About the Creation of Sensor of New Firefighting, Devices Based on Nanostructures for Determination of Carbon Monoxide and Carbon Dioxide Components

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Abstract. The article is devoted to the study of methods of detecting CO₂ molecules using boron carbon nanotubes of type BC₅. The article also compares the mechanisms of attachment of the molecule CO₂ to the surface of the modified carboxyl group of the nanotube. The main method used in the work is the density functional theory (DFT) method within the B3LYP functional. As a result of the work, the most likely method of catching carbon dioxide molecules using boroncarbon nanotubes was established and the physicochemical characteristics of these phenomena were determined.

1. Introduction

Upon contact of two chemical elements, their physicochemical properties change. One such property is the conductive characteristics of the samples. This rule underlies the construction of nano sensors for smart devices. In 2000, Kong et al. described an experiment [1] in which a single layer carbon nanotube showed a change in conductivity upon contact with nitrogen oxide and ammonia. At the same time, an instant change in the properties in the system was recorded, which allows accelerating the response time of the fire sensor. It is worth noting that the advantage of using nanomaterials lies in the possibility of detecting micro amounts of matter in the room under normal conditions. Metal oxide sensors required a temperature of about 200 °C for normal operation [2]. [1] describes a sensor operating at room temperature. And this device is restored in the following conditions: in one hour after annealing in 200°C or in 12 h at the room temperature under a stream of pure argon.

As mentioned above, the low reduction capacity of the nanodetectors is one of the main disadvantages. The reason for this can be explained by the high specific surface area of univariate nanomaterials [3]. Therefore, a number of researchers are considering other methods of cleaning nanosensors, except annealing. For example, [4] proposes the use of UV radiation instead of annealing to purify impurity atoms and molecules.

Collins and colleagues (Collins et al., 2000) [5] described in their work that single-layer carbon nanotubes are susceptible to the presence of oxygen. They measured electrical resistance and thermal EMF when the partial pressure of oxygen in the medium changed from 10⁻⁸ to 10⁻¹⁰ Torr. The authors also experimentally determined the change in electron density of carbon nanotubes placed on a gold substrate under the influence of oxygen or pure argon by scanning electron spectroscopy. The study
showed that not all single-walled carbon nanotubes are sensitive to oxygen, and when argon, helium and nitrogen interact with them, no special effects are found.

Separately, it is worth noting low selectivity of sensors based on carbon nanotubes with respect to specific gases and vapors [6]. In the case of simultaneous detection with a sensor based on carbon nanotubes of water and nitrogen oxide, their detection signals can hide each other. While adsorption of nitric oxide to the surface of carbon nanotubes leads to an increase in electrical conductivity, water has the opposite effect (i.e., leads to a decrease in electrical conductivity). To get rid of this shortcoming, Evans and coauthors (Evans et al., 2016) mixed nanotubes with zeolite [7]. While pure nanotubes are unable to detect nitric oxide in a moist environment due to the above features, nanotubes associated with a hydrophilic zeolite are successfully detected. The reason for this is that the zeolite "catches" water molecules before they can reach the surface of carbon nanotubes, which in turn only feel nitric oxide.

Thus, nanoelectronics has a huge undiscovered potential in the field of instrument making, namely, the creation of sensors [8-11] with increased selectivity and recall to specific gases.

In recent decades, carbon nanotubes containing boron atoms have shown good sorption properties compared to pure nanotubes. Therefore, an interesting research task is to study the possibility of using borocarbon nanotubes as a base material for creating a sensor for fire protection devices. Nanostructured material will allow at the molecular level to record the presence and concentration of toxic gases harmful to the human body.

2. Calculation model
To study the sensitivity of nanostructures to carbon dioxide molecules, the process of their interaction with a borocarbon nanotube of type BC5 was simulated. To perform model experiments, the method of density functional theory was used [12, 13]. At the first stage, the attachment of molecules to its surface was simulated. The molecule approached the nanotube with a pitch of 0.1 Å along the perpendicular connecting the molecule and the adsorption center. The calculations made it possible to establish the energy of the interaction process, the changes of which are shown in Figures 4 and 5.

We previously investigated the possibility of modifying the boroncarbon nanotube with a carboxyl group [3]. This modification improves the sensory properties of nanostructures. Therefore, the next step of our research was to consider the mechanism of interaction between the modified boroncarbon...
nanotube and the carbon dioxide molecule. The carbon dioxide molecule was attached in two variants shown in Figures 2 and 3.

Figure 2. Carbon dioxide molecule adsorption model together with carboxyl group on surface of BC₅-nanotube on carbon atom.

Figure 3. Carbon dioxide molecule adsorption model together with carboxyl group at edge of BC₅-nanotube on carbon atom.

3. Results and discussion
The results of computer modeling of adsorption processes showed that there is a change in the energy of the system with the formation of a minimum when molecules approach the surface of the nanotube at positions above the boron and carbon atoms (position II and III). At all other positions on the energy curves there were no minimums, which suggests that adsorption at these points is impossible.
After studying the attachment of the carbon dioxide molecule to the surface of the nanotube, two options for attaching this molecule to a modified carboxyl group nanotube were considered, as shown in Figures 2 and 3. The calculations made it possible to construct the surface profiles of potential energy shown in Figure 5.

**Figure 4.** Normalized profile of potential energy of adsorption of carbon dioxide molecule on surface of BC₅ nanotube.

**Figure 5.** Carbon dioxide adsorption potential energy profile together with carboxyl group on carbon atom BC₅ nanotubes.

All results obtained during the model experiment are shown in Table 1.
Table 1. The main characteristics of the sorption processes.

| Sorption center    | Adsorption distance, Å | Adsorption energy, eV |
|--------------------|------------------------|-----------------------|
| C atom             | 3                      | 1.4                   |
| B atom             | 2.9                    | 1.6                   |
| COOH surface       | 3.3                    | 0.9                   |
| COOH edge          | 3.2                    | 0.94                  |

The quantum-chemical calculations made it possible to establish that the adsorption of a carbon dioxide molecule is possible when the molecule is located above the boron and carbon atoms of the surface of the boroncarbon BC₅ of the nanotube. When this molecule is attached to the carboxyl group of the modified nanotube BC₅, adsorption occurs in both cases considered.

When the molecule is attached to a pure nanotube, the amount of adsorption energy is greater than when in contact with a modified nanostructure. Thus, it can be concluded that the first two mechanisms under consideration are the most likely to be implemented in fire protection devices.

At the same time, a change in electron density near the adsorption center was observed. At the same time, in the case of a boron atom, density is transferred to a carbon dioxide molecule, and when interacting with a carbon atom, towards the surface of the nanotube.

4. Conclusion
The BC₅ nanotubes in question can be considered as fire detectors for capturing carbon dioxide. The operation of the sensors is based on adsorption of CO₂ molecules with subsequent detection, possible due to a change in the conductive properties of nanobjects.

Since chemical adsorption is realized when carbon dioxide molecules interact with the nanotube, the nanostructures considered BC₅ can also be used as filters for purifying air from CO₂.

Note here that nanotube modification does not improve sorption properties. Therefore, the manufacture of such nano-sensors will not require additional sample preparation of nano-objects.

5. References
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