Research into boron-carbon nanotube modified by alkaline metal atoms

S V Boroznin*, E V Boroznina, I V Zaporotskova, O A Davletova, N P Polikarpova

Volgograd State University, Volgograd 400062, str. Bogdanova, 32

**Corresponding auhtor's e-mail: sboroznin@mail.ru*

Received 10 October 2014, www.cmnt.lv

Abstract

All articles *must* contain an abstract. The abstract follows the addresses and should give readers concise information about the content of the article and indicate the main results obtained and conclusions drawn. As the abstract is not part of the text it should be complete in itself; no table numbers, figure numbers, references or displayed mathematical expressions should be included. It should be suitable for direct inclusion in abstracting services and should not normally exceed 200 words. The abstract should generally be restricted to a single paragraph. These pages provide you with instructions on how to use this word template to prepare your paper according to the required layout and style for CM&NT papers.

Keywords: boron-carbon nanotubes, ionic-built covalent-cyclic cluster model, quantum chemical calculations, adsorption, metal superlattice.

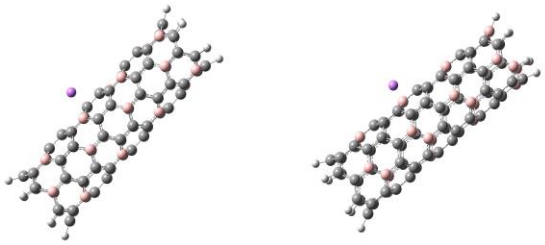
1 Introduction

The discovery of carbon NTs in the early nineties was followed by intensive investigation into their electronic structure and energy spectrum parameters as well as physical and chemical properties. Along with studying of nanotube properties researchers started searching for ways to modify NTs and fabricate structures having new mechanical, electronic and other properties. Due to high surface activity, nanotubes can be used as basis for fabricating various types of composites. In particular, it was found that introduction of metal atoms between the tubulene layers leads to the formation of nanotube based composite structures such as hollow alternating metallic supercells, nanotube conductors in semiconducting coating, etc., that possess new conducting, magnetic and electrical properties [1].

However, apart from carbon nanotubes, current research focuses on theoretical and experimental investigation of non-carbon nanotubes, namely recently discovered boron-carbon nanotubes of BC3 type. Research conducted into the electron structure and energy characteristics of this class of non-carbon structures showed that boron-carbon nanotubes (BCNTs) as well as carbon nanotubes of "zigzag" type represent a class of narrow gap semiconductors [2-6] whereas the study of BCNTs surface activity revealed that they display better adsorption properties in respect to certain elements that CNTs [7-12]. That is why one of the most interesting aspects of BCNTs study is research into the interaction mechanism of alkaline metal atoms with the BCNT external surface.

The present paper presents calculations of alkaline metal atoms (AM) (Li, Na, K) adsorption on the boron-carbon BC3 nanotubes (6, 0) type external surface with the view of exploring a possibility to fabricate boron-carbon nanotube based metal-phase composites.

As geometrical models of the studied tubulenes we selected clusters containing six hexagon boron-carbon cycles located on the tube perimeter and four elementary layers located along the tube axis. Since a nanotube is an infinite structure hydrogen pseudo atoms were used to complete loose chemical bonds on the nanotube edge. A model of a covalent cyclic cluster built in via ionic bonding in the framework of the semi-empirical quantum chemical MNDO calculation procedure was applied [1]. Two possible positions of carbon and boron atoms in respect to a lithium atom on the tube external surface in BC_3-tubulenes clusters are shown in Figure 1.



a) b)

FIGURE 1 BC3 nanotube (6,0) with an absorbed lithium atom on the nanotube surface: a) type A of C and B atoms positions; b) type B of C and B atoms position

