https://doi.org/10.22226/2410-3535-2022-3-214-218

Sensory properties of carbon nanotubes containing impurity boron atoms

S. V. Boroznin†, I. V. Zaporotskova

†boroznin@volsu.ru

Volgograd State University, Volgograd, 400062, Russia

Nanotubes, being one of the most demanded nanotechnology materials, are finding new areas of application. One of these areas is their use as highly sensitive sensors. However, in the practical application of nanotubes, it often turns out that, despite the positive sorption properties, a change in their electronic state does not occur after the capture of the analyte. This fact significantly complicates the possibility of their use as sensory nanosensors. One of the ways to improve the electronic properties of carbon nanotubes by creating heterostructures on their surface is modification with various atoms. At the same time, one of the most effective substances for carrying out the substitution reaction is boron. It makes it possible to create a redistribution of electron density on the surface of nanotubes without introducing significant changes in the topology of the nanotube surface. This article analyzes a model experiment to study the possibility of using the nanotubes themselves as highly sensitive nanosensors in relation to carbon dioxide molecules.

Keywords: carbon nanotubes, boron-carbon nanotubes, structural modification, sensor properties, adsorption, semiconductor nanomaterials.

1. Introduction

Recently, there has been an increase in research related to the sensory properties of nanomaterials, since this will both increase the sensitivity of existing sensors [1] and offer new nanoelectronic solutions for controlling them [2]. Since the discovery of carbon nanotubes, a large number of works have been devoted specifically to this area of research [3]. Single-walled carbon nanotubes (CNTs) attract close attention of researchers due to their unique surface, mechanical, chemical, and electrical properties [4–6]. Various possibilities of using carbon nanotubes in industry, including gas sensors, have been investigated, since they change their electrical and conductive properties under the influence of adsorbed atoms and molecules [7–9]. At the same time, carbon nanotubes have a number of other advantages compared to materials traditionally used in the sensor industry, including the well-established technology for their production, the possibility of repeated use, a large range of gases for which they can be applied [10] in combination with high sensitivity [11]. Currently, the study of gas sensors is extremely important for both industry and the environment [12]. Due to their high specific surface area and structure similar to a hollow cylinder [13], carbon nanotubes have found active application as biological, chemical, and electromechanical sensors of gas atoms [14]. Real experiments only confirm the stated assumptions [15]. Quantum-chemical calculations using Density Functional Theory (DFT) are a real possibility to predict the physical and chemical properties of materials. Model experiments make it possible to create a detailed structure of a carbon nanotube and get an idea of its basic physical and chemical properties. Carrying out theoretical calculations will also save some of the time and resources that are usually spent on experiments in laboratory conditions, when it is necessary to select precursors and experimental conditions.

But without a connection with real research, it becomes unclear which way nanomaterials scientists should move in the study of new materials. For example, recent reports on new methods for fabricating multiwalled carbon nanotubes doped with boron atoms are of great interest from both research and industrial points of view. In particular, the production of boron-carbon nanotubes by catalytic pyrolysis [16,17], electric arc discharge [18], various chemical reactions [19,20], spark plasma sintering [21], and laser evaporation [22] has been reported. However, among these methods, chemical vapor deposition (CVD) has been recognized as the most promising and efficient method because it facilitates the production of boron-doped carbon nanotubes in high yield without by-products. In [23], the possibility of modifying nanotubes with a number of materials for using them as highly sensitive sensors for detecting phosgene molecules is considered, but as shown in article [24], in reality, only carbon nanotubes modified with boron are successfully observed, despite the many proposed substances for modification. Therefore, the most significant will be a comparison of the sensory properties of pure carbon nanotubes and those modified with boron in relation to the poisonous gas — phosgene. It turned out that successful adsorption, or rather physical attachment due to van der Waals forces, is possible for both types of nanotubes. However, when attached to a pure carbon nanotube, phosgene does not have a significant effect on the electronic energy structure and, accordingly, does not change the conductive characteristics of the

material, which makes it difficult to detect using CNTs. When modifying boron atoms are added, the adsorption process is accompanied by the appearance of additional levels in the nanotube zone friction and the transfer of electron density from the phosgene molecule to the nanotube surface is observed. Therefore, carbon boron-containing nanotubes are a more preferable material for creating nanosensors, according to theoretical calculations.

