

Structural and electronic properties of Li_n , B_n , N_n and O_n ($n = 1 - 4$) clustering on graphene: Density Functional Theory calculations with dispersive forces correction

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Abstract:

Density Functional Theory calculations are performed to study the adsorption of Li, B, N, and O clusters on graphene and to clarify the interaction of these atoms with a graphene sheet. The stable structures, the adsorption and interaction energies and the Density of States (DOS) of atom-graphene systems are calculated. The obtained results show that light atoms on graphene are governed by physisorption/chemisorption mechanisms with and without clustering occurrence. More interestingly, the formation of diatomic molecules is noticed. For example, Li atoms prefer to be physisorbed whereas B atoms prefer the clustering configuration on the graphene sheet. For N and O atoms, the molecule formation is preferred to the clustering one. The electronic structure of studied systems is analyzed by performing densities of states calculations. The results show that electronic structures are affected by the increasing concentration and the nature of adsorbed light atoms.

Keywords: Graphene; Adsorption; Clustering; Electronic properties; Van de Waals; DFT

1. Introduction

Graphene, a single-atom thick carbon nanosheet, has emerged as a versatile material with distinctive properties originating from its two-dimensional (2D) honeycomb lattice [1–4]. Graphene is the basic material to form nanotubes, fullerenes and graphite. It attracts attention not only as part of nanocarbons but also for its own interesting electronic, mechanic, and optical properties [5], which make it a good candidate for many applications. Therefore, there have been many theoretical and experimental attempts to apply metal-embedded graphene to gas storage, sensing materials, catalyst, biodevices, low-dimensional transport and magnetic structures, and other applications [6–11]. This is due to the combination of the high chemical property of metal atoms and the large surface area of graphene. The graphene and nanoscale carbons are particularly suitable for the stabilization of metal particles while maintaining excellent mass transfer properties, which is important in catalytic studies. In electronic applications, materials with a tunable bandgap are very interesting. Therefore, several studies

have reported possible graphene-like structures [12, 13] by reducing the graphite thickness and achievement of mono-layer and multi-Layer graphene sheets [14]. In other hand, doped-graphene systems show small bandgap by breaking the symmetry. In addition, their electronic structure and stability are highly affected by graphene interaction with atomic defects. For example, the doping graphene with N atoms is generally suggested for this kind of applications because of its high efficiency.

However, there is a major obstacle for metal-graphene complex since metal atoms prefer to aggregate without difficulty [15, 16]. For example, in Li ion batteries [17], it was reported that the Li cluster formation on graphene declines the charge/discharge capacity of a battery when graphene is used as an anode material. Knowing that the interaction of atoms with graphene is a feasible way to open an energy gap for graphene, it is still difficult to understand the stability, the structural as well as the electronic and the magnetic properties of such systems. In spintronic devices, the application of graphene must include a ferromagnetic spin injector. It is then important to study the atom clustering on

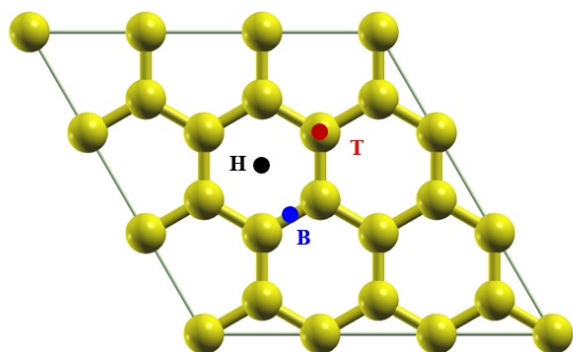


Figure 1. The three high symmetrical adsorption sites on graphene: Hollow (H), Bridge (B), and Top (T).

graphene knowing that clustering could greatly affect the long-term device stability. Recently, small ferromagnetic conductors have been used as spin injectors in graphene-based spintronics devices.

In this work, we study Li, B, N, and O clustering on graphene using the Density Functional Theory (DFT) and the Generalized Gradient Approximation (GGA). To take into account the Van der Waals (VdW) interaction effects, we have added Dispersive Force correction (DF) to the standard DFT functional. The paper is organized as follows. In Section 2, we present a brief description of the computational methods based on the Density Functional Theory (DFT). In Section 3, we present the obtained results of Li, B, N, and O clustering on graphene. The obtained results are discussed and compared with available data in the literature. The concluding remarks are given in Section 4.

