UDC 539

Dft Study Of Few-Layer Graphene-Metal Composites

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Graphene and it's few-layer configurations are the multi-functional materials for a wide range applications. Particularly, they can be used in production of composites, based on metal, ceramic, polymer matrices, as elements of reinforcement. Taking into consideration the fact of some difficulties of graphene application, such as surface chemical inertness and sliding between the layers of graphene sheets under stressed state, here we perform the computer simulation study of radiation defects which make possible the formation of stable graphene-metal structures. Performed quantum mechanical calculations revealed that that few-layer graphene – metal (Cu, Al, Li) fast bonds can be induced due to production of radiation structural defects.

Key words: Graphene, radation defects, graphene metal structure, strnctural defects
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1 Introduction

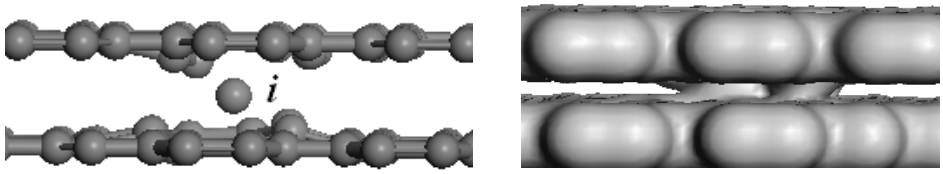
It is known that graphene and few layer graphene nanostructures are considered as promising materials in production of electronic devices, electrical sources, in particular, lithium-ion batteries, elements of reinforcement in production of composite materials [1-8]. It should be noticed that many difficulties concerning graphene's usage originate from its rather closed sp2 electronic structure. In practice it results in week interfacial bonding between graphene fragments and matrices when using it as filler substance, for example, in decreasing the part of graphene's surface transferring stress between reinforcement particle and matrix under of the composite. This obviously limits the level of ultimate strength that can effectively be transferred from graphene's element to the matrix. It is one of the barriers on the way of wide application of graphene based elements in new materials production. For example, composite material on the base of copper with graphene fragments as filler would be a material possesses very high heat conductivity combined with high stiffness and strength. On the other hand, Al – based composite with graphene filler would be very useful material because of unique combination of high strength with light weight. Our recent theoretical investigations [4-6] allow to propose, that radiation defects in carbon nanostructures like carbon nanotubes and graphene based materials can essentially improve binding ability of graphene's surface with metallic materials due to production of additional fast covalent bonds. Moreover, it has been stated that so called "bridge-like" radiation defects can link together nanostructures of fillers (particularly, few layer graphene fragments) making them and composite itself much more stiffer and stronger and improving isotropy of physical properties, like electro- and heat conductivity. Unfortunately, it is not easy to observe radiation defects directly and to make reasonable interpretations of experimental measurements of material's characteristics. In this situation computer simulation of radiation defects in carbon nanostructures becomes of great importance. Recently in the papers [1-4] physical and structural characteristics of single vacancies and complex defects, involving only carbon atoms were theoretically studied. It was established that vacancy zone in graphene raveled out in symmetrical way with increasing the hexagons parameter from 2.46 Å to 2.72 Å. The energy of relaxation of a vacancy's zone was calculated as large as 1.6 eV [4]. Recently nanomaterials based on ultra-thin graphite have also found a use in the technological field relating to production of lithium-ion rechargeable batteries, as possible storing elements for lithium atoms. But there are some obstacles on this way of application, linking for example, with deformation of cells which results in limitation of a charge capacity and the life-time of devices [7,8]. Taking all above into account, searching the possible ways to improve the relevant properties of few layer graphene nanostructures are of great interest. Obviously, performing the direct experiments with structures mentioned above is rather difficult problem. In this

situation computer simulation becomes a scientific instrument of a large importance. In our paper the energetic and structural characteristics of complex defects in graphene and few-layer graphene involving metallic atoms and clusters have been studied by quantum- mechanical calculations, based on density functional theory (DFT).