In order to eliminate the influence of boundary effects, we modelled the process so that adsorbed atoms (Li, K, Na) bound either to a carbon or boron atom located approximately in the middle of the boron-carbon nanotube cluster. The adsorption process for alkaline metal atoms was modeled in increments of 0,1 Å in the direction of the perpendicular to the tube axis passing through the boron or carbon atom on which the adsorption takes place. The geometrical parameters of the system were optimized in quantum-chemical calculations. As a result of calculations we obtained the potential energy curves of these processes. Analysis shows that all the curves for the nanotubes reveal the presence of energy minimum that enabled us to conclude that atoms adsorbed on the BC_3 tubulene external surface formed stable

adsorption complexes (Figures 2–5). Adsorption energy values were calculated as the difference between the total energy value of non-interacting adsorbent model of a corresponding atom and a related adsorption complex, formula (1):

$$E_{ad} = E_{ad.c.} - (E_{tub} + E_{H,\,Cl,\,O,\,F}). \quad (1)$$

Adsorption energy values E_{ad} for Li, K, Na atoms and corresponding adsorption distances R_{ad} are shown in Table 1.

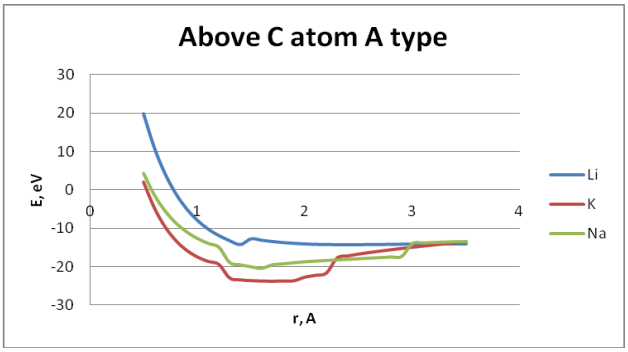


FIGURE 2 The energy curve of the alkaline metal atoms adsorption process on the boron-carbon nanotube A type (6, 0) external surface (C atom)

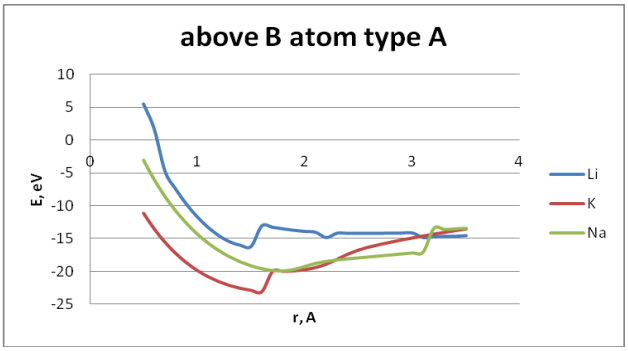


FIGURE 3 The potential energy curve of the alkaline metal atoms adsorption process on the boron-carbon nanotube A type (6, 0) external surface (B atom)

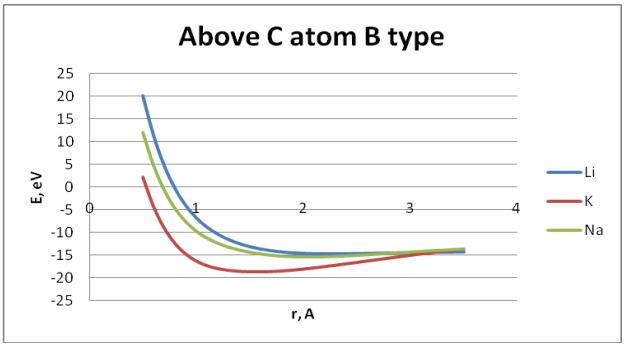


FIGURE 4 The potential energy curve of the alkaline metal atoms adsorption process on the boron-carbon nanotube B type (6, 0) external surface (C atom)

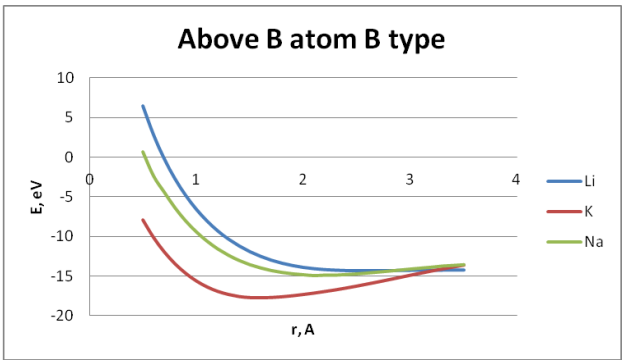


FIGURE 5 The potential energy curve of the alkaline metal atoms adsorption [process on the boron-carbon nanotube B type (6, 0) external surface (B atom)

