecules. It gives fairly accurate results for most types of systems and properties, although there may be exceptions, for example, for systems with strong electron interactions.

2.4 Basis set 6-31G

The 6-31G basis set is one of the most common basis sets in the quantum chemistry method for calculations of molecular systems. It was developed in 1980 as part of the Hartree-Fock method.

The name 6-31G denotes the basic characteristics of the basis set. The number "6" indicates the number of Gaussian functions used to describe the electron shell of the atoms in the molecule, and the numbers "3" and "1" indicate the number of Gaussian functions used to describe d and p type functions, respectively.

Thus, for atoms that can form bonds in a molecule, such as carbon, oxygen, and nitrogen, six Gaussian functions are used to describe the 1s, 2s, and 2p orbitals. For atoms that do not form bonds in the molecule, such as noble gases, only one Gaussian function is used to describe the 1s orbital.

The 6-31G basis set also includes additional functions that take into account the polarization of the electron clouds of the atoms and improve the accuracy of the calculations. For example, for each atom, additional functions like d and p are added, which describe the polarization of its electron shell in response to the charges and fields of neighboring atoms.

The 6-31G basis set is commonly used for calculations of molecular systems in organic chemistry, and gives fairly accurate results for most types of systems and properties, although there may be exceptions for complex systems, such as metal complexes or biological molecules, where more complex basis sets may be needed.

3 Research results

3.1 The functionalization process of a boron-carbon nanotube

To improve the sensor properties of the BC nanotube, its surface was functionalized with an amine group (-NH_2), the presence of which can lead to increased sensitivity of nanotubes to various atoms and molecules.

Functionalization of the boron-carbon nanotube surface was performed by attaching an amine group to two possible nanotube surface centers in 0.1 Å increments: 1 - surface carbon atom (C); 2 - nanotube surface boron atom (B). The functional group was placed approximately in the center of the boron-carbon nanotube cluster to eliminate the effect of edge atoms. At each step, the system was optimized to obtain an energetically advantageous geometry of the attached functional group.

When the BC nanotube is functionalized with an amine group at the first possible center, namely the carbon atom, the minimum distance at which a chemical bond is formed between the nanotube and the amine group is 1.5 Å, which corresponds to an energy of 2.05 eV. The bandgap width in this case is 0.81 eV, while the unmodified boron-carbon nanotube has a bandgap width equal to 1.06 eV. When functionalized to a boron atom, the minimum distance at which a chemical bond is formed between the nanotube and the amine group is 1.6 Å, which corresponds to an energy of 1.63 eV. The bandgap width is 0.84 eV. In both cases, there is an electron density transfer between the nanotube and the amine group. It can be concluded that the conductivity in the system is provided not only by the electron transfer, but also by the change in the band gap width in the obtained complexes. The distances and interaction energies are reflected in the curve in Figure 2.

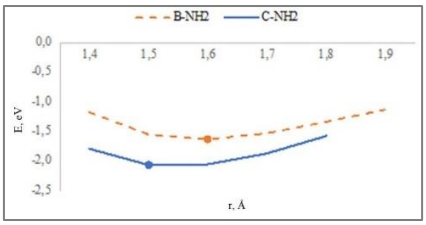

Fig. 2. Functionalization curve of a nanotube with an amine group.

Figure 3 shows density of states (DOS) plots showing the contribution of the amine group to the band structure of a boron-carbon nanotube.

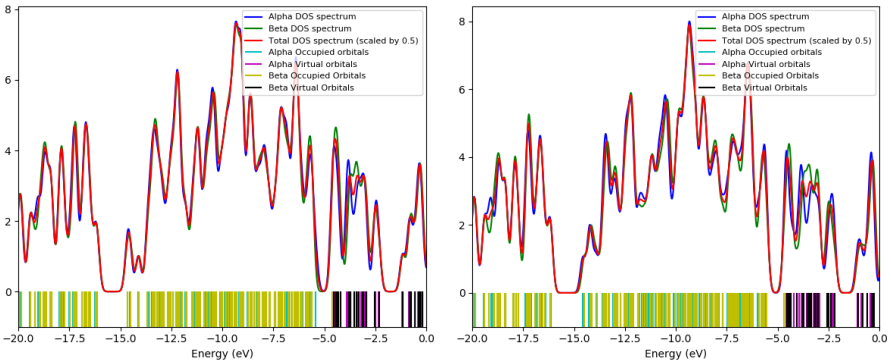

Fig. 3. Density of states plots of the nanotube functionalization process: on the left, per surface carbon atom; on the right, per surface boron atom.

3.2 Sorption interaction of the complex with alkali metal atoms

The alkali metal atoms (lithium, sodium, potassium) were approached to the obtained " BC-NH_2" complex to determine the distance and sorption interaction energy, namely, with a step equal to 0.1 Å to one of the hydrogen atoms of the functional group. Based on the simulation results, energy curves (Fig. 4) showing the interaction distance and the corresponding sorption interaction energy of alkali metal atoms and a functionalized boron-carbon nanotube were constructed.