2 Modeling and calculations

2.1 Bridge-like radiation defects

Recently we reported results of computer simulations and studies of energetic and structural characteristics of stable radiation defects like vacancies and carbon-carbon dumbbells in graphene and relative nanostructures [4-6]. In this paper we focus on complex radiation defects in carbon nanostructures, which involve atoms of metals. All calculations were performed by density functional theory with using a procedure of optimization on energy. The first model which we consider is a special configuration, which is called a "bridge-like defect" and consists of two vacancies, faced each other, produced in both of graphene sheets and interstitial carbon atom (*i*) caught between them (Fig. 1).



a) b)

Figure 1 – a) A typical configuration of a bridge-like radiation defect.
a) the atomic structure of defect with interstitial *i*;
b) The distribution of the electron charge with the density equal to 1.3 el /A^3

The essential feature of this defect is that two graphene sheets are linked with fast covalent bond. Moreover, neighboring atoms pulling in the gap between sheets, facilitating additional bonds in the zone of the defect. The electron charge distribution calculated for high value of electron density presented in Fig.1b proves existing of additional bonds between graphene sheets. The total binding energy for this defect was calculated as large as 9.5 eV.

2.2 Graphene-copper composition

Preliminary DFT calculations were performed for metallic atoms (Cu, Al, Li) placed in special positions of high symmetry (Fig.2) on the surface of ideal graphene gave values of the binding energies of metal atoms on the graphene surface nearly zero.

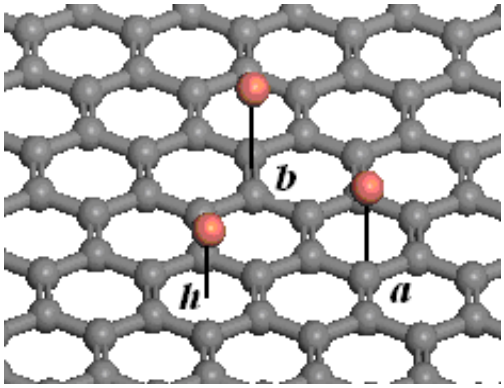


Figure 2 – Possible positions of metallic atoms (Cu, Al, Li) arranged on graphene surface in sites of the high symmetry: h – over the center of a hexagon;
a- over a carbon atom, b – over the center of the C-C bond

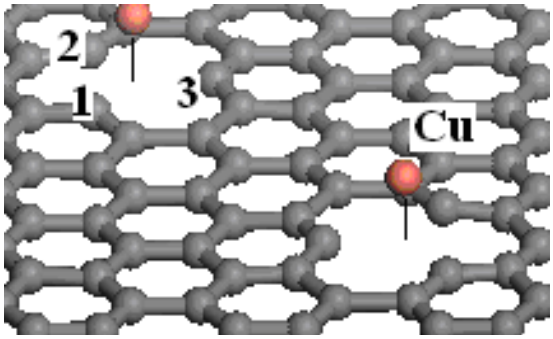


Figure 3 – Single Cu atoms linked with vacancies in graphene

Fig. 3 illustrates a computer model of possible composition Cu – vacancy. In this case calculation gave the binding energy of a Cu atom as large as 1.1 eV with distance from graphene sheet as large as 1.5 Å. Dimension parameters of the vacancy (distances D_{ij} between carbon atoms 1,2,3 in the graphene sheet) are as follows: D_{12}= 2.91 Å; D_{23} = D_{31} = 2.96 Å;

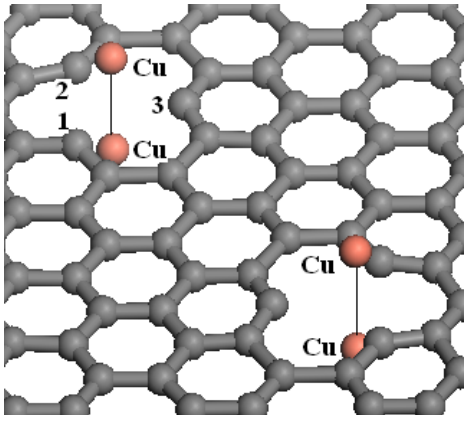


Figure 4 – Graphene with two Cu-dumbbells bonded with vacancies

More complex configuration – a dumbbell of Cu atoms linked with a vacancy one can see in Fig.4. Parameters of the vacancy after energy optimization: all three distances are equal: D_{12}= D_{23} = D_{31} = 2.9 Å ; The Cu atom binding energy is equal to 1.8 eV with the distance between copper atoms (the length of the dumbbell) equals 2.8 Å.