TABLE 1 The adsorption energies E_{ad} for Li, K, Na atoms and corresponding adsorption distances R_{ad}. Letters C and B denote an approximation to boron and carbon atoms, respectively

	Li		**K**		**Na**	
	C	*B*	*C*	*B*	*C*	*B*
Type A						
E_{ad}, eV	14,21	15,97	23,73	23,13	20,33	19,94
R_{ad}, Å	1,4	1,4	1,7	1,6	1,6	1,8
Type B						
E_{ad}, eV	14,63	14,28	18,7	17,77	15,4	14,98
R_{ad}, Å	2,3	2,6	1,6	1,6	2,1	2,1

The charge distribution over the metal atoms indicates that electron transfer to boron and carbon atoms located on the nanotube external surface takes place, which increases the number of majority charge carriers in tubulenes; as a result BC_3 nanotubes, which we had previously classified as narrow-gap semiconductor, begin to take on metallic properties (the occurrence of surface conductivity is attributed to electrons from metal atoms).

2 Regular binding of alkaline metal atoms to the BC_3nanotubes (6,0) type B surface

On performing calculations of single alkaline metal atoms adsorption on the boron-carbon nanotube external surface that has shown that interaction between metal atoms and BC_3 tubulenes is possible, it seemed interesting to study the possibility of alkaline metal atoms regular binding (modification) to this type of tubulene to find out whether metal-phase boron-carbon based composites can be fabricated. We chose BC_3 nanotubes (6,0) type B that interact with alkaline metal atoms located over carbon or boron atoms on the BC_3 tubulene external surface as shown in Figure 6. In the selected positions the distance between metal atoms is taken to be 4.2 Å. It is known that lattice parameters for alkaline metals are 3.5 Å (for Li) and 4.2 Å (for Na) [13], that is, they are in good agreement with the values we obtained for interatomic distances Li-Li, Na-Na or K - K. Thus, alkaline metal atoms that bind to the external nanotube surface can be considered one-dimensional metallic cells (further called a superlattice on boron-carbon nanotube external surface), and the distances between the atoms can be called superlattice constants.

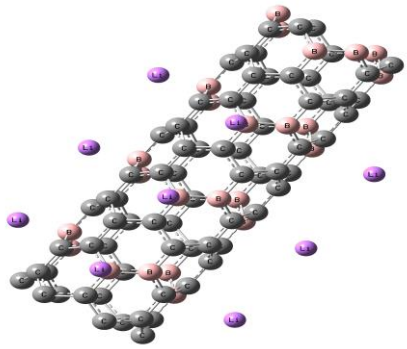


FIGURE 6 Extended elementary cell (6, 0) modified by Li atom

To study the electron energy structure of the described nanosystems a BC_3 - type (6,0) tubulene cluster consisting of ninety-six nanotube atoms and nine alkaline metal atoms located above the tubulene surface and forming superlattices either of rectangular or rhombic type was selected. Calculations were performed by applying the procedure described in the previous section. Bond length between the boron and carbon atoms were taken to be equal to 1.44 Å, and the distance between the metal atoms and tubulene surface atoms corresponded to the values obtained in the study of single Li, K, Na adsorption. Calculations allowed us to build one-electron spectra of the nanocomposites under study and then compare the values with the ones obtained for the energy spectrum of pure - BC_3 tubulene (Figure 7). The values of the bandgap ΔE_g are seen in Table 2. Figure 7 shows that the band gap structure in boron-carbon nanotubes modified by Li atoms when compared to pure BC_3 tubulenes does not change within a predetermined degree of accuracy. In BC_3 tubulenes modified by K atoms the band gap value approaches zero that reveals the presence of metallic conductivity. Nanotubes modified by Na atoms have a slight increase in the band gap, but, nevertheless, the structure can be classified as a narrow-gap semiconductor. Analysis of the charge reveals that likewise in the case of single atom adsorption electron density is transferred from alkaline metal atoms on the BC_3 tubulene surface atoms (Table 2).