Researchers [25] used a manufactured composite nanofilm of boron-containing nanotubes with gold nanoparticles to determine dopamine and adrenaline in biological samples. The conducted studies have shown that the analysis of the content of dopamine and adrenaline in pig blood using nanosensors based on carbon nanotubes modified with boron and gold nanoparticles is effective, accurate and reproducible. That is, this material can be successfully applied in practice in other biological samples. The data also behaved when uric acid was added to the samples. That is, there was no blurring and overlapping of the peaks. The ability to determine the content of dopamine and adrenaline remained at the same high level as before.

The examples discussed above describe cases of using modified carbon nanotubes as sensors. In both cases, the use of this nanomaterial is extremely important and allows solving significant research and industrial problems. However, in these studies, in one case, carbon nanotubes modified only with boron atoms are considered, and in the other case, additionally with gold nanoparticles. Therefore, an interesting research task is to find out whether such a type of nanomaterial as a boron-carbon nanotube requires additional modification or not? To clarify this circumstance, we carried out a model experiment to study the sensor properties of a conventional boron-carbon nanotube containing 15% impurity boron atoms and modified with a carboxyl group with respect to a carbon dioxide molecule, since this type of modification is well known and the technology for obtaining carboxylated carbon nanotubes has been established [7].

2. Materials and methods

To construct a model of a nanoobject, the mechanism of modification of a BC_5 nanotube by a carboxyl group upon attachment of the a-COOH group to the surface of boron-carbon tubulene was studied (Fig. 1) [26].

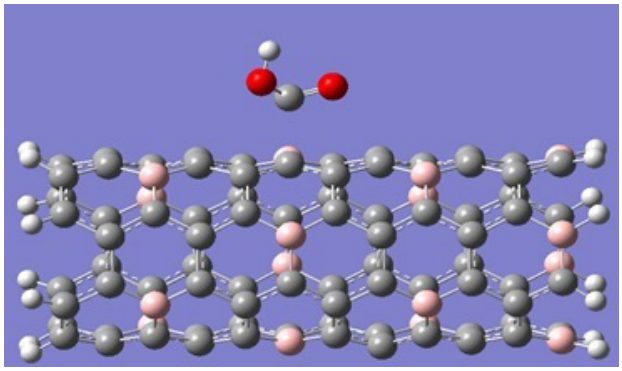

Fig. 1. (Color online) Variant of the orientation of the carboxyl group relative to the surface of nanotube.

As the most probable adsorption centers in the interaction of a carbon boron-containing nanotube with a COOH group, we chose surface atoms of the BC_5 nanotubes: a carbon atom for the first variant (I) and a boron atom for the second variant (II). When calculating the interaction mechanisms, a carbon boron-containing nanotube was studied within the framework of the MC model using the density functional theory (DFT) method. The cluster length was chosen so as to avoid the influence of edge effects on the process, namely, five rings made by hexagons along the central axis of the nanotube with a total length of 0.15 nm were considered. Pseudo-atoms with the required valency were used to compensate for broken chemical bonds at the cluster boundary. In the case under consideration, hydrogen atoms, playing the role of pseudoatoms, are well suited for this role.

The process of adsorption of the carboxyl group for variant I was modeled as follows: the -COOH group approached step by step the carbon atom of the surface of the borocarbon nanotube located approximately in the middle of the cluster. The performed calculations within the framework of the B3LYP functional and the 6-31 G basis helped to determine the energy of the system at each stage, as a result of which it became possible to plot the dependence of the energy on the interaction distance between the COOH group and the nanotube in the case of the adsorption center located on the carbon atom of the BC_5-type nanotube.

The shape of the potential energy surface profiles showed that the interaction of the carboxyl group with the nanotube leads to its adsorption, which leads to the surface modification of the tubulen. The fact of adsorption confirms the presence of a minimum on the profile of the potential energy surface at a distance characteristic of the formation of a chemical bond between the atoms included in the nanostructures under study. For the formation of the adsorption complex "BC_5-nanotube-COOH" the following process parameters were set: $r_{ad} = 0.2$ m, $E_{ad} = -5.89$ eV.

The next process of adsorption of the carboxyl group for variant II was modeled in the same way: the carboxyl group approached step by step the boron atom of the surface of the boron carbon NT. Based on the results of quantum chemical calculations, the profiles of the potential energy surfaces of the processes of adsorption of the carboxyl group on the boron atom of the surface of carbon boron-containing (4, 4) nanotubes of the BC_5 type were constructed. An analysis of the energy curves also showed that there is an energy minimum on the potential energy surface profile at a distance characteristic of chemical adsorption. In the case of localization of the adsorption center near the boron atom of the surface of a BC_5 nanotube, the main parameters for the formation of the adsorption complex are as follows: $r_{ad} = 0.21$ nm, $E_{ad} = -5.89$ eV.

