NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (1), P. 101–106

SENSOR PROPERTIES OF CARBOXYL-MODIFIED CARBON NANOTUBES

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PACS 00.30.91

This paper studies the sensor activity of carboxyl-modified single-walled carbon nanotubes (zig-zag, arm-chair type) to atoms and ions of alkali metals Na, Li, K. The mechanism of the carboxyl binding to the open border of the semi-infinite carbon nanotube is investigated. Calculations of the interaction processes between the sensor and sample alkali atoms and alkaline ions are performed. The process of scanning a sample surface site with atoms of metals under consideration is modeled and the functional carboxyl group chemical activity is defined. The research is performed by the MNDO method within the framework of the molecular cluster model and DFT method.

Keywords: sensor properties, carbon nanotube, sensory activity, functional carboxyl group, alkali metals, chemical active sensor, semi-empirical scheme MNDO, DFT method.

1. Introduction

In recent years carbon nanotubes have been regarded as a material of wide potential application, a commercial product and a subject of marketing research [1-7]. Their unique quasi-1D structure and extended curved π-bonding configuration define the nanotubes' remarkable structural, electronic and mechanical properties. Besides the above described characteristics, nanotubes possess high sorption activity [8], and owing to this valuable feature they can act as an effective adsorbent of various particles and, consequently, have a great potential for the development of chemical and biological sensors based on their sensitivity to their chemical environment [9,10]. It has been reported that devices with boundary modified carbon nanotubes can be successfully used as sensors. For example, an atomic force microscope with a specially selected functional group located at the end of the cantilever tip [11] can function as a sensor and is suitable to investigate the chemical composition of a sample surface. S.S. Wong, E. Josevlevich et. al. [11] report that carboxyl-modified carbon nanotubes have been fabricated experimentally. Theoretical simulations [12-14] demonstrate that carboxyl-modified carbon nanotubes are sensitive to ethanol, and the gases NO, and NO_2.

We assume that the potential of modified nanotubes' application as sensors is not limited to gases and can be suitable to detect other elements, for example, metals. Before [15] we investigated the mechanism of the carboxyl group binding to the open border of the semi-infinite carbon nanotube. In the present paper we performed calculations to study its sensitivity to atoms and ions of some alkali metals. Finally, we simulated the scanning process of a sample surface site and studied the functional group sensor activity to atoms of alkali metals.

2. The interaction mechanism between single-walled carboxyl-modified carbon nanotubes and atoms of alkali metals

We investigated the mechanism of interaction between some alkali atoms (potassium, sodium, lithium) and the boundary oxygen and hydrogen atoms of the carboxyl group – COOH on the border of carbon nanotube of (6, 0)-type (Fig. 1a) or (6, 6)-type. The process was simulated by an incremental approach when sample atoms moved to the O or H atoms of the functional group (Fig. 1b). The energy curves of the "nanotube + COOH - metal atom" system are presented in Fig. 2, 3, where each curve shows a minimum corresponding to the formation of bonds at certain distances. Analysis of the binding energies revealed that all the curves are characterized by barrier-free nature. Table 1 shows the main characteristics of Li, Na, K binding process to the boundary atoms (oxygen and hydrogen) of the carboxyl group that modifies the open border of the (6, 0) or (6, 6) carbon nanotubes. The obtained results allowed us to draw the following conclusion: since the interaction distances corresponding to the minimum on the interaction energy curves are long, there exists a weak van der Waals interaction between the atoms of the functional group and metal atoms. This is a very important result confirming that the designed sensor can undergo multiple uses without being destroyed.