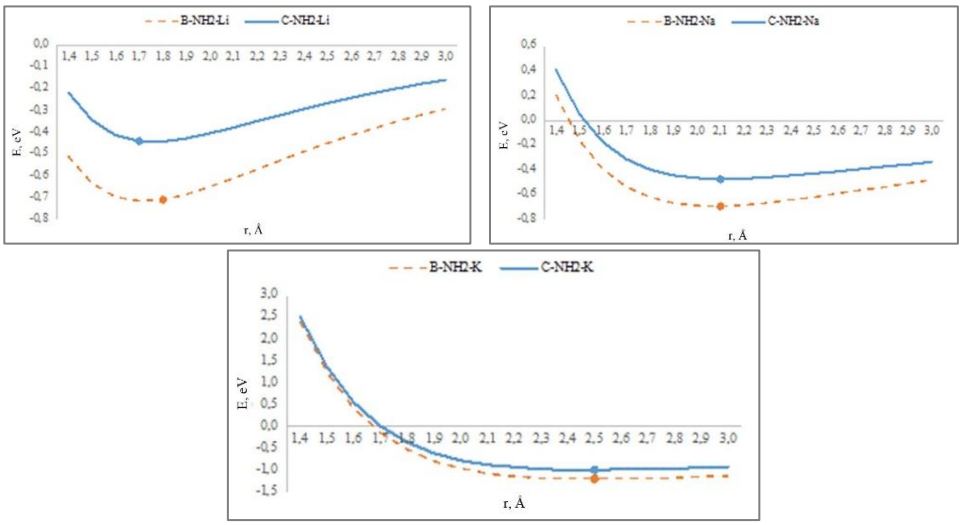

Fig. 4. Energy curves showing the distance and interaction energies of the BC-NH_2 complex with alkali metal atoms.

Analysis of the results showed that the interaction of the selected metal atoms with the hydrogen atom of the group is barrier-free. In addition, because of the sufficiently large interaction distance between the amine group and the alkali metals (it corresponds to the minimum on the energy curve), this interaction can be qualified as a weak van der Waals interaction, which allows multiple use of the sensor, since no chemical bonds are formed between it and the alkali metal atom. The sensor modified by the amine group is able to

register the change in the Schottky barrier value between the electrodes of the sensor device and the "BC-NH_2" system. The defined interaction parameters are shown in Table 1.

Table 1. Characteristics of the sorption interaction between a functionalized boron-carbon nanotube and alkali metal atoms.

	PC: atom C		PC: atom B	
	r_{int}, Å	E_{int}, eV	r_{int}, Å	E_{int}, eV
Li	1.9	-3.08	1.8	-3.67
Na	2.1	-2.60	2.1	-3.14
K	2.5	-2.71	2.5	-3.15

3.3 Scanning a virtual surface containing alkali metal atoms

Once the distances at which the functionalized nanotube interacts with alkali metal atoms were known, an arbitrary virtual surface, on which the presence of these atoms is implied, was scanned to evaluate the sensory interaction between them and the "BC-NH_2" complexes. The scanning was performed along the hydrogen atoms of the amine group at the distance obtained from item 3.2. This path is shown by the dotted line in Figure 5.

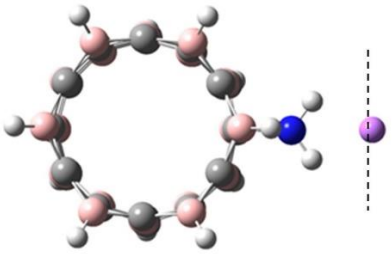

Fig. 5. Scanning direction of the lithium atom (pink ball) along the hydrogen atoms of the amine group.

The data obtained are shown in Table 2. The distance of 2.6 Å corresponds to the position of the studied atoms exactly between the hydrogen atoms of the amine group.

Table 2. Characteristics of sensory interaction when scanning a virtual surface.

	PC: atom C		PC: atom B	
	$r_{s\text{-}int}$, Å	$E_{s\text{-}int}$, eV	$r_{s\text{-}int}$, Å	$E_{s\text{-}int}$, eV
Li	2.6	-3.18	2.6	-3.89
Na	2.6	-2.78	2.6	-3.35
K	2.6	-2.82	2.6	-3.29

4 Conclusions

To summarize, we can conclude that the boron-carbon nanotube studied in this work is capable of functionalization with an amine group, and has conductivity, which is important for sensor systems. The modified nanotube showed the ability to interact with alkali metal atoms (Li, Na, K), and was able to detect them on an arbitrary surface. Such systems can act as sensitive elements of sensor devices and detect not only micro quantities of alkali metals,

but also other types of contaminants, such as toxic gases and harmful chemicals that degrade the environment.

The work was carried out within the framework of the state task of the Ministry of Science and Higher Education of the Russian Federation (topic "FZUU-2023-0001).

References

1. S. V. Boroznin, Z. A. Zhitnikov, I. V. Zaporotskova, N. P. Boroznina, AIP Conf. Proc. **7** (2020)
2. S. V. Boroznin, O. A. Kakorina, I. A. Kakorin, E. S. Dryuchkov, *"Smart technologies" for society, state and economy*, 277-287 (2021)
3. I. V. Zaporotskova, E. S. Dryuchkov, N. P. Boroznina, Rus. Microelectronics **40**, 644-648 (2021)
4. I. V. Zaporotskova, E. S. Dryuchkov, D. E. Vilkeeva, KEM **887**, 23-27 (2021)
5. I. V. Zaporotskova, E. S. Dryuchkov, M. F. Chesheva, D. A. Zvonareva, NBI Technologies **15**, 27-34 (2021)
6. W. Koch, M.C. Holthausen, *Wiley-VCH*, Weinheim (2002)
7. Tirado-Rives, Julian & Jorgensen, William, J. Chem. Theory Comput. **4**, 297-306 (2008)
8. V. Maslov, Optics and Spectroscopy **101**, 853-861 (2006)