Investigation of interaction of borocarbon nanotubes with gas phase atoms

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Abstract. During the study of adsorption interaction by computer modeling, it was found that adsorption of oxygen, fluorine and chlorine atoms is possible on the surface of a carbon nanotube. In the course of comparing the surface sorption activity of BC\textsubscript{5} nanotubes with respect to various chemical elements, it was found that the interaction of the oxygen atom with the surface of the borocarbon nanotube is the most energetically advantageous. The introduction of boron atoms promotes a more active addition of oxygen, fluorine and chlorine atoms to the surface of the nanotube, that is, structural modification leads to an increase in the sorption activity of carbon nanotubes.

1. Introduction

Nowadays, the technology has reached such a level of perfection that the micro-components of modern technology are becoming less relevant, gradually being replaced by nanocomponents. The main element of nanotechnology are nanomaterials, whose dimensions lie within 1-100 nm [1-3], which have new unique properties and characteristics. 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.

Nanotubes are extended cylindrical structures with a diameter of one to several tens of nanometers and a length of several micrometers, consisting of one or more rolled-up hexagonal graphite planes and usually ending in a hemispherical head. Their surface is made by regular six-membered carbon cycles (hexagons). Depending on the conditions of production, single-layer or multi-layer nanotubes with open or closed ends are formed. Single-walled nanotubes - SWNT consist of a single shell of carbon atoms, and Multi-walled nanotubes – MWNT consist of many grouped carbon tubes. The currently accepted classification [1-4] is based on this principle of subdivision of tubular structures. The most common forms of nanotubes are extended multilayer structures with closed ends: extended surfaces are formed by hexagons, and the turns leading to the rounding of the ends of the tubes and their closure are five - membered graphite rings (pentagons).

A model of an idealized single-layer nanotube is presented in Figure 1. Such a tube ends with hemispherical vertices containing, along with regular hexagons, also six regular pentagons. The
presence of pentagons at the ends of the tubes allows us to consider them as the limiting case of fullerene molecules, the length of the longitudinal axis of which significantly exceeds their diameter.

![Atomic structure of closed single-layer carbon nanotubes.](image)

The unique mechanical, sorption, electrical and magnetic properties of nanotubes provide a breakthrough in nanoelectronics and semiconductor technology.

The trend towards increasing miniaturization of electronic devices entails the need to develop a new level of integration—the nanoscale. As a result, there was a need to obtain transistors, wires with sizes ranging from 1 to 20 nanometers. The solution to this problem was in 1985. the discovery of nanotubes, but they began to study only since 1990, when they learned to get in sufficient quantities, and their history of development began in 1991.

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, the sorption activity of nanotubes, making them more sensitive to the presence of various substances. That is, the possibilities of using nanotubes as elements of electronic devices are expanding, including such devices as display panels, discharge tubes, anodes in lithium batteries, hydrogen storage materials, energy conversion, composites (fillers or coatings), absorbing and shielding electromagnetic radiation, nanoprobe, sensors, sensors, supercapacitors, etc. [4, 5].

It was found that carbon nanotubes have high surface activity, which made it possible to obtain various nanocomposites based on them, which have found wide application in nanoelectronics. Due to the abnormally high specific surface, in which the whole mass is concentrated, carbon nanotubes, whose surface is modified by substituting boron atoms to form various structures, exhibit extremely high sorption properties and characteristics [6, 7].

Modification of the surface of carbon nanotubes significantly increases their sorption characteristics, as well as stabilizes the geometric shape in the interaction of different atoms with the surface of such a nanotube, which makes them a promising material as an object of research, as well as for further practical application. For example, the borocarbon nanotubes considered in the article [8-12], regardless of the type of chirality and diameter, have the properties of semiconductors. Due to this stability, it can be expected that borocarbon nanotubes will be in demand as functional elements of a new generation of electronic devices.

In addition, the introduction of gas phase atoms between the layers of multilayer nanotubes will allow to create nanotube conductors in a semiconductor shell and other composite structures based on nanotubes with new conductive, magnetic and electrical properties.

2. Materials and methods
In this study, a computer simulation of the adsorption of an oxygen atom on the surface of a borocarbon BC₃ nanotube was carried out. The calculations were carried out within the framework of the molecular cluster model.

