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About Using Carbon Nanotubes with Amino Group Modification as Sensors

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The article represents the research of single-walled carbon nanotubes with amino group modified sensor activity to metal atoms and their ions. The process of the amino group binding to the open edge of the nanotube has been perfomed. Investigation of the interaction between the nanotube, used as sensor, and metal atoms and ions are represented. The mechanism of scanning process in relation to atoms of metals has been modeled and the chemical activity of amine group is defined. The calculations have been carried out by the MNDO method within the framework of the molecular cluster model.

Keywords: Carbon nanotube, Sensory activity, Functional amino group, Boundary modification, MNDO method.

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1. INTRODUCTION

One of the most important aims of the nanotechnology development is the creation of miniature and, at the same time, high effective equipment.

The opening of the carbon nanotubes (CNTs) is one of the most significant achievement of modern science [1-4]. The carbon nanotubes have high sorption activity and they are used as adsorbents of different particles [5]. Thus, in addition to their conductivity state, make their application as chemical and biological sensors possible [6]. The authors [7] tell us about investigation of the gas sensors. Their work based on the adsorption of the gas-phase molecules. During the sorption process the molecule gives of accept the electron, so it leads to the changing of the CNTs electrical properties. In the paper [8] authors report about sensibility of CNTs to the ammonia and nitrogen dioxide. The modification of CNTs using functional groups leads to electronic properties changing and higher sorting.

The carbon nanotubes with boundary carboxyl group (-COOH) modification have been experimentally obtained [9]. The multi-walled nanotube used in the experiment. The nanotubulene was fixed on the gold pyramid of the silica cantilever device of the microscope. The top of the nanotube has been made shorter on the oxygen atmosphere using the voltage between the nanotube and the mica surface with niobium layer on it. The carboxyl group (–COOH) is obtained on the open edge of the nanotube. The carboxylated carbon nanoubes are sensible to the vapors of the ethanol, NO, CO and NO_2 [10-12]. Fu et al. [12] represented the results of the experiment that showed the carboxylated carbon nanotubes sensibility to the CO gas. There is no reaction between pure carbon nanotube and that gas.

However, there are a lot of experimental researches of the nanotube's sensory properties but there are a few papers that describe the theoretical investigation of the modified with active groups carbon nanotubes.

We assume that the modified carbon nanotubes may be used not only as gas sensors. It is possible to use boundary modified nanotubes for identification of another chemical elements (for example - metals). It is possible to determine not only the metal atoms themselves, but also and their ions, included in the different hells and alcalies.

We investigated the bonding possibility between functional groups –COOH and NO_2 to the carbon nanotubulene. Also we made a research of this modified system activity to the atoms and ions of alkaline metals [13].

In this paper we represent the results of the theoretical investigation of interaction processes between boundary modified system "CNT-amino group" and atoms and ions of alkaline metals (lithium, sodium, potassium). The surface containing atoms and ions of metal scanning processes have been modeled. The sensory activity of the probe system has been obtained. The calculations carried out using molecular cluster (MC) model with the MNDO method.

We assume that this research will be actual one because of its subject, which will make the number of the activity group using for boundary modification bigger.

2. INVESTIGATION OF THE MECHANISM OF CARBON NANOTUBE BOUNDARE FUNCTIONALIZATION WITH AMINO GROUP

We made a research of the carboxyl group binding mechanism to the open border of the nanotube. Since the nanotube chirality does not affect sensor activity, the choice of the nanotube type is not treated as an important factor. In our case the choice was determined by the simplicity of the nanotube (6, 6) structure. We performed calculations of single-walled carbon nanotube (6, 6) within the framework of the molecular cluster using semi-empirical scheme MNDO [14]. One border of the cluster was completed with pseudo atoms of hydrogen and the carboxyl group (-NH_2) bound to a carbon atom on the other end of the cluster border.

The geometry of the system was optimized while calculations were being performed. The calculations allowed us to define peculiarities of the amino group spatial orientation in relation to the nanotube border, find out its geometrical parameters and calculated charge distribution in the system. The system was found to have the following characteristics: the amino group bound to the nanotube at an angle of 114°, C-N bond lengths were 1,35 Å and the N-H bond length was found to be 1 Å; the charges on the functional group atoms were: on the nitrogen atom $q_N = –0,22$; on hydrogen atoms $q(1) = + 0,2$; $q(2) = + 0,21$.