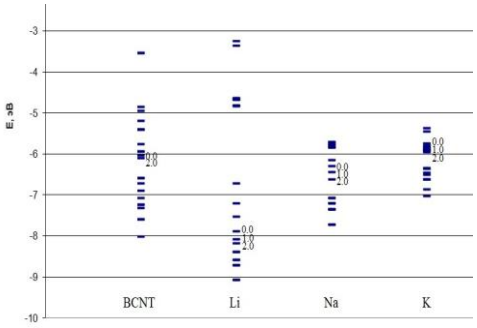


FIGURE 7 One-electron energy spectra of BC_3-tubulenes (6, 0)

TABLE 2 Energy characteristics of modified boron-carbon tubulenes type B (6, 0); Q - charges on alkaline metal atoms; ΔE_g – bandgap (eV)

	Q	**ΔE_g, эВ**
BCNT		0,14
BCNT +9Li	0,96	0,2
BCNT +9K	0,96	0,01
BCNT +9Na	0,92	0,15

3 Conclusions

Calculations reveal that surface modification of boron-carbon nanotubes with alkaline metal atoms (Li, K, Na) leads to metallization of the tube external surface. The optimum adsorption distance was found and adsorption energy values were calculated. It can be assumed that a regular adsorption process on the external nanotube surface will cause the "metal - metal" transition. It means that by introducing, for example, metal atoms between the layers of multi-walled tubulenes alternating hollow metal superlattices can be fabricated as well as other nanotube based composite structures having novel conductive, magnetic and electrical properties. Surface modification of boron-carbon nanotubes with metal atoms does not change their conductivity , but leads to the formation of free charge carriers on the tube surface, thereby ensuring the emergence of transition “narrow-gap semiconductor – metal” in the obtained metal-phase boron-carbon nanotube based composites.

References

[1] Zaporotskova IV 2009 Carbon and un-carbon nanomaterials and composite structures on their base: structure and electronic properties Volgograd: Volgograd State University Publishing 490 p
[2] Liu X M, Gutiérrez H R, Eklund P C 2010 Electrical properties and far infrared optical conductivity of boron-doped single-walled carbon nanotube films *J Phys: Cond Matter* **22** 334223
[3] Debnarayan J, Sun C-L, Chen L-C, Chen K-H 2013 Effect of chemical doping of boron and nitrogen on the electronic, optical, and electrochemical properties of carbon nanotubes *Progress in Materials Science* **58** 565-635
[4] Ayala P, Reppert J, Grobosch M, Knupfer M, Pichler T, Rao A M 2010 Evidence for substitutional boron in doped single-walled carbon nanotubes *Appl Phys Lett* **96** 183110–3
[5] Panchakarla L S, Govindaraj A, Rao C N R 2010 Boron-and nitrogen-doped carbon nanotubes and graphene *Inorg Chim Acta* **363** 4163–74
[6] Zaporotskova I V, Boroznin S V, Perevalova E V, Polikarpov D I, 2012 Electronic structure and characteristics of certain types of boron containing nanotubes *Vestnik VolGU*: ser 10 *Innovatsionnaya deyatelnost* **6** 81-6
[7] Boroznin S V, Boroznina E V, Zaporotskova I V, Polikarpov D I 2013 Adsorption of atomic hydrogen on the surface of the boron-carbon nanotubes *Russian Journal of General Chemistry* **83**(3) 1580-5
[8] Boroznin S V, Zaporotskova I V, Boroznin S V 2012 Investigation of oxidation in boron-containing nanotubes *Nanoscience and Nanotechnology Letters* **4** 1096-9
[9] Boroznin S V, Boroznina E V, Zaporotskova I V, Polikarpov D I, Polikarpova N P 2013 Hydrogenation of boron-carbon nanotubes *Nanoscience and Nanotechnology Letters* **5** 1-6
[10] Boroznin S V, Boroznina E V, Zaporotskova I V, Polikarpov D I 2013 About hydrogen adsorption on the boron-carbon nanotube surface *Journal of General Chemistry* **83**(8) 1351-6
[11] Boroznin S V, Boroznina E V, Zaporotskova I V, Polikarpov D I, Krutoyarov A A 2013 Vacancy transport properties in boron-carbon BC_3 nanotubes *Physics of wave processes and radio systems* **16**(2) 14-8
[12] Perevalova E V, Zaporotskova I V, Zaporotskova N P 2011 Boron Nanotubes: Sorption Properties and Proton Conductivity *Nanoscience and Nanotechnology Letters* **3**(6) 1-6
[13] Penkalya T M 1972 Essay about crystal chemistry Leningrad: Chemistry 496 p *(in Russian)*