Obviously, production of such defects with metallic dumbbells allows to get higher amount of Cu in the composition. It should be also noticed that graphene structure displayed no signs of non-uniformity between the two dumbbells.

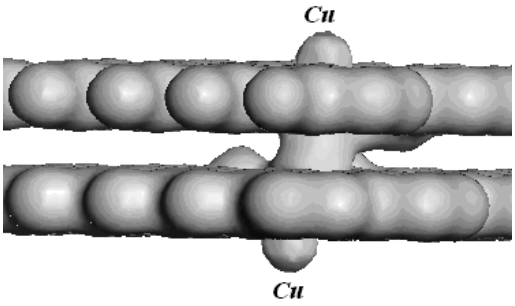


Figure 5 – Bridge-like defect with copper atom attached over vacancies (the distribution of electron charge calculated at density of charge as large as 1.2 el / Å^3)

Much more complex defect configuration is presented in Fig.5. It is a bridge like defect, linking two graphene sheets with two attached Cu atoms on the graphene surfaces.The binding energy of a Cu atom in this configuration is as large as 1.2 eV.

2.3 Graphene-aluminium composition

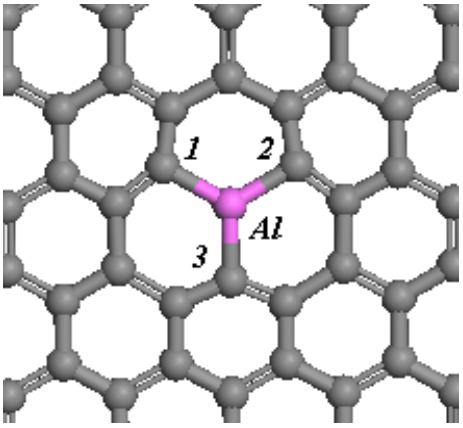
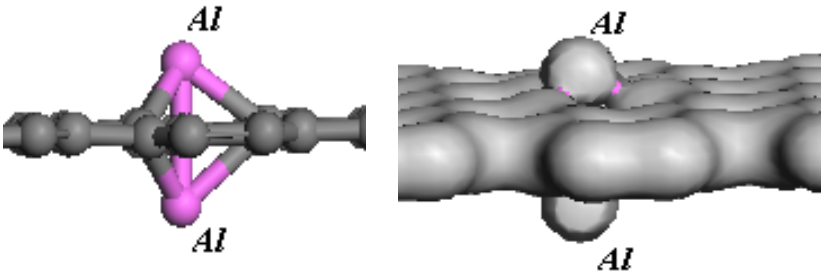


Figure 6 – 2D defect in graphene involving a vacancy linked with Al atom

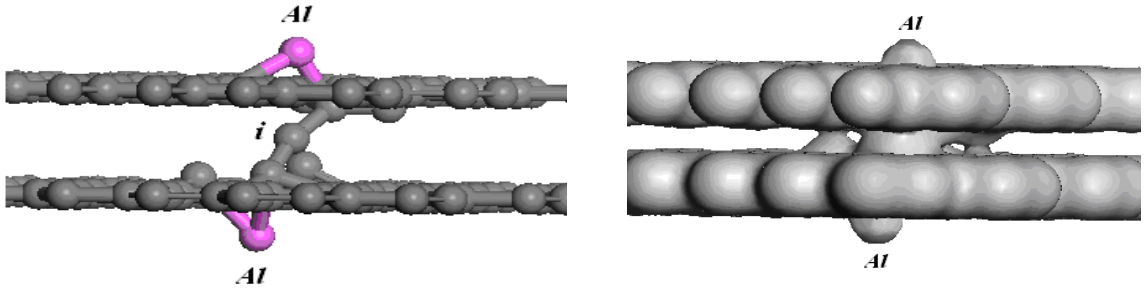
The computational model of a relatively simple defect configuration *Al* – V is presented in Fig.6. After the procedure of optimization on energy had been performed, the vacancy zone has increased in size and Al atom occupied its equilibrium position in the graphene's plane. Distances between Al atom and the nearest carbon atoms (marked as 1,2,3) are the same and equal to 1.71 Å. The binding energy of Al with graphene is equal to 3.6 eV.