The process of amino group (–NH_2) binding to the selected C atom on the nanotube border was modeled by incremental method (in increments of 0,1 Å) along the direction perpendicular to the nanotube border and towards a N atom. As a result, the energy curve for the process of interaction in the system "nanotube –NH_2" was built, which is shown in Fig. 1. The normalized curve clearly shows energy minimum that corresponds to the chemical bond formation between the nanotube and the functional group.

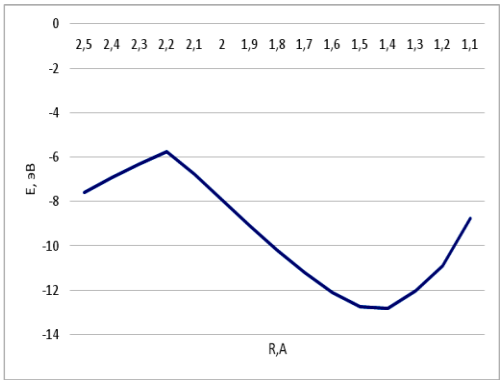

Fig. 1 – The energy curve of the amino group binding to a C atom on the nanotube border

Thus, the performed calculations proved that creation of highly sensitive and chemically active probes based on single-walled carbon nanotubes modified with the functional amino group is possible.

2.1 Investigation of the Interaction Mechanism between Single-walled Carbon Nanotubes Modified with the Functional Nitro Group and Atoms of Alkali Metals

We investigated the mechanism of sensor activity in relation to some alkali atoms (potassium, sodium, lithium and their ions) and the boundary hydrogen atom of the amine group - NH2. The process has been modeled by moving of the sample atoms to the H atom of the functional group (Fig. 2). The energy curves of the systems "nanotube + NH_2 - metal (or ion)" are presented in Fig. 3, where each curves show a minimum corresponding to the creation of bonds. Analysis of the binding energies showe that all processes are characterized by barrier-free nature. Table 1 shows the basic characteristics of investigated processes.

The obtained values allowed us to make the following conclusion: because of long interaction distances corresponding to the minimum on the energy curves, the nature of the bond is a weak Van-der-Waals bond between the atoms of the sensor and metal atoms.

This is a significant result confirming that the modeled sensor can undergo multiple uses without being destroyed. Had chemical bond formation between the sample metal atoms and the amino group occurred, it would have resulted in the sensor destruction.

Thus, the obtained results proved possibility of interaction between the boundary hydrogen atoms of the functional amino group and atoms metals.

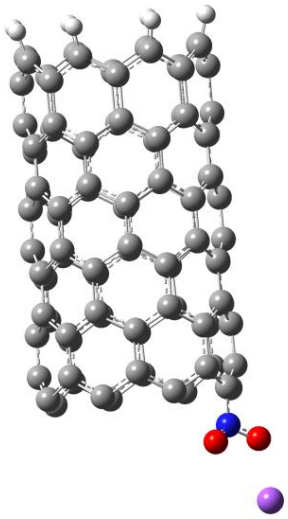

Fig. 2 – Carbon nanotubes with modified amino group

Table 1 – The main characteristics of Na, K, Li, binding process to the boundary H atom of amino-modified carbon nanotube (6, 6), where R_{int} – interaction distance between a metal atom and atom of amino group, E_{int} – interaction

Atomic bonds	R_{int}, Å	E_{int}, eV (MNDO)	The charge on the metal atom
Li-H	1.8	– 1.17	+ 0,6
Na-H	1.6	– 1.9	+ 0,6
K-H	1.6	– 3.6	+ 0,6
Li^+-H	1.5	– 2.15	+ 0.6
Na^+-H	1.2	– 2.78	+ 0.6
K^+-H	2	– 5.54	+ 0.6