Authors

Sergei Boroznin , 08.03.1987, Volgograd, Russian Federation

Current position, grades: associate professor, PhD, Institute of priority technologies Volgograd State University
University studies: Volgograd State University
Scientific interest: nanotechnology, nanostructures and atomic clusters, boron-carbon nonmaterial, solid state physics
Publications: 52 published scientific works, including 7 in journals included in the database Scopus
Main: [1] Zaporotskova I V, Boroznin S V, Boroznina E V, Plikarpova N P 2014 Boron-carbon Nanotube Modification Using Alkaline Metal Atoms *Journal of nano-and electronic physics* **6**(3) 03006-1 – 03006-2.
[2] Boroznin S V, Zaporotskova I V, Polikarpov D I, Boroznina E V 2013 Adsorption of atomic hydrogen on the surface of the boron-carbon nanotubes *Russian Journal of General Chemistry* **83**(3) 1580-5
[3] Boroznin S V, Zaporotskova I V, Boroznina E V, Polikarpov D I, Polikarpova N P 2013 Hydrogenation of boron-carbon nanotubes *Nanoscience and Nanotechnology Letters* 5(11) 1195-1200
Experience: The holder of a scholarship of the President of the Russian Federation, Head of the grant of the Volga, participation in the grant of the Ministry of Education "study of the structure, physico-chemical and dynamical properties of nanostructures",defended PhD thesis on "boron nanotubular structures: the structural features and properties (2013)

Irina Zaporotskova , 12.11.1963, Melitopol, Ukraine

Current position, grades: professor, Doctor of Physical and Mathematical Sciences
University studies: Volgograd State University, Molecular physics, Solid State Physics
Scientific interest: nanotechnology, boron-carbon nonmaterial, nanocomposites.
Publications: 326 publications
Recent main:
[1] Zaporotskova I V, Boroznin S V, Boroznina E V, Polikarpov D I 2013 Vacancy Transport Properties in Boron–Carbon BC3 nanotubes *Nanoscience and Nanotechnology Letters* **5** (11) 1164-8
[2] Zaporotskova I V, Polikarpova N P, Ermakova T A, Polikarpov D I 2013 Carbon Nanotubes, New Material for Purification of Water–Ethanol Mixtures from Isomers of Propanol *Russian Journal of General Chemistry* **83**(8) 1601–6
[3] Zaporotskova I V, Anikeev N A, Kojitov L V, Davletova O A, Popkova A V 2014 Theoretical Studies of the Structure of the Metal-carbon Composites on the Base of Acryle-nitrile Nanopolimer *Journal of nano- and electronic physics* **6**(3) 03035-1 - 03035-3
Experience: since 2008 - the managing editor of the journal "Bulletin of the Volga. Series 10: Innovation activities; since 2007 - the head of Research and Education Center VolSU "Nanomaterials and Nanotechnologies", repeatedly participated in conferences, symposiums, forums and academic seminars of national and international level.