In addition to surface modification, the mechanism of edge functionalization is also encountered in the literature [26]. To determine a more probable way of functionalization, the process of carboxyl group addition to the open boundary of the BC_5 boron-carbon nanotube was simulated.

A fragment of a boron-containing nanotube interacting with a carboxyl group to determine the possibility of edge functionalization was modeled as follows [27]. The end face of the nanotube cluster closest to the group was open, while

the other end (to simulate a nanotube of infinite length) was closed by hydrogen pseudoatoms. Two variants of the addition of a carboxyl group were studied: I) to the carbon atom at the NT boundary, II) to the boron atom.

The process of addition of the carboxyl group for variant I was modeled as follows: the -COOH group approached the carbon atom at the boundary of the borocarbon NT step by step. After carrying out quantum-chemical calculations, it became possible to obtain the profile of the potential energy surface of the interaction of the carboxyl group with the open boundary of the nanotube. The profile view demonstrated the possibility of attaching a group to the NT boundary, this is illustrated by the minimum energy value on the curve (Fig. 2). For the approach of the carboxyl group to the C atom at the tubulene boundary, the localization point of the energy minimum is at a distance of 0.16 nm from the boundary, the adsorption energy is −0.78 eV.

The next process of addition of the carboxyl group for variant II was modeled as follows: the carboxyl group step by step approached the boron atom located at the open end of the BC_5 type carbon boron containing NT. The quantum-chemical calculations carried out made it possible to construct a graph of the dependence of energy on the distance of interaction of the phenomenon under study. The potential energy surface profile shown in Fig. 3 allows us to conclude that it is possible to create a nanosensor complex for this option: the distance between the functional group and the nanotube is 0.16 nm, the adsorption energy is −0.79 eV.

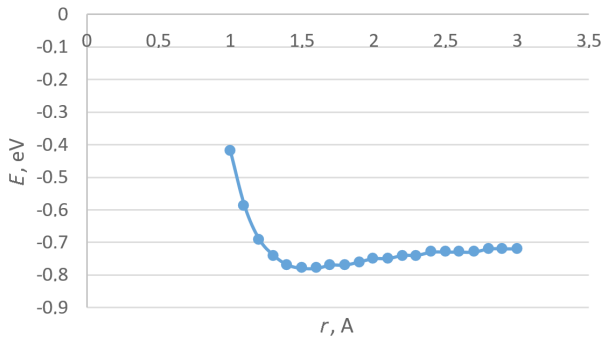

Fig. 2. Energy curve of the process of interaction of the carboxyl group oriented to the carbon atom with the open boundary of the BC_5 nanotube of the (4, 4) type.

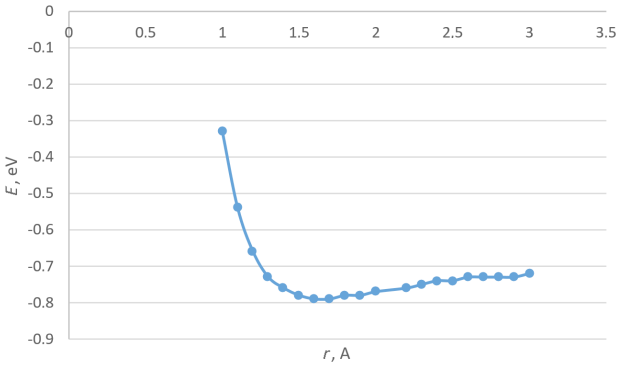

Fig. 3. Potential energy profile of the process of addition of a carboxyl group to the boron atom of the open boundary of the BC_5 nanotube.

3. Results

To study the sensitivity of nanostructures to carbon dioxide molecules, the process of their interaction with a boron-carbon nanotube of the BC_5 type (4, 4) was simulated. At the first stage, the attachment of molecules to its surface was simulated. The molecules were oriented perpendicular to the surface of the nanostructure in the positions shown in Fig. 4.

