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**Short Communication**

# Comparative Analysis of Sensor Activity of Carbon Nanotubes Modified with Functional Groups

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This article presents theoretical study of sensor activity of nanosystems based on a carbon nanotube modified with functional group (carboxyl, aminogen, nitrogroup) on some metal atoms and ions. Calculations were performed within the frameworks of molecular cluster model with application of semiempirical MNDO method and density functional theory DFT. The mechanism of binding functional groups to the open border of single-walled zig-zag carbon nanotubes for the purpose of formation of a chemically-active sensor based on them has been investigated. Main geometric and electron energy characteristics of built systems have been defined. Interaction of the sensors built in this fashion with atoms and ions of some metals: potassium, sodium, lithium has been investigated.

**Keywords:** Carbon nanotube, Sensory activity, Functional nitro group, Functional amino group, Functional carboxyl group, Boundary modification.

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## 1. INTRODUCTION

Variety of new mechanical, electric and magnetic properties of nanotubes may contribute to breakthrough in electronic technology and nanoelectronics. CNT possess extraordinary electronic properties [1, 2]. Carbon nanotubes have high sorption activity [3]. This feature makes it possible to apply them as chemical and biological sensors taking into account their conductivity state [4]. Some research papers discuss gas sensors based on clean CNT, as well as CNT modified with functional groups [5-9]. Modification of CNT with functional groups changes electronic properties of nanotubes, and increases selectivity and response to particular gases and molecules.

The devices that utilize boundary modifiied carbon nanotubes, for example atomic force microscope that has a nanotube with an individually selected functional group on its tip, may serve as sensors. The majority of research papers is focused on use of carboxyl - COOH group. In the course of experiment carbon nanotubes with one of the borders modified with carboxyl group attached have been obtained.

Apart from carboxyl group, CNT can be modified by means of organic chemistry methods with other functional groups, for instance, with frequently used and known aminogen group $NH_2$ which reactivity is subject to presence of a lone-electron pair, or nitrogroup $NO_2$, one of the strongest electron withdrawing group. Tran et al. [10] studied the effect of -$NH_2$ functionalized single-walled carbon nanotubes on $NO_2$ gas. Aminogen group acts as a charge carrier of semiconducting CNT, and, therefore, the number of electrons transferred from a nanotube to $NO_2$ molecule increases.

The authors have studied the attachment mechanism of a functional group - COOH [11] and $NH_2$ [12] to a carbon tube, and investigated activity of these modified systems with regard to atoms and ions of alkali metals. Not least important and interesting is a study of implementation of boundary functionalization of a carbon nanotube with nitrogroup, and comparative analysis of a probe activity on the basis of obtained nanosystems.

This article presents comparison results of theoretical research of attachment mechanism of functional groups to an open border of a semiconducting single-walled carbon nanotube in order to confirm possibility of formation of a chemically-active probe. Processes of interaction between built boundary modified systems with atoms and ions of some metals are also studied . Besides, the authors analyse scan processes of random surfaces that contain atoms and ions of metals carried out by the probe obtained, and determine the most active group to be used as a sensor probe system with regard to chosen particles. Calculations are performed within the frameworks of molecular cluster modules with well-known calculation methods: semiempirical method MNDO for the quantum chemical calculation [13] and DFT [14-16] method that is one of the widely used and universal methods.

## 2. COMPARATIVE ANALYSIS OF INTERACTION OF ALKALI MATALS WITH BOUNDARY ATOMS OF OXYGEN AND HYDROGEN OF FUNCTIONAL GROUPS

The authors have studied the mechanisms of attachment of functional groups (carboxyl, aminogen and nitrogroup) to a single-walled carbon achiral nanotube of semiconducting type. Semi-infinite molecular cluster module and calculations methods MNDO and DFT were used. In order to define infinity of one edge, dangling bonds on the borderline were saturated with pseudo atoms of hydrogen, while groups -COOH, -$NN_2$, -$NO_2$ (Fig. 1) were attached to the other edge.

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When CNT is modified with nitrogroup there occurs transfer of electron density from the functional group

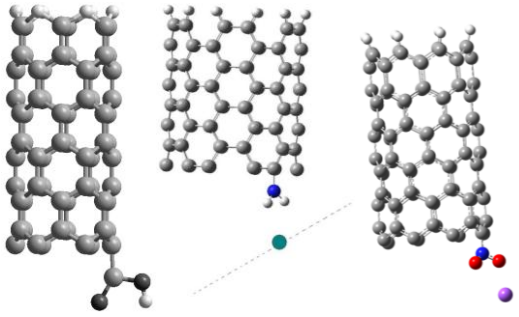


**Fig. 1** – Molecular cluster of a semi-infinite CNT with border-modifying functional groups: a) – COOH; b) – $NH_2$; c) – $NO_2$

that changes the number of charge carriers in a nanotube and makes provisions for conductivity in the system which resembles earlier results [12, 13].

