Features of sorption and sensory interaction of boron-nitride nanotubes with alkali metal atoms

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Abstract. Theoretical studies of sorption and sensory interaction of modified boronitride nanotube with functional amine group (-NH₂) are presented in this article. The study is conducted on alkali metal atoms. The results presented in this paper can form the basis of a highly effective sensor for determining the presence of certain elements contained in ultra-small quantities.

1. Introduction

Today, research and the use of intelligent nanotubes as nano-sensors is rapidly growing, since their unique characteristics can be used in biological and medical sciences, in the field of quality control, in the identification of materials for law enforcement needs, and the like. Bio- and nano-sensors are used to diagnose and treat individual diseases. For these areas, findings on the oscillatory behavior of carbon nanotubes (NTRs) as bio-/nano-sensors are used. Hauptmann et al. [1] proposed an ultrasonic sensor for process monitoring and chemical analysis. Microcantilever sensors were studied by Thundat and colleagues [2], who investigated the effects of damping, surface stress and mass load. Ilic et al. [3] worked on a mechanical resonance examination of a biological detector. They demonstrated that the immunospecific biological detector is a mechanical oscillator with microparticles and a silicon nitride cantilever.

The resonance frequency of the OSUNT cantilever with the attached mass sensor was investigated by Wu et al. [4]. Work [5] describes the study of calibration of bio/nanodetectors based on UNT. They showed an excellent mass distribution over the frequency shift of the nanotube remarkably.

Nano-mechanical sensors based on ONT have been proposed by Joshi et al. [6]. Similarly, NSCs as nanosensors for the recognition and detection of gas atoms were analyzed in [7].

In works [8-10], the authors describe the features of modifying carbon and boron-carbon nanotubes with various functional groups. These studies prove the possibility of determining the sorption and sensory activity of the resulting nanosystems with respect to various elements, including alkali metal atoms and gas molecules.

However, research on new nanotubular materials that have superior UNT characteristics is now becoming increasingly relevant.

Recently, due to the brilliant characteristics of boron-nitride nanotubes (BNNT) compared to CNT, nanotechnologists decided to use BNNT for their unique chemical, electrical and mechanical properties [11-18].
Ciofani et al. [19] investigated the behavior of BNNT, which act as an innovative nanodetector to solve nanomedicine problems. A comprehensive study of single-walled boron-nitride nanotubes as bio-/nano-sensors was proposed in [20]. The above studies are based on the classical theory of continuous medium mechanics without taking into account dimensional-dependent methods that can lead to incorrect and inaccurate results for interpreting the mechanical behavior of BNNT as bio-/nano-sensors. Therefore, to avoid possible errors in modeling nanotubes, it is important to use a suitable small-scale theory to analyze this type of nanostructure.

In view of the above, a deeper study of the various properties of boron-nitride nanotubes, especially their sorption and sensory properties, is relevant. This paper presents theoretical studies related to the modeling of the boron-nitride modified system and calculations of the interaction energy for this system with alkali metal atoms. Interaction energy calculations have been performed using the DFT method.

2. Methods
According to Density Functional Theory, the properties of a many-electron system including energy, can be defined by using an electron density functional. The system is described by electronic density as \( \rho(r) \):

\[
\rho(r) = \int \cdots \int | \Phi_i \rangle \langle \Phi_i | d\sigma_1 d\sigma_2 \ldots d\sigma_n
\]  

Function is defined in all space. The integral from electronic density on all space gives full number of electrons. Kinetic energy of electrons is described obviously in approach of independent particles, a classical part of potential energy is described using Coulomb's law. Exchange and electronic correlation are considered approximately.

Electronic correlation is defined as the effect caused by the instantaneous Coulomb repulsion of electrons. Its account results in lower value of total energy of a system. The specified effect is not considered in Hartree-Fock's method. The energy change caused by these instant Coulomb interactions is called energy of correlation:

\[
E_{\text{cor}} = E_{\text{ex}} - E_{\text{HF}} < 0
\]  

Electronic correlation is significant for investigation of the effects that depend on excited states. Also, this correlation is not described in the one-determinant approach.