The CO_2 molecule approached the boron or carbon atoms of the surface, located in the center of the cluster, so that the process under study would not be affected by boundary effects. The molecule approached the nanotube with a step of 0.01 nm along the perpendicular connecting the molecule and the adsorption center. In this case, one of the oxygen atoms of the carbon dioxide molecule was chosen as the nearest atom to the surface of the nanotube, and the nanotube itself was oriented along the perpendicular to the longitudinal axis of the nanotube so that the bond angle between the O atoms was 180°. Calculations made it possible to calculate the energy of the interaction process, the changes in which depending on the distance between the molecule and the atom of the nanotube surface are shown in Fig. 5. The graph shows the change in the interaction energy when a carbon dioxide molecule approaches different atoms of the nanotube surface [27]. The interaction energy was −1.6 eV at a distance of 0.28 nm when the molecule interacted with a boron atom and −1.2 eV at a distance of 0.3 nm for the case of approaching a carbon atom (Fig. 6).

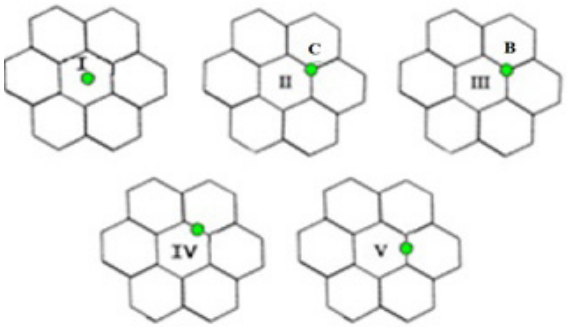

Fig. 4. (Color online) Variants of the orientation of the carbon dioxide molecule relative to the surface of nanotubes. The green marker corresponds to the location of the carbon dioxide molecule above the nanotube. The carbon dioxide molecule is oriented perpendicular to the surface of the nanotube.

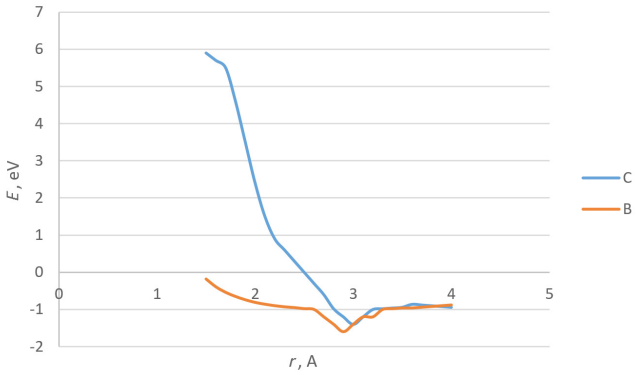

Fig. 5. (Color online) The energy curve of the interaction of CO_2 with the surface of the unmodified nanotube BC_5 when attached to atoms C or B constituting the surface of the nanotube.

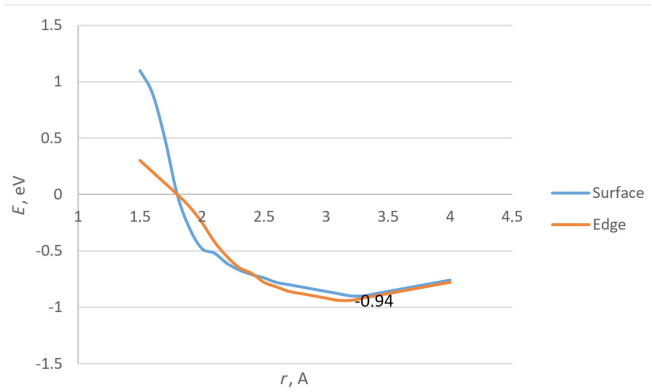

Fig. 6. (Color online) Potential energy surface profile of the interaction of a carbon dioxide molecule with a sensor complex consisting of a carbon boron-containing nanotube of the BC_5 type and a carboxyl group attached to it. "Surface" corresponds to the case of surface modification of a nanotube with a functional group, and "Edge" corresponds to boundary functionalization.

To compare the efficiency of capturing CO_2 molecules by a BC_5 carbon boron nanotube modified with a carboxyl group, the mechanisms of its interaction with a carbon dioxide molecule were considered. Namely, the oxygen atom of the carboxyl group was chosen as the adsorption center, since earlier, when performing similar calculations, this center showed better efficiency compared to the hydrogen atom chosen as second adsorption center. The carbon dioxide molecule, as in the case of interaction with an unmodified tube, was oriented by the oxygen atom so that it was perpendicular to the nanotube axis.

When studying the boundary modification, the oxygen atom was also chosen as the adsorption center of the functional group. The molecule interacted with the system, approaching it with an edge oxygen atom, and was located parallel to the nanotube axis.