Interaction mechanism of atoms and ions of sodium, potassium and lithium with functionalized groups and single-walled nanotubes has been implemented by means of building the model of step-by-step approximation of atoms or ions of metals to atoms of hydrogen and oxygen that belong to functional groups located on the boundary of CNT.

Table 1 shows some characteristics of process of attachment of atoms (ions) Na, K, Li to boundary atoms of modifying group.

**Table 1** – Characteristics of process of attachment of atoms of sodium, potassium, lithium to boundary atoms of functionalizing group: $r_{вз}$ – distance of interaction between atom O or H of a functional group and atom of metal, $E_{вз}$ - relevant interaction energy

| Interatomic bond (group - COOH) | $r_{вз}$, Å | $E_{вз}$, eV (MNDO) | $E_{вз}$, eV (DFT) | Metals atomic charge |
|---|---|---|---|---|
| Na – O | 2,2 | – 4.23 | – 3.21 | + 0.7 |
| Na – H | 1.8 | – 3.03 | – 1.77 | + 0.7 |
| K – O | 2.5 | – 4.00 | – 4.30 | + 0.4 |
| K – H | 1.8 | – 2.41 | – 1.04 | + 0.4 |
| Li – O | 2.0 | – 5.45 | – 4.39 | + 0.9 |
| Li – H | 1.9 | – 5.90 | – 4.62 | + 0.9 |
| Interatomic bond (group – $NH_2$) | $r_{вз}$ , Å | $E_{вз}$, эВ (MNDO) | $E_{вз}$, эВ (DFT) | Metals atomic charge |
| Na – H | 1.6 | – 1.90 | – 2.43 | + 0.7 |
| K – H | 1.6 | – 3.60 | – 3.22 | + 0.4 |
| Li – H | 1.8 | – 1.17 | – 1.0 | + 0.7 |
| Interatomic bond (group – $NO_2$) | $r_{вз}$, Å | $E_{вз}$, eV (MNDO) | $E_{вз}$, эВ (DFT) | Metals atomic charge |
| Na – O | 2.3 | – 3.07 | – 3,24 | + 0.7 |
| K – O | 2.8 | – 3.26 | – 4.02 | + 0.7 |
| Li – O | 2.1 | – 1.97 | – 2.12 | + 0.7 |

Comparison analysis of the results has shown that a carbon nanotube modified with carboxyl group interacts with atoms of metals most actively, besides the interaction with oxygen atoms is the most favourable. Also, all the systems obtained between atoms of a functional group and chosen atoms (ions) of metals have weak van der Waals interaction that is defined by quite long distances corresponding to minimum on energy curve. Therefore, it proves resistance of such probe in the course of its multiple application, as damage that might have been caused to a probe due to formation of chemical bonding with chosen atoms of alkali metals will not happen. In addition thereto, electron density is transferred from atoms (ions) of metals to atoms of a boundary modified probe system which increases the number of carriers in it and governs change of its electric properties.

## 3. COMPARATIVE ANALYSIS OF SENSOR ACTIVITY OF MODIFIED NANOTUBULAR SYSTEMS

Further the authors investigated sensor activity of CNT modified with active groups by means of scanning random surface that contains atoms or ions of earlier chosen alkali metals Na, Li, K. Atom (or ion) step-by-step approached a boundary modified nanotubular system along a straight parallel border of a nanotube located over earlier interaction distance. The calculation results were used to plot energy curves of interaction, a few of which are depicted in Fig. 2. Table 2 shows the bonds resulted from energy calculations.

Comparative analysis of the results has shown that the carbon nanotubes boundary modified with a functional group become chemically-sensitive to chosen metals. This is evidenced by minimums on energy curves that reflect interaction of atom (or ion) with a nanotube modified with chosen functional group.

**Table 2** – Some characteristics of interaction between boundary modified carboxyl, aminogen and nitrogroups of a nanotubular system with Na, $Na^+$, K, $K^+$, Li, $Li^+$: $r_{int}$ - sensor interaction distance, $E_{int}$ - sensor interaction energy

| Atom/ion (group - COOH) | $r_{nt}$, Å | $E_{int}$, eV |
|---|---|---|
| Na | 3.0 | – 0.64 |
| K | 2.5 | – 1.77 |
| Li | 3.0 | – 0.93 |
| $Na^+$ | 2.6 | – 1.73 |
| $K^+$ | 2.8 | – 1.76 |
| $Li^+$ | 3.0 | – 1.63 |
| Atom/ion (group – $NH_2$) | $r_{nt}$, Å | $E_{int}$, eV |
| Na | 1.9 | – 3,12 |
| K | 2.0 | – 5.47 |
| Li | 2.0 | – 2.25 |
| $Na^+$ | 1.2 | – 2.05 |
| $K^+$ | 1.4 | – 5.54 |
| $Li^+$ | 1.5 | – 2.15 |
| Atom/ion (group – $NO_2$) | $r_{nt}$, Å | $E_{int}$, eV |
| Na | 1.2 | – 2.87 |
| K | 2.2 | – 2.09 |
| Li | 1.7 | – 2.56 |
| Na+ | 1.1 | – 0.10 |
| K+ | 1.4 | – 0.96 |
| Li+ | 1.5 | – 0.10 |