2. Density Functional Theory (DFT) calculations

All calculations of the present study were performed using the framework of the Density Functional Theory (DFT) [18]. The Quantum Espresso program package was used to study the stability of nX clusters ($X = \text{Li, B, N, O}$; $n = 1 - 4$) adsorption on a graphene sheet [19]. We used a plane-wave basis set for the expansion of the single particle Kohn–Sham wave functions. The Generalized Gradient Approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE) [20] was employed in a spin-polarized scheme including the Ultra-Soft Pseudo-Potential (USPP) of Vanderbilt [21] with nonlinear core corrections. For the convergence, relaxation parameters were performed over the Monkhorst Pack meshes of $8 \times 8 \times 1$ k-points along the three basic axes in reciprocal space. A plane-wave basis up to a kinetic cut-off of 400 eV was selected. All systems are allowed to fully relax using a Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme. The convergence of the force between atoms is lower than 0.004 eV/\AA and the maximum displacement is 0.002 \AA . In our calculations, the Van der Waals (VdW) interactions between the adsorbed nX clusters and graphene are taken into account using the Dispersive Force (DF) correction (DF). Dispersion Forces arise from the mutual dynamic polarization of the electronic clouds of two or more atoms. London developed a formula to explain the intermolecu-

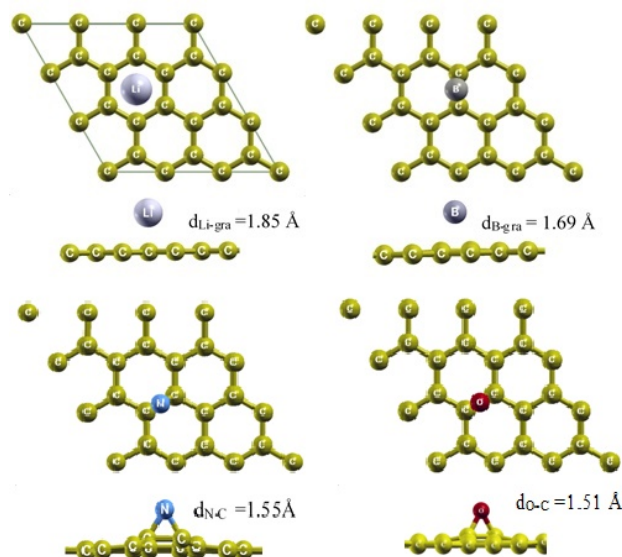


Figure 2. Equilibrium relaxed structures of one X atoms adsorbed on a 4×4 graphene sheet. $X = \text{Li, B, N}$ and O .

lar attractions that exist between nonpolar molecules [22]. DF correction models the long-range attractive potential of Dispersive Forces in terms of pair-wise atomic potential proportional to C_6R^{-6} , where R is the interatomic distance and C_6 is the interaction parameter (0.75 in this study).

The graphene is described using the supercell approach where a single layer is separated from its image along the z -axis by 27 \AA , which ensures a convergence precision of the total energy within 10^{-5} eV/atom . For this purpose, a 4×4 graphene supercell (32 C atoms) was considered for one, two, and three atoms defect adsorption. For the single atom, the adsorption was performed in three different sites: Top (T), Hollow (H) and Bridge (B), as shown in Fig. 1. The Top site is directly above a C atom; the Hollow site is at the center of a hexagon formed by six C atoms and the Bridge site is at the middle of the C-C bound. For two and three atoms adsorption, several configurations were considered taking into account previous equilibrium positions of one atom and only favorable configurations were considered. Accordingly, nX clusters-graphene systems were fully relaxed to equilibrium geometries.

3. Results and discussion

3.1 Structural and energetic properties

Equilibrium structures and equilibrium distances between nearest-neighbor adsorbed atoms and graphene atoms are reported in Fig. 2 and Fig. 3.

a. A single X atom adsorption on graphene

In the single atom case, the results show that Li and B atoms do not bound to a graphene surface as shown in Fig. 2. The B atom prefers the bridge site with the minimum adsorption energy of -1.188 eV and the equilibrium distance to the graphene surface of 1.69 \AA . However, the Li atom prefers the hollow site with the minimum adsorption energy of -0.759 eV and the equilibrium distance to the graphene surface of 1.85 \AA . For the graphene, interatomic distances between C atoms are not affected and remain unchanged