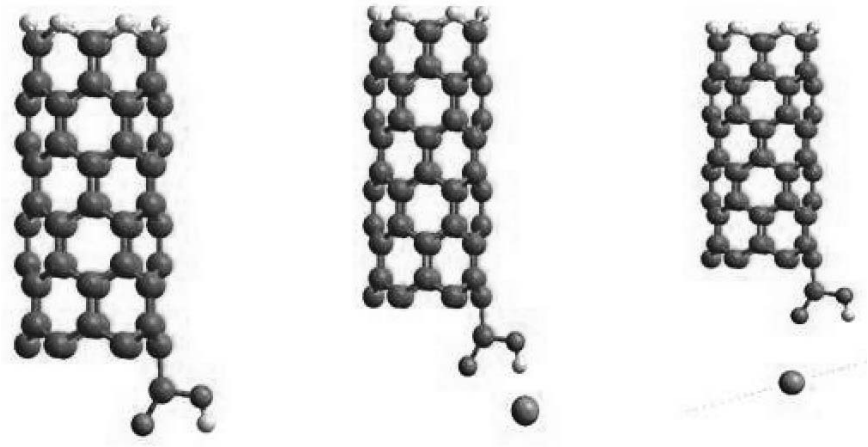
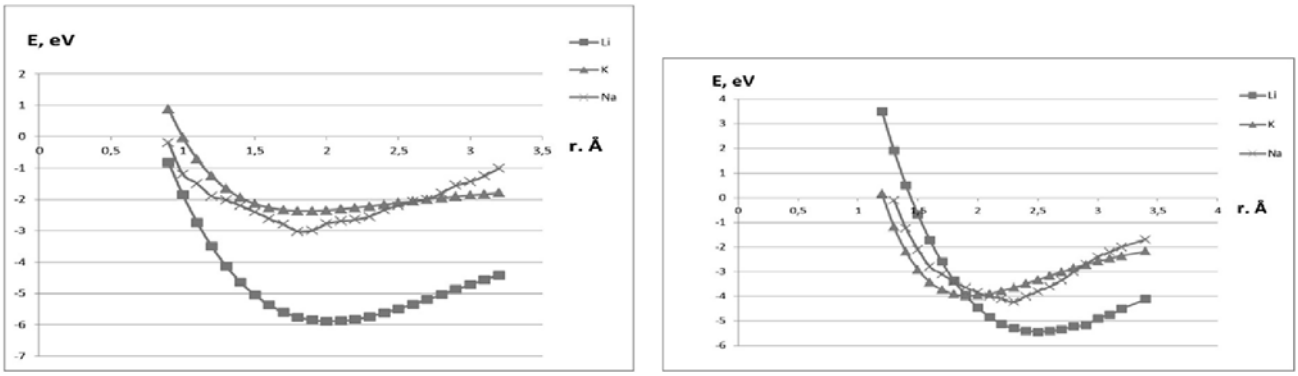


Fig. 1. The model of a sensor based on the modified (6,0) carbon nanotube: (a) the model of semi-infinite carbon nanotube (6,0) with the functional carboxyl group (-COOH) on the open border; (b) the model of incremental approach of a Na atom to the H atom of carboxyl group; (c) modeling of the scanning process of a random surface site with a Na atom, the dots indicate Na atom migration with respect to the modified nanotube

Thus, the obtained results proved the possibility of interaction between the boundary atoms of the carboxyl group and atoms of sample alkali metals.

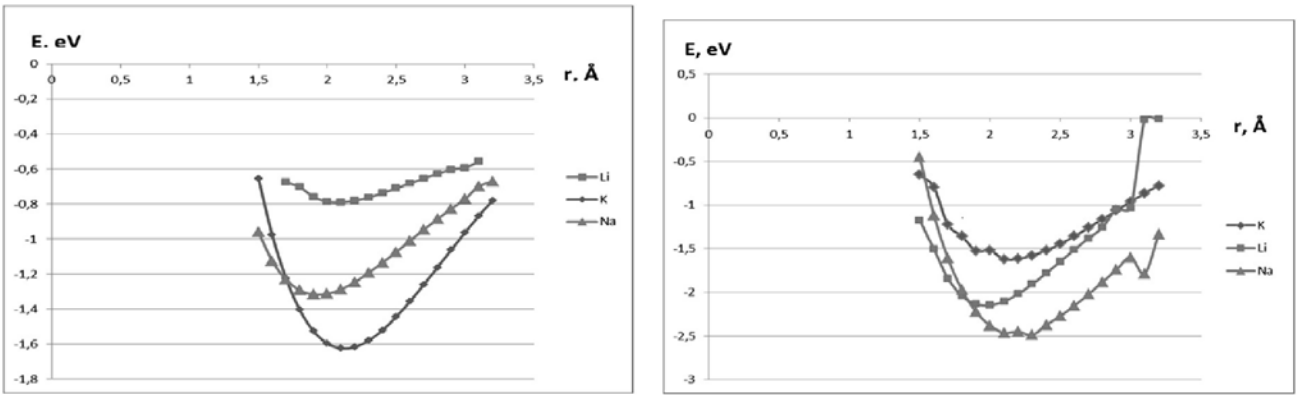
3. Sensor properties of the carboxyl-modified carbon nanotube