## 4. CONCLUSIONS

Theoretical research the authors undertaken have proved possibility of creation of a high-sensitivity sensor

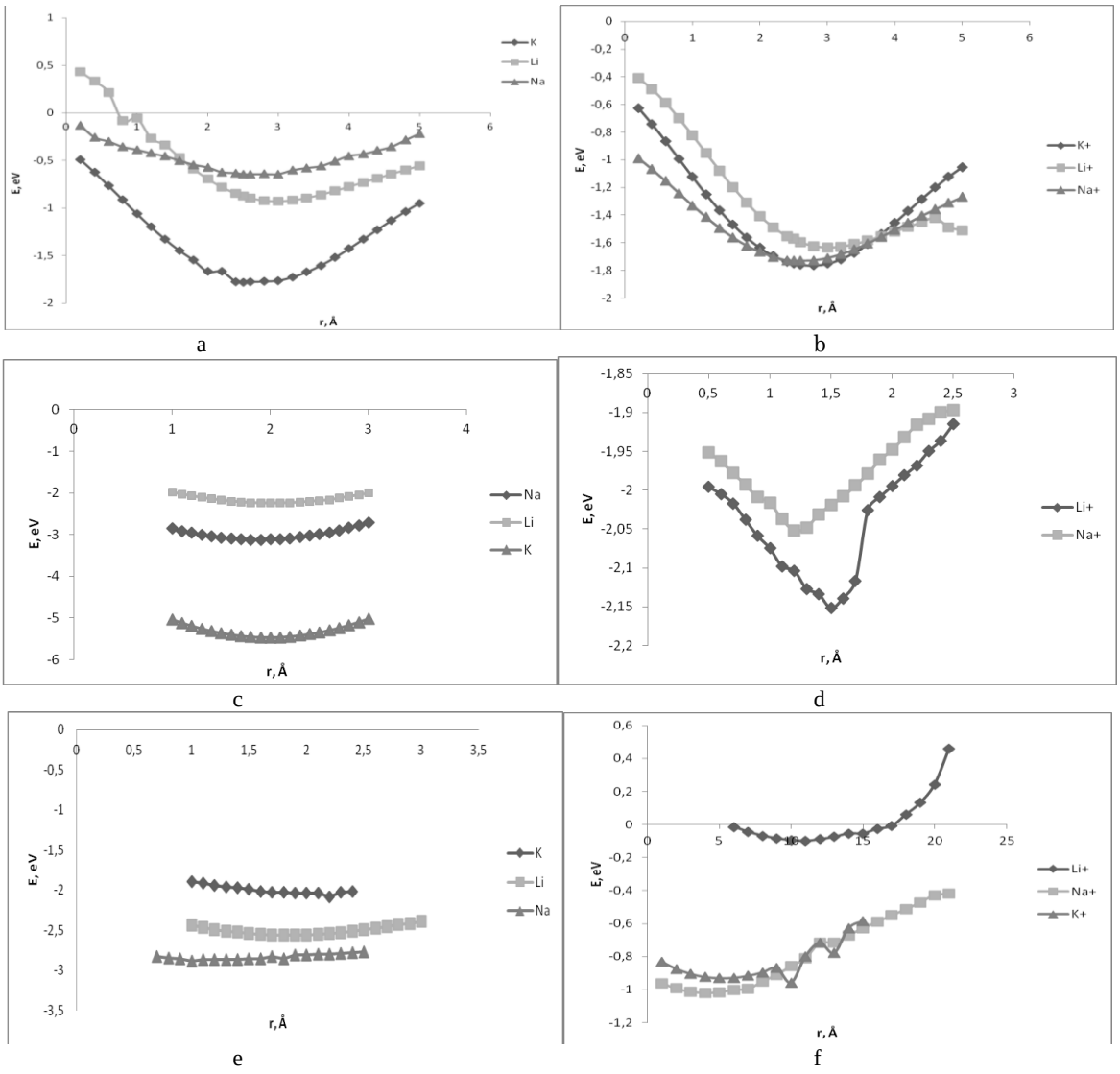


**Fig. 2** – Energy curves of interaction between atoms (or ions) of metal and a boundary modified nanotubular structure; 0 point corresponds to the point located under atom H of carboxyl group, as well as one of atoms H of aminogen group and atom O of nitrogroup: a), b) group - COOH; c), d) for group – $NH_2$ ; e) f) for group – $NO_2$

based on the most advanced up-to-date nanomaterial – the carbon nanotube boundary modified with chemically active functional groups; and comparative analysis has stated that the most sensitive sensor with regard to metal atoms is CNT modified with aminogen group. The sensors created in such manner will possess significant selectivity and respond to presence of ultra-low amount of substances, including metals found in salts and alkali, and offer great opportunities of their further use in chemistry, biology, medical science, and etc.

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