Practical application of DFT resulted in two theorems proved by Hoenberg and Kohn in 1964 and generalized then in the papers of several authors. The first theorem claims that any property of the main condition of this system is described only by electronic density \( \rho(r) \). It is important to emphasize that this theorem is proved only for the main condition of a molecule and, strictly speaking, DFT is not the exact theory for the excited states. The second theorem establishes the variation principle in DFT: if \( E_0 \) is exact energy of the main state, then for any other electronic density \( \rho \), which can be also approach to the true electronic density of the main state, the ratio of \( E[\rho] \geq E_0 \). This theorem makes it possible to determine the \( E_0 \) of the basic state and the corresponding density of states as in the calculation methods based on the wave function. In general, DFT has an excellent ratio of accuracy and computing expenses that allow using this method for solving a huge number of problems of a quantum-chemical research [21].

3. Results of the study
Based on the results of our previous studies, which consisted in computer modeling of the process of joining the functional amine group (-NH2) to the open border of boron-nitride nanotube [22], the tasks of determining the presence of sensory interaction between the modified amine group with boron-nitride nanotube and potassium, lithium and sodium atoms were set.

Previously, the sorption interaction distance of metal atoms was established when they were attached to the hydrogen atom of the amine group (Table 1).
Table 1. The adsorption distances $R_{ad}$ for Li, K, Na atoms.

| Atom | The adsorption distances $R_{ad}$ |
|------|----------------------------------|
| Li   | 3.8                              |
| Na   | 2.9                              |
| K    | 3.4                              |

The simulation and determination of the presence of the sensory interaction of the nanosystem with the selected metal atoms was carried out as follows. An arbitrary surface containing the metal atom to be examined at a distance that had been calculated previously was scanned. As a result, a model of interaction was calculated and graphs of energy versus the position of a metal atom in a relative group were plotted (Fig. 1-3). In the graph, the location of the atom at the point 15 corresponds to its place under the functional group.

Figure 1. Graph of interaction energy versus distance between hydrogen atom of amine group and lithium atom.

Figure 2. Graph of interaction energy versus distance between hydrogen atom of amine group and sodium atom.

Figure 3. Graph of interaction energy versus distance between hydrogen atom of amine group and potassium atom.
In the course of research, a comparative table of characteristics of the scanning process of an imaginary surface containing alkali metal atoms was compiled.

**Table 2.** The main characteristics of scanning an arbitrary surface containing alkali metal atoms: adsorption distance $R_{\text{ad}}$, interaction energy $E_{\text{ad}}$ for Li, Na, K.

| Atom | The adsorption distances $R_{\text{ad}}$ | Adsorption energies $E_{\text{ad}}$ |
|------|----------------------------------------|-----------------------------------|
| Li   | 3.8                                    | -2.694                            |
| Na   | 2.9                                    | -3.498                            |
| K    | 3.4                                    | -4.323                            |

After analyzing the obtained results, it was found that the most active sorption and sensory interaction is observed between the modified boron-nitride nanotube and the potassium atom. Thus, it can be seen that as the element sequence number increases in the periodic system, the interaction energy increases. This can be explained by the fact that with an increase in the sequence number there is an increase in the atomic nucleus and an increase in the distance of the extreme orbital from the center of the atom, which leads to easier formation of generalized energy levels that facilitate interaction between substances.

**4. Conclusion**

Theoretical studies showed the possibility of creating ultra-sensitive chemically active probes based on a boron-nitride nanotube modified by a functional group. These systems have proved sensory to alkali metals (lithium, sodium, potassium). The interaction between the nanosystem and metal atoms occurs due to the small Van der Waals forces. Due to this type of interaction between the probe tube system and the identified metals, the probe can be reused, since the presence of a chemical bond would lead to the destruction of the sensor during its operation. The charge carrier in such a nanotubular system is an electron supplied by the attached functional groups.

Also, different values of the interaction energy arising at different interaction distances indicate the presence of selectivity of this nanosystem. Such systems can find their application in the field of biomedical sensors, sensors for establishing air quality in residential and industrial premises, sensor devices for detecting micro amounts of a substance. The use of chemically modified nanotubes, including in atomic power microscopy, is a way to create probes with clearly expressed chemical characteristics.

**5. References**

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