We investigated the sensor properties of (6, 0) and (6, 6) carbon nanotubes modified by carboxyl group to sodium, potassium, lithium atoms and their ions Na^+, K^+, Li^+. We studied the process of scanning the surface with an atom (or ions) to be initialized, and defined the functional group activity to the sample element. The process was simulated by incremental approach of a metal atom (or ion) to the functional group. The atom followed



(a) (b)

FIG. 2. The energy curves of interaction between the nanotube (6,0) modified by carboxyl group (-COOH) and atoms of alkali metals: (a) between atoms of metals and the hydrogen atom in the group; (b) between atoms of metals and the oxygen atom in the group



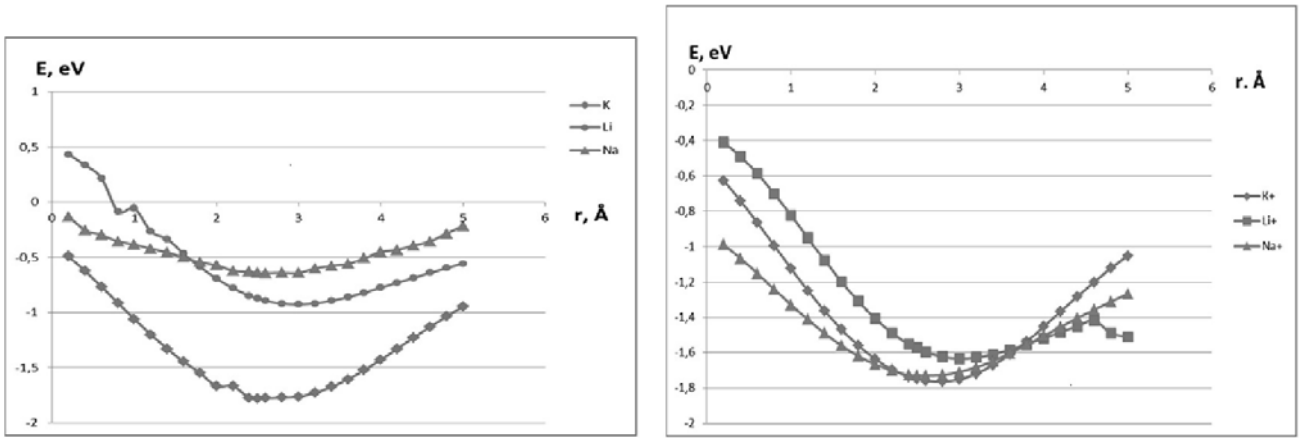
(a) (b)

FIG. 3. The energy curves of interaction between the nanotube (6,6) modified by carboxyl group (-COOH) and atoms of alkali metals: (a) between atoms of metals and the hydrogen atom in the group; (b) between atoms of metals and the oxygen atom in the group

the path parallel to the modified border of the nanotube (Fig. 1c). The interaction energy curves (Fig. 4, 5) showed that the nanotube with the functional group is chemically sensitive to atoms and ions of sample metals: each curve has a characteristic minimum that indicates the formation of interaction between an atom (or an ion) of metal and the carboxyl group (co-called sensor interaction). It has to be pointed out that the minimum on each curve is located nearly beyond the boundary oxygen atom of the carboxyl group (-COOH). 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 and radicals that can be experimentally detected by the change in the potential of the sensor system based on the nanotube with the functional group.