The model of a molecular cluster is connected with the separation of a fragment in a solid body and the calculation of its electronic structure on the basis of methods developed in the theory of molecules.
Fictitious atoms (pseudoatoms) are placed on the line of broken bonds, trying to take into account the influence of the nearest neighbors of the boundary atoms of the cluster.

Molecular systems contain fewer atoms than real solids, their symmetry group is poorer. Therefore, the application of molecular models in the theory of the electronic structure of solids must be due to the physical essence of the problem under consideration. The use of quasi-molecular models is expedient, first of all, in the study of those phenomena in solids that can not be described in the framework of the zone theory. Such phenomena include adsorption and catalysis associated with processes on the surface of crystals, essential for practical applications of effects in solids, due to the presence of impurities or structural defects, etc. In the framework of quasi-molecular models it is possible to describe many local properties of solids such as the redistribution of electron density around a single atom, the nature of its interaction with its nearest neighbors. These properties are essential for describing solids with a physically isolated individual atom or group of atoms (local center, adsorbed molecule or atom).

The choice of a quasimolecule modeling a crystal turns out to be quite a difficult task, the solution of which is impossible in isolation from the symmetry of the considered systems. It is usually assumed that the cluster modeling the crystal must have the point symmetry of the latter. In accordance with this, the approximation of "spheres of interaction" is used: in a solid, a Central atom and several coordination spheres surrounding it are distinguished.

The choice of the method of setting the boundary conditions, as a rule, is determined by the calculated system and the task. The technique of boundary atoms, which saturate the broken external valence bonds of the cluster, is often used. For this purpose, monovalent atoms are usually used, having approximately the same electronegativity as the atoms of the crystal. This approach was successfully applied, for example, in the calculations of molecular clusters of diamond and graphite, in which hydrogen atoms replaced the missing atoms of the crystal. The selection of parameters for pseudoatoms is carried out in such a way that the following conditions are met: a) the energies of the molecular orbitals of the cluster must qualitatively correctly convey the nature of the energy zones of the crystal; b) the ratio between charges on atoms due to the stoichiometry of the crystal must be correctly transmitted; c) the solution must be stable during the expansion of the cluster. This approach is acceptable when the boundary atom of the cluster has one broken bond. If a boundary atom has two or more broken bonds, the application of the method of closing them by pseudoatoms becomes difficult.

![Figure 2](image-url)  
**Figure 2.** Variants of the orientation of the oxygen atom relative to the surface of the nanotubes.
At the moment there are five options for the orientation of the oxygen atom on the nanotube surface: I) above the centre of the hexagon of the nanotube surface, II) and III) above a boron atom or carbon, these types of nanotubes, IV) and V) above the middle of the connection between the closest atoms of the hexagon of the nanotube surface. In this work, the variant III of oxygen adsorption on the surface of a borocarbon nanotube was chosen. The approximation process was modeled by a stepwise approximation with a step of 0.2 Å of the adsorbed atom to the surface of the nanotube (Figure 2).

3. Results and discussion
The oxygen adsorption process for variant III was modeled as follows: the O atom was stepwise approaching the carbon atom of the surface of the borocarbon nanotube. The calculations made it possible to construct energy curves of adsorption processes for these variants and types of nanotubes under consideration. Analysis of the energy curves showed that for this variant, oxygen adsorption is possible on the surface. This is illustrated by the presence of a minimum on the energy curves corresponding to the case of physical adsorption of the O atom.

During the analysis of the energy curve of the process of joining an oxygen atom to the surface of a borocarbon nanotube (Figure 3), a table was formed showing the values of the interaction energy depending on the distance of the adsorbing atom O relative to the nanotube thickness (Table 1).

![Figure 3. The potential energy profile of the oxygen atom adsorption process on the carbon atom of the BC₅ nanotube.](image-url)
Table 1. The main electron-energy characteristics of the adsorption process of the O atom on the surface of the BC$_5$ borocarbon nanotube for this variant of the orientation of the O atom relative to the tubulene surface.

| $R_{AD}$, Å | $E_{AD}$, eV  |
|-------------|--------------|
| 3.0         | -3510.565    |
| 2.8         | -3510.574    |
| 2.6         | -3510.586    |
| 2.4         | -3510.601    |
| 2.2         | -3510.622    |
| 2.0         | -3510.646    |
| 1.8         | -3510.670    |
| 1.6         | -3510.685    |
| 1.4         | -3510.671    |
| 1.2         | -3510.590    |