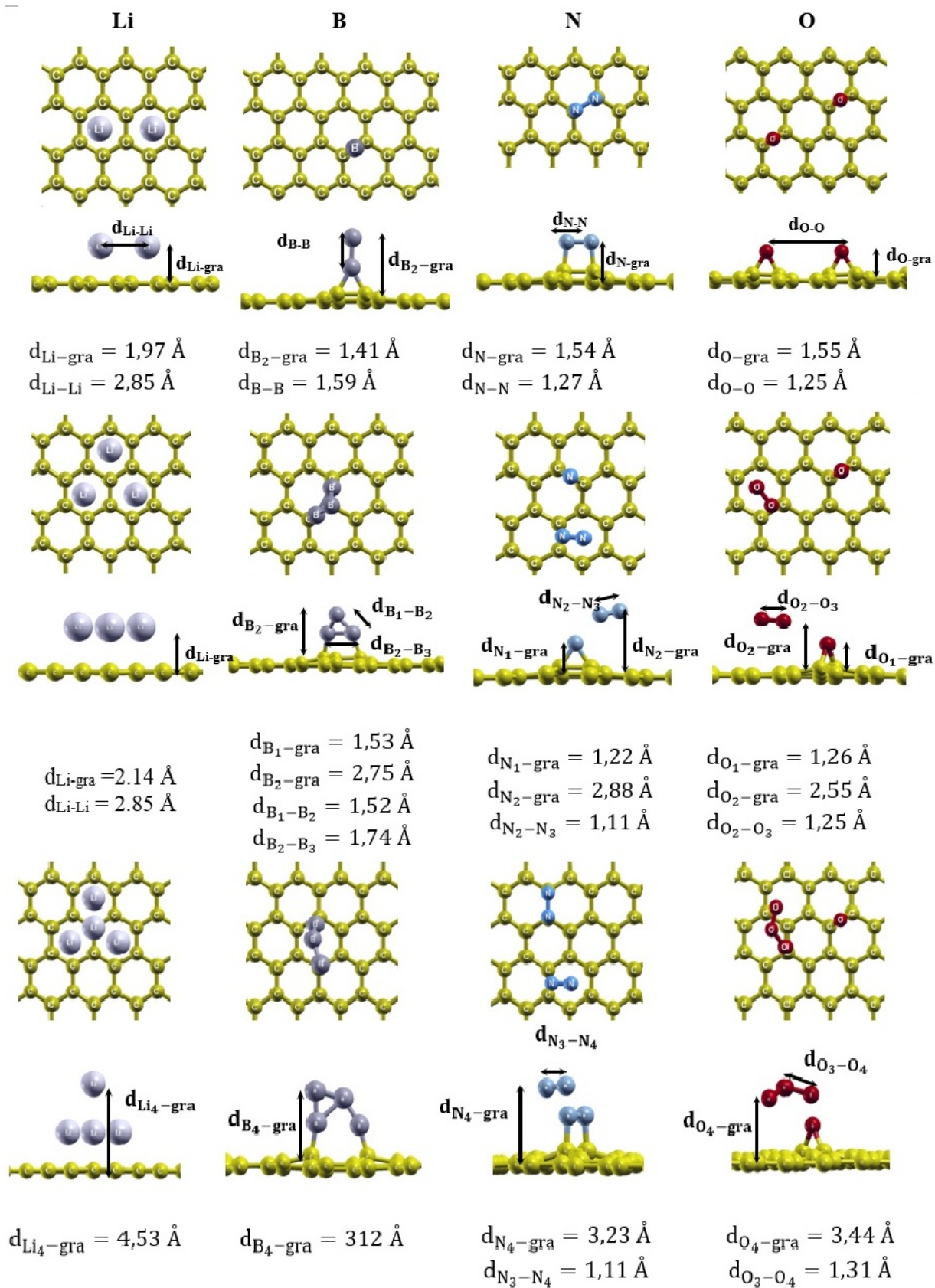


Figure 3. Equilibrium relaxed structures of nX atoms ($n = 2 - 4$) adsorbed on a 4×4 graphene sheet.

in the presence of Li and B. Taking into account the above results, Li and B atoms prefer to be physisorbed. These

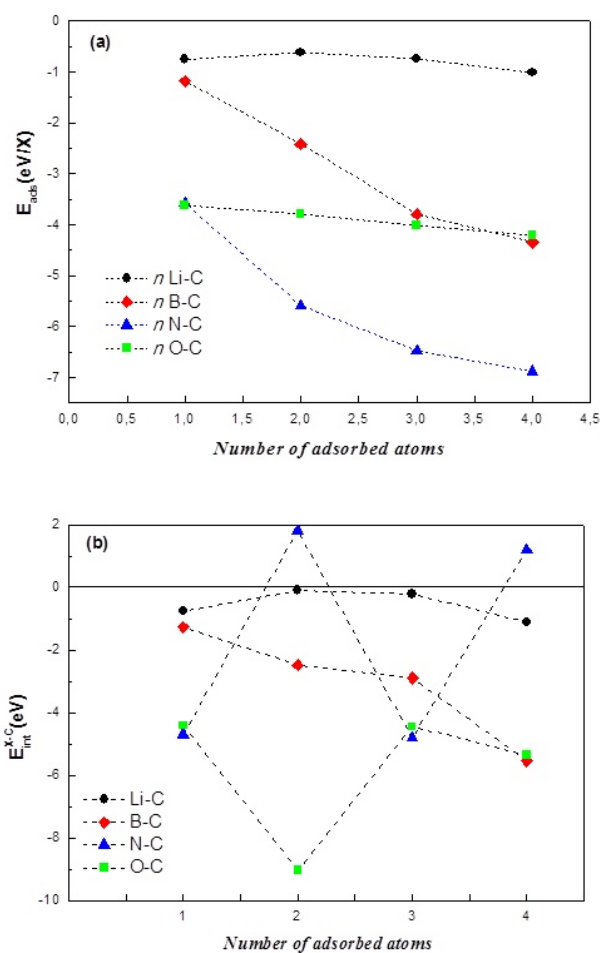


Figure 4. The adsorption energy, E_{ads} , for nX atoms on a graphene sheet and (b) $X-C$ interaction energy, $E_{int}^{(X-C)}$, as function of the number of adsorbed atoms, n .