Evgenia Boroznina, 01.11.1980, Volgograd, Russian Federation

Current position, grades: associate professor, PhD
University studies: Volgograd State University, Atomic physics
Scientific interest: nanotechnology, boron nanomaterial, nanotubes.
Publications: 50
Main: [1] Zaporotskova I V, Boroznin S V, Boroznina E V, Polikarpova N P 2014 Boron-carbon Nanotube Modification Using Alkaline Metal Atoms *Journal of nano- and electronic physics* **6**(3) 03006-1 – 03006-2
[2] Zaporotskova I V, Boroznin S, Boroznina E, Zaporotskov P A, Davletova O A 2014 Migration processes on the surface of carbon nanotubes with substitute boron atoms *Nanosystems: physics, chemistry, mathematics* **5**(1) 107-12
[3] Boroznin S V, Zaporotskova I V, Polikarpov D I, Boroznina E V 2013 Adsorption of atomic hydrogen on the surface of the boron-carbon nanotubes *Russian Journal of General Chemistry* **83**(3) 1580-6
Experience: In 2012, defended his thesis on "Nanotubular form boron: features the electron energy structure and conducting properties." Boroznina Eugene participated in the grant of the Ministry of Education "study of the structure, physico-chemical and dynamical properties of nanostructures."

Olessya Davletova, 19.12.1981, Buzinovka, Volgograd region, Russian Federation

Current position, grades: associate professor, PhD
University studies: Volgograd State University, Computer modeling of nanostructures
Scientific interest: nanotechnology, pirolyzed poliakrilonithril, quantum-chemistry calculations.
Publications: [1] Zaporotskova I V, Anikeev N A, Kojitov L V, Davletova O A, Popkova A V 2014 Theoretical Studies of the Structure of the Metal-carbon Composites on the Base of Acryle-nitrile Nanopolimer Journal of nano- and electronic physics 6(3) 03035-1 - 03035-3
[2] Zaporotskova I V, Boroznin S, Boroznina E, Zaporotskov P A, Davletova O A 2014 Migration processes on the surface of carbon nanotubes with substitute boron atoms Nanosystems: physics, chemistry, mathematics 5(1) 107-12
[3] Zaporotskova I V, Kravchenko A A, Ermakova T A, Davletova O A, Zaporotskova I V, Korchagina T K, Popov U V, Kalmikova G A 2014 The semi-empirical research of the adsorption of biologically active molecules on the outer surface of carbon nanotubes *Nanosystems: physics, chemistry, mathematics* **5**(1) 98-100
Experience: She defended her thesis on "The structure and electronic properties of the pyrolyzed polyacrylonitrile." (2010), has scientific journal articles from the list of HAC and included in the Scopus database, is the deputy director of the Institute of priority technologies Volgograd State University in social work.

Natalia Polikarpova, 11.03.1989, Volgograd, Russian Federation

Current position, grades: associate professor, PhD
University studies: Volgograd State University, Spectroscopy
Scientific interest: nanotechnology, sensor activity of nanostructures, quantum-chemistry calculations.
Publications: 47
Main: [1] Zaporotskova I V, Boroznin S V, Boroznina E V, Plikarpova N P 2014 Boron-carbon Nanotube Modification Using Alkaline Metal Atoms Journal of nano-and electronic physics 6(3) 03006-1 – 03006-2.
[2] Polikarpova N P, Vilkeeva D E, Polikarpov D I, Zaporotskova I V 2014 Sensor properties of carboxyl-modifies carbon nanotubes *Nanosystems: physics, chemistry, mathematics* **5**(1) 101-6
[3] Polikarpova N. P., Vil'keeva D. E., Zaporotskova I V 2013 Sensor Activity of Carbon Nanotubes with a Boundary Functional Group Nanoscience and Nanotechnology Letters **5**(11) 1169-73
Experience: Has 47 scientific publications, including 4 articles in journals included in the Scopus database. In defended her thesis on "SENSORY PROPERTIES OF SEMICONDUCTOR Nanotubular SYSTEM "(2013), takes part in the grant of Ministry of Education 'Study of the structure, physical, chemical and dynamical properties of nanostructures'