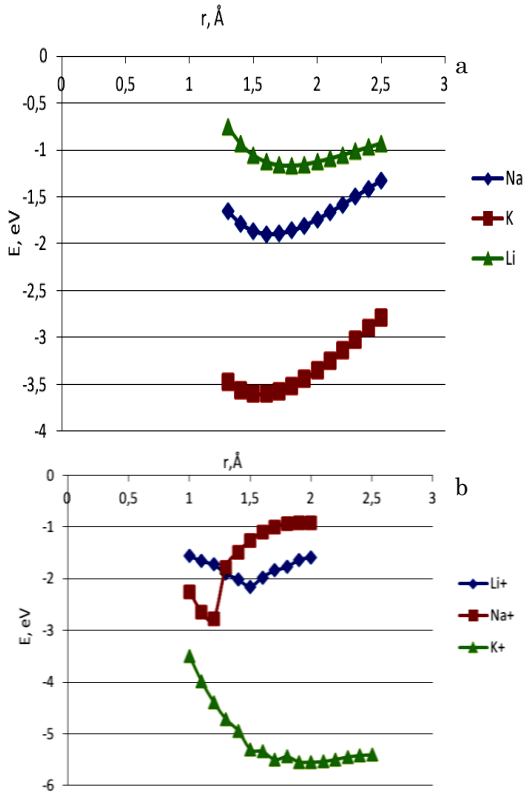

Fig. 3 – The energy curves of interaction between the nanotube modified by amino group (–NH_2) and a) atoms of metal Li, Na, K; b) ions of metal Li^+, Na^+, K^+

3. STUDY OF SENSOR PROPERTIES OF THE NANOTUBE MODIFIED BY AMINO GROUP

We made a research of sensor properties of a carbon nanotube modified by amino group to metal atoms and ions. We investigated the mechanism of scanning the surface with an atom to be initialized, and defined the functional group activity to the atoms of Li, Na, K. The process has been modeled by approach of the metal atom to the functional group. The atom followed the way parallel to the modified border of the nanotube.

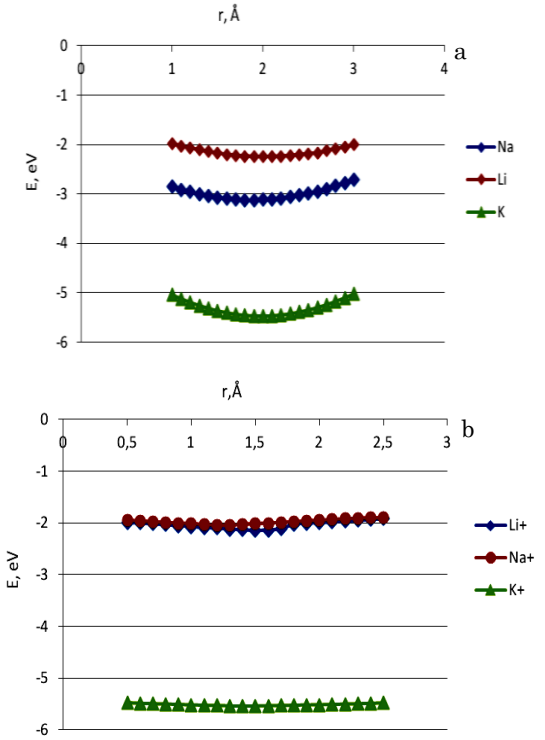

Fig. 4 – The energy curve of interaction between atoms of a metal and boundary atoms hydrogen of the functional amino group obtained by modeling the scanning process a) for metal atoms Na, K, Li; b) for ions Na^+, K^+, Li^+

Table 2 – The main characteristics of the interaction process between the amino-modified nanotube (6, 6) and atoms and ions obtained from scanning the surface, where $R_{s\text{-int}}$ – sensor interaction distance, $E_{s\text{-int}}$ – sensor interaction energy

Atom	$R_{s\text{-int}}$, Å	$E_{s\text{-int}}$, eV
Na	1.9	– 3.12
K	2.	– 5.47
Li	2	– 2.25
Na^+	1.2	– 2.05
$5K^+$	1.4	– 5.55
Li^+	1.5	– 2.15

The interaction energy curves (Fig. 4) showed that the nanotube with the functional group is chemically sensitive to atoms of metals: obtained curves have characteristic minimum on each one that indicates the formation of chemical or physical bond between an atom of metal and the amino group. The sensor interaction distances and sensor interaction energies are shown in Table 2.

The results obtained from the calculations demonstrate that modified carbon nanotubes can be used as sensors for specific elements that can be experimentally detected by the change in the potential of the sensor system based on the nanotube with the functional amino group.

4. CONCLUSIONS

Theoretical and experimental research prove the unique properties of the carbon nanotubes. These properties are depended form the nanotubes modification. Carbon nanotubes modified with amino group ($–NH_2$) have the same sensory properties as carbon nanotubulenes modified with carboxyl group (-COOH) and nitro group ($–NO_2$). Therefore the creation possibility of high efficient sensor on the basis of the carbon nanotube modified with functional group selective to metals is proved. The possibility of many times sensor using without its damage is also proved.

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