a) b)

Figure 7 – A complex dumbbell-like defect of Al atoms in graphene vacancy:
a) atomic structure; b) the electron charge distribution by the density equal to 1.4 el / Å^3

Fig.7 presents configuration of *Al* – dumbbell placed at the vacancy. The equilibrium distance between Al atoms equals 2.5 Å, the binding energy is as large as 2.9 eV. The electron charge distribution with high electron density proves existing fast bonds between Al and vacancy.



a) b)

Figure 8 – A complex "bridge-like defect"-Al atoms configuration in two-layer graphene:
a) the atomic structure; b) the electron charge distribution

Fig. 8 shows the bridge-like defect with aluminum atoms attached at the surfaces in the defect area. The binding energy of *Al* in this configuration is as large as 1.5 eV. The binding energy between graphene sheets due the single bridge-like defect is as large as 9.3 eV.

2.4 Graphene- lithium system

It is well known, that ultra thin graphite and few layer graphene particles can be used as cells for a storage of Li atoms in lithium ion batteries production technologies. Moreover, the existence of bridge-like defects essentially improves one more important feature of lithium ion sources: it obviously enlarges the permeation and mobility of Li ions through graphene cells. Therefore, radiation modification of graphene cells with bridge-like defects might become a key technology to improve mechanical and electrical properties of lithium ion electrical sources, that results, in particular, in the essential enlargement of charge capacity, dimension stability and life-time of Li –ion-based electrical elements. Fig. 9 shows a possible configuration of a Li-Li dumbbell bonded with a vacancy with binding energy 0.9 eV / atom Li. The distance between Li atoms and graphene is equal to 1.1 Å. The calculation has been performed by the electron charge density equals 0.2 el / Å^3. Obviously, this kind of defects can also be in general useful for holding Li by graphene structures.

Obviously, Li atoms diffuse into and out of the electrodes when the batteryis charged or discharged. These cycling motion can caused changes in size of lithium storing cells. Therefore computer simulation of possible dimension changes of graphene cells was also performed. A typical result of modeling presented in Fig. 10 illustrate very important feature of graphene – based system for storing lithium that

can be called as dimension instability. One can see the noticeable deformation of graphene sheets in perpendicular direction. Similar effects are also possible to be displayed in ultra-thin graphite particles when using for Li storing in lithium ion batteries. This phenomena can significantly limit a capacity of such batteries and cut their life-time by using ultra-thin graphite- and graphene- based elements for storing of Li. One can think that it is impossible in principle to improve the state. But some results of computer simulations and calculations of possible configurations of few layer graphene cells contained Li which are given below, show, that situation becomes much better when graphene sheets of the cell are linked together with a fast bridge-like radiation defect, which makes the cell much more stiffer and improves its dimension stability.