The chlorine adsorption process for variant III was modeled in a similar way as in the case of oxygen interaction, namely: the Cl atom was stepwise approaching the carbon atom of the surface of the borocarbon nanotube. The calculations were carried out within the framework of the molecular cluster model using the Gaussian program. The calculations made it possible to construct energy curves of adsorption processes for these variants and types of nanotubes under consideration. Analysis of the energy curves also showed that for these variants, chlorine adsorption is possible on the surface (Figure 4). This is illustrated by the presence of a minimum on the energy curves corresponding to the presence of physical adsorption of the Cl atom (Table 2).

![Figure 4](image-url)
Table 2. The main electron-energy characteristics of the adsorption process of the Cl atom on the surface of the BC$_5$ borocarbon nanotube for this variant of the orientation of the Cl atom relative to the tubulene surface. $E_{AD}$-adsorption energy, eV; $R_{AD}$ - adsorption distance, Å.

| $R_{AD}$, Å | $E_{AD}$, eV   |
|-------------|---------------|
| 3           | -3893.970     |
| 2.8         | -3893.961     |
| 2.6         | -3893.968     |
| 2.4         | -3893.978     |
| 2.2         | -3893.971     |
| 2           | -3893.956     |
| 1.8         | -3893.920     |
| 1.6         | -3893.829     |
| 1.4         | -3893.641     |
| 1.2         | -3893.233     |
| 1           | -3892.301     |

The fluorine adsorption process for option III was modeled similarly to the two interaction processes described above: the F atom was stepwise approaching the carbon atom of the surface of the borocarbon nanotube.

Figure 5. The potential energy profile of the fluorine atom adsorption process on the carbon atom of the BC$_5$ nanotube.
The calculations were carried out within the framework of the molecular cluster model using the GaussView 5.0 program. The calculations made it possible to construct energy curves of adsorption processes for these variants and types of nanotubes under consideration. Analysis of the energy curves showed that, as for the two above-described variants, fluorine adsorption is possible on the surface and occurs barrier-free. This is illustrated by the same presence of a minimum on the energy curves corresponding to the case of chemical adsorption of the atom F (Figure 5, table 3).

Table 3. The main electron-energy characteristics of the adsorption process of the F atom on the surface of the BC₅ borocarbon nanotube for this variant of the orientation of the F atom relative to the tubulene surface. E_{AD}-adsorption energy, eV; R_{AD} - adsorption distance, Å.

| R_{AD}, Å | E_{AD}, eV |
|-----------|------------|
| 3         | -3535.20   |
| 2.8       | -3535.20   |
| 2.6       | -3535.20   |
| 2.4       | -3535.22   |
| 2.2       | -3535.21   |
| 2         | -3535.23   |
| 1.8       | -3535.24   |
| 1.6       | -3535.25   |
| 1.4       | -3535.21   |
| 1.2       | -3535.09   |
| 1         | -3534.76   |

4. Conclusion
During the study of adsorption interaction by computer modeling and calculations, it was found that on the surface of a carbon nanotube, in which every sixth carbon atom is replaced by a boron atom (the structure of a borocarbon nanotube of type BC₅), adsorption of oxygen, fluorine and chlorine atoms is possible. The study of the mechanism of adsorption of the oxygen atom to the surface of the tube found that the process of joining is more energy-efficient when the adsorbing atom is located above the carbon atom. In the course of comparison of surface sorption activity of BC₅ nanotube with respect to various chemical elements, namely selected atoms of the gas phase, it was found that the interaction of the oxygen atom with the surface of the borocarbon nanotube is the most energetically advantageous.

Comparison of adsorption of gas phase atoms on the surface of structurally modified substitutive boron atoms BC₅ nanotubes with adsorption on the surface of unmodified carbon nanotube [13] allowed to conclude that the introduction of boron atoms promotes more active attachment of oxygen, fluorine and chlorine atoms to the surface of the nanotube. Structural modification leads to an increase in the sorption activity of carbon nanotubes. Also, as in the case of unmodified carbon nanotubes, they interact with the Van-der-Waals forces, which allows the resulting structure to be used as an element of the sensor device to determine the micro-quantity of the substance, and also guarantees the repeated use of such a device without time and additional influences to restore the sensor by desorption.
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