results were confirmed by previous studies [23–26]. Several authors have found that the most favorable adsorption site for the Li atom is the hollow. The equilibrium distance to the graphene is 1.84 Å in ref [23], 1.71 Å in ref [24] and 1.67 Å in ref [25]. In addition, Li et al. [26] have indicated that the most favorable site for B is the bridge site at 1.69 Å from the graphene surface. However, the N and O atoms prefer to be bounded to two carbon atoms in the bridge site forming a triangle with two carbon atoms below, as shown in Fig. 2. The distance between N and O atoms and the graphene is 1.61 Å and 1.51 Å, respectively. The presence of N and O has affected the planer configuration of C atoms at the adsorption site. Interatomic distances between N-C and O-C are 1.55 Å and 1.51 Å, respectively. These distances are smaller than Li and B ones. Accordingly, N and O have reduced the overlap of the electron cloud between two carbon atoms at the adsorption site. In addition, adsorption energies are predicted to be -3.564 eV and -3.597 eV for N and O, respectively. Consequently, from the perspective of bond length and the reported values of the adsorption energy, N and O are strongly bounded to two carbon atoms. These facts mean that N and O are chemisorbed.

The adsorption of N and O atoms has induced a deforma-

tion of the graphene lattice. However, Li and B are rather far from the graphene and the its lattice is not deformed. The results concerning the adsorption of O on graphene are in good agreement with ref [27].

b. The adsorption of nX atoms on graphene

By increasing their coverage, Li atoms have preferred the hollow site as show in Fig. 3. The relaxed configurations are represented with equilibrium atomic distances. As reported in Fig. 3, Li-graphene distances increase as the Li coverage increases. However, Li-Li distances remain unchanged (2.85 Å). This value is slightly smaller than the distance between the Li-Li distance in the bulk bcc-Li (3.01 Å [28]). This means that a formation of Li-cluster is not favored. The distance between Li atoms and graphene is smaller than Li-Li one. This means that the physisorption of Li atoms on graphene is significant without deformation of the graphene sheet. Moreover, the adsorption site of the fourth Li atom is localized above the other three atoms. Li-Li distances on the same layer are identical to that of three Li atoms adsorbed on graphene with the distance between the fourth Li atom and others atoms is 3.05 Å. This behavior is the consequence of the Li clustering occurrence. This result is confirmed by G. Yang et al. [29] which have indicated that the stability of Li on graphene is due to the Li cluster configuration with increasing Li content.

For two B atoms, the first one is bounded to carbon atoms in bridge sites and the second one is vertically bounded to the first one. The B-B bond is 1.59 Å and the adsorption energy is -2.41 eV/B. For three and four B atoms, the equilibrium structure has indicated that two B atoms are bounded to the graphene sheet and other B atoms are bounded to each other in a triangular form. It can be concluded that the adsorption of B atoms on graphene has preferred the clustering configuration.

For two N atoms, the relaxed structure shows that two atoms are bounded to two surface carbon atoms while remaining bounded to each other with a bond length of 1.27 Å. The adsorption energy is -5.576 eV/N. Moreover, when three and four N atoms are adsorbed, two of them form a free dimer with an interatomic distance of 1.11 Å.

For two O atoms, the epoxy group is formed in the vicinity of each other. However, for three O atoms adsorbed on graphene, two atoms have formed a free dimer with a bond length of 1.25 Å. The remaining O atom is chemisorbed on the graphene sheet. When four O atoms are adsorbed, the relaxed structure has shown the formation of a free trimer (ozone) with a bond length of 1.31 Å and an angle of 117.21°. This indicates that oxygen atoms have a strong tendency to form a molecular structure on graphene.

The bond length values of free 2N, 2O, and 3O are similar to experimental molecular counterparts which are 1.098 Å, 1.208 Å, and 1.28 Å [30], respectively. The adsorption of B, N, and O atoms has stretched the C-C bound to 1.52 Å, 1.55 Å, and 1.51 Å, respectively. This means that the planar form of graphene was altered. As a consequence, the graphene sheet was distorted and atoms settle into a valley created by them