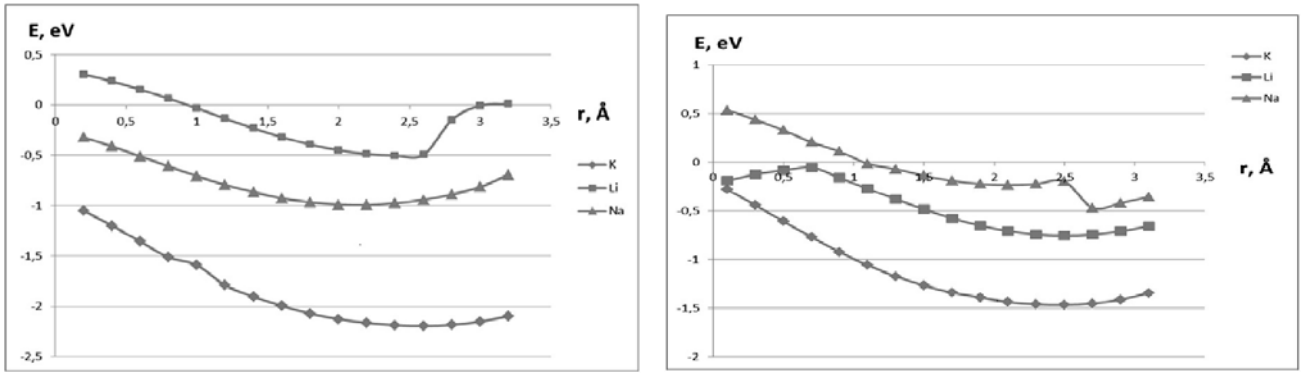
TABLE 1. The main characteristics of Na, Na^+, K, K^+, Li, Li^+ binding process to the boundary O and H atoms of carboxyl-modified carbon nanotube (6, 0) and (6, 6), where r_{int} — interaction distance between a metal atom and the O (or H) atoms of carboxyl group, E_{int} — interaction energy (MNDO and DFT methods)

Atomic bonds	r_{int}, Å	E_{int}, eV (MNDO)	E_{int}, eV (DFT)
Carbon nanotube (6, 0)-type			
K – O	1,9	-3,98	-4,30
K – H	2,1	-2,70	-1,04
Li – O	2,5	-5,44	-4,39
Li – H	2,0	-5,89	-4,62
Na – O	2,2	-4,23	-3,21
Na – H	1,8	-3,03	-1,77
Carbon nanotube (6, 6)-type			
K – O	2,1	-1,62	-1,83
K – H	2,1	-1,62	-1,45
Li – O	1,9	-2,14	-2,53
Li – H	2,1	-0,79	-1,96
Na – O	2,3	-2,48	-1,68
Na – H	1,9	-1,32	-1,33



(a) (b)

FIG. 4. The energy curves of interaction between atoms (ions) of metal and boundary atoms of the functional carboxyl group of (6,0) carbon nanotube obtained by modeling the scanning process, a distance of 0 AA corresponds to a point beyond the hydrogen atom: (a) for metal atoms K, Li, Na, (b) for metal ions K^+, Li^+, Na^+



(a) (b)

FIG. 5. The energy curves of interaction between atoms (ions) of metal and boundary atoms of the functional carboxyl group of (6,6) carbon nanotube obtained by modeling the scanning process, a distance of 0 AA corresponds to a point beyond the hydrogen atom: (a) for metal atoms K, Li, Na, (b) for metal ions K^+, Li^+, Na^+

TABLE 2. The main characteristics of the interaction process between the carboxyl-modified nanotube (6, 0) and (6, 6) and Na, Na^+, K, K^+, Li, Li^+ obtained from scanning the surface, where r_{s-int} - sensor interaction distance, E_{s-int}- sensor interaction energy, MNDO method

Atom/ion	r_{s-int}, Å	E_{s-int}, eV
Carbon nanotube (6, 0)-type		
K	2,5	-1,77
K^+	2,8	-1,76
Li	3,0	-0,93
Li^+	3,0	-1,63
Na	3,0	-0,64
Na^+	2,6	-1,73
Carbon nanotube (6, 6)-type		
K	2,5	-2,20
K^+	2,5	-1,47
Li	2,5	-0,50
Li^+	2,5	-0,76
Na	2,2	-0,99
Na^+	2,2	-0,23

4. Conclusion

This paper studies sensor properties of carboxyl-modified single-walled "zig-zag" and "arm-chair" carbon nanotubes to atoms and ions of alkali metals Na, Li, K. Calculations of the interaction processes between the sensor and sample alkali atoms and alkaline ions are performed. The research is performed by the MNDO method within the framework of the molecular cluster model and DFT method. The interaction energy curves showed that the nanotube with the carboxylate functional group is chemically sensitive to atoms and ions of sample metals: each curve has a characteristic minimum that indicates the formation of

interaction between an atom (or an ion) of metal and the carboxyl group (co-called sensor interaction). The performed theoretical studies prove the possibility of developing a sensor that responds to the presence of ultra-low quantities of materials and has a big potential for its application in chemistry, biology, medicine, etc.

Acknowledgements

The research has been supported by grant from the Ministry of Education and Science of the Russian Federation, project 14.B37.21.0080.

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