All results obtained during the simulation experiment are presented in Table 1.

Table 1. Main energy parameters of the attachment of a carbon dioxide molecule to a BC_5 nanotube without modification and NT modified with a COOH group.

Adsorption Center	r_{ad}, nm	E_{ad}, eV
C atom	0.3	1.2
B atom	0.28	1.6
COOH to the surface	0.33	0.9
COOH to the edge	0.32	0.94

4. Discussion

The results of computer simulation of the processes showed that the energy of the system changes with the formation of a minimum when a molecule approaches the surface of an unmodified nanotube when it is located above the boron and carbon atoms (positions II and III) (Fig. 4) indicates the possibility of adsorption at these points. Thus, the performed quantum-chemical calculations have established that the adsorption of a carbon dioxide molecule is possible when the molecule is located above the boron and carbon atoms of the surface of the boron-carbon BC_5 nanotube, as shown in Fig. 4.

The studied BC_5 nanotubes can be considered as elements of fire sensors for identifying carbon dioxide. When a carbon dioxide molecule was attached to the surface of the nanotube, a change in the band gap of the system was observed, as shown in Table 2. The operation of sensors is based on the adsorption of CO_2 molecules with subsequent detection, which is possible due to a change in the conductive properties of nanoobjects. When this molecule is attached to a nanotube modified with a BC_5 carboxyl group, adsorption occurs in both cases considered.

Table 2. Change in the band gap of a carbon boron-containing nanotube of the BC_5 type upon interaction with a carboxyl group and a carbon dioxide molecule.

Type of nanostructure	Adsorption center	ΔE_g, eV
BC_5 type Nanotube		0.47
Nanotube + COOH (boundary functionalization)	C atom	0.28
	B atom	0.24
Nanotube + COOH (surface functionalization)	C atom	0.19
	B atom	0.07
CO_2 + BC_5 nanotube	C atom	0.46
CO_2 + BC_5 nanotube	B atom	0.46

At the same time, nanotube modification does not improve the sorption properties of boron-carbon tubulene containing 15 percent of impurity substitutional boron atoms. Therefore, the manufacture of such nanosensors will not require additional preparation.

It was found that the appearance of impurity boron atoms makes it possible to discover new facets in the field of industrial use of carbon nanotubes. To use them as sensor devices, it becomes extremely important to introduce precisely impurity boron atoms, since, as a number of previous studies have shown, it is the heterostructure that makes it possible to make a carbon nanotube more sensitive to various effects of chemicals. In this case, only boron atoms, due to their spatial and electronic characteristics, can be built into the surface of a carbon nanotube without a significant change in its surface topology. A change in the electronic structure, on the other hand, entails an increase in the sensitivity of nanosensors with respect to various substances.

It is known that when conducting an experiment, additional alloying elements are often used, which make it possible to increase the sensitivity of sensors. In the case of boron-containing nanotubes, such studies are also observed, showing their effectiveness. But do they have any purpose? To answer this question, let's turn to the conclusions of the last part of the article.

When a molecule is attached to a pure unmodified nanotube, the adsorption energy in both cases is higher than when it comes into contact with a modified nanostructure in the case of its modification with a carboxyl group. A change in the electron density near the adsorption center was observed. In the case of interaction with the boron atom of the surface, the density is transferred to the carbon dioxide molecule, and in the case of interaction with the carbon atom, it is transferred towards the surface of the nanotube.

5. Conclusion

Thus, we can conclude that the mechanisms under consideration are the most likely to be implemented, which can be used to create new generation fire-fighting devices using CNT-based nanostructures. This allows us to conclude that to control the sorption properties of carbon nanotubes in order to use them in fire-fighting devices, it is sufficient to modify them with impurity boron atoms without introducing additional functional groups.

Acknowledgements. This research was funded by the Ministry of Science and Higher Education of the Russian Federation No. MK-2089.2021.1.2.