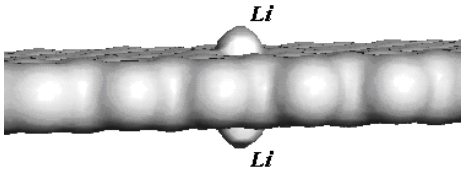


Figure 9 – The electron charge distribution in a Li – dumbbell in graphene's vacancy

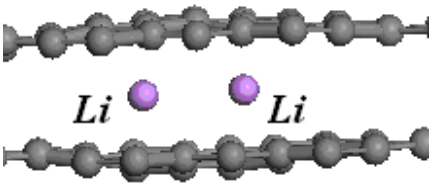
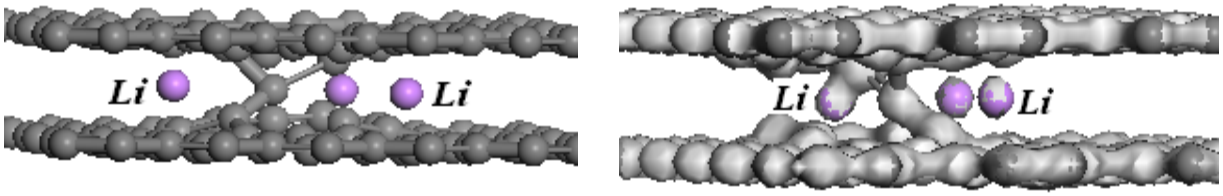


Figure 10 – A computer model of storing lithium atoms between graphene sheets



a) b)

Figure 11 – Li atoms stored in a two layer graphene cell, with a bridge-like radiation defect.
a) the atomic structure of defect; b) the electron charge distribution at the charge density equals 0.6 el / Å^3

One can see that the cell simulated with defect shows no signs of noticeable deformation (Figure 11). Fig 11, b represents the distribution of electron charge in the area near the bridge-like defect and one can see, that although there is a possibility of originating the fast bond between Li and bridge-like defect (Li atom on the left side) but mainly two layer graphene cell can be used for nearly full recycling storage of Li.

One more important characteristic of lithium-ion devices is the effective mobility of Li in the structure of batteries. Therefore the simulation of possible ways of Li motion are of great interest. In particular, the possibility of direct passing of Li through single vacancy and bivacancy inside graphene cells was investigated. Fig 12 presents a scheme of possible way for Li passing through holes in graphene sheet.

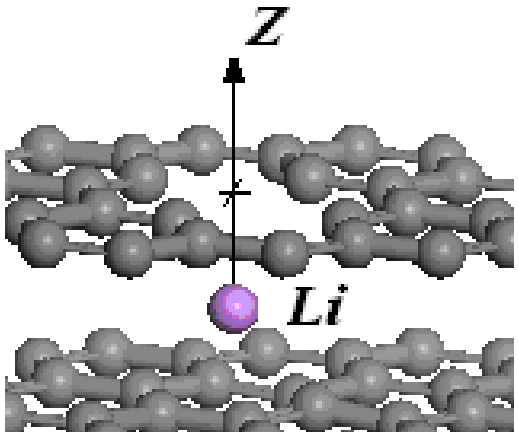


Figure 12 – A possible configuration of two-layer graphene with Li atom encapsulated between them, moving through bi-vacancy

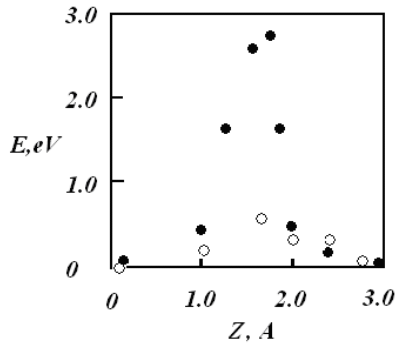


Figure 13 – The energy barrier existing by permeation of Li through vacancy or bivacancy in graphene

Figure 13 represents the results of DFT calculations, using optimization on energy, which show the existing of a potential barrier on the way of Li atom passing through graphene sheet with a single vacancy (black marks) or bivacancy (empty marks). The zero point of Z axis is placed in initial position of Li atom at the center between graphene sheets.

3 Conclusion

Computer simulations and quantum mechanical calculations of single and few-layer graphene -metal compositions have been performed in order to predict their energetic and structural characteristics. It was revealed that radiation modification of few layer graphene might become a key technology to improve physical-mechanical properties of ultra-thin graphite particles and few layer graphene structures as reinforcement elements of composites and as nanocells which serve as possible storing elements for lithium atoms in lithium-ion batteries production technologies.

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