References

1. R.K. Pandyan, S. Seenithurai, M. Mahendran. Indian Journal of Physics. 86 (8), 677 (2012). Crossref
2. M.S.A. Bistamam, M.A. Azam. Results in Physics. 4, 105 (2014). Crossref
3. A.A. EL-Barbary, K.M. Eid, M.A. Kamel, H.M. Osman, G.H. Ismail. J. Surf. Eng. Mater. Adv. Technol. 4, 66 (2014). Crossref
4. M.A. Azam, M.W. A. Rashid, K. Isomura, A. Fujiwara, T. Shimoda. Adv. Mater. Res. 620, 213 (2013). Crossref
5. M.A. Azam, N.H. Jantan, N. Dorah, R.N.A.R. Seman, N.S.A. Manaf, T.I.T. Kudin, M.Z. Yahya. Mater. Res. Bull. 69, 20 (2015). Crossref
6. R.N. A. R. Seman, M.A. Azam, A.A. Mohamad. Renew. Sustain. Energy Rev. 75, 644 (2017). Crossref
7. I.V. Zaporotskova, N.P. Boroznina, Y.N. Parkhomenko, L.V. Kozhitov. Modern Electronic Materials. 2, 95 (2016). Crossref
8. D.Z. Kutlubaev, D.V. Makaev, P.N. D'yachkov. Journal of inorganic chemistry. 56 (8), 1301 (2011). Crossref
9. P.N. D'yachkov, D.Z. Kutlubaev, D.V. Makaev. Physical Review B. 82, 035426 (2010). Crossref
10. D. Jung, M. Han, G. Lee. Sens. Actuators A: Phys. 211, 51 (2014). Crossref
11. M. Roberts, M. LeMieux, Z. Bao. ACS Nano. 3, 3287 (2009). Crossref
12. D. Ruixue, Y. Yintang, L. Lianxi. J. Semicond. 30, 114010 (2009). Crossref
13. S. Gowtham, R.H. Scheicher, R. Ahuja, R. Pandey, S. Karna. Phys. Rev. B. 76, 033401 (2007). Crossref
14. D.S. Rawat, M.M. Calbi, A.D. Migone. J. Phys. Chem. C. 111, 12980 (2007). Crossref
15. M.T. Baei, A.R. Soltani, A.V. Moradi, M. Moghimi. Monatsh. Chem. 142, 573 (2011). Crossref
16. A.A. Koós, F. Dillon, E.A. Obraztsova, A. Crossley, N. Grobert. Carbon. 48, 3033 (2010). Crossref
17. M.A. Mamo, A.O. Sustaita, Z.N. Tetana, N.J. Coville, I.A. Hümmelgen. J. Mater. Sci. Mater. Electron. 24, 3995 (2013). Crossref
18. R. Czerw, P.W. Chiu, Y.M. Choi, D.S. Lee, D.L. Carroll, S. Roth, Y.W. Park. Curr. Appl. Phys. 2, 473 (2002). Crossref
19. S. Shiraishi, M. Kibe, T. Yokoyama, H. Kurihara, N. Patel, A. Oya, Y. Kaburagi, Y. Hishiyama. Appl. Phys. A. 82, 585 (2006). Crossref
20. Y.A. Kim, S. Aoki, K. Fujisawa, Y.I. Ko, K.S. Yang, C.M. Yang, Y.C. Jung, T. Hayashi, M. Endo, M. Terrones, M.S. Dresselhaus. J. Phys. Chem. C. 118, 4454 (2014) Crossref
21. Y. Sato, H. Nishizaka, K. Motomiya, G. Yamamoto, A. Okubo, H. Kimura, M. Ishikuro, K. Wagatsuma, T. Hashida, K. Tohji. ACS Appl. Mater. Interfaces. 3, 2431 (2011). Crossref
22. J.L. Blackburn, Y. Yan, C. Engtrakul, P.A. Parilla, K. Jones, T. Gennett, A.C. Dillon, M.J. Heben. Chem. Mater. 18, 2558 (2006). Crossref
23. S.S. Katta, S. Yadav, A. Pratap Singh, B. SanthiBhushan, A. Srivastava. Applied Surface Science. 588, 152989 (2022). Crossref
24. S.V. Sawant, A.W. Patwardhan, J.B. Joshi, K. Dasgupta. Chemical Engineering Journal. 427, 131616 (2022) Crossref
25. N.G. Tsierkezos, U. Ritter, Y. Nugraha Thaha, A. Knauer, D. Fernandes, A. Kelarakis, E.K. McCarthy. Chemical Physics Letters. 710, 157 (2018). Crossref
26. N.P. Boroznina, I.V. Zaporotskova, S.V. Boroznin, L.V. Kozhitov, A.V. Popkova. Russ. J. Inorg. Chem. 64 (1), 74 (2019). Crossref
27. N. Boroznina, I. Zaporotskova, S. Boroznin, L. Kozhitov, P. Zaporotskov. World Congress on Recent Advances in Nanotechnology. Lisbon, Portugal. (2020) pp. 125-1-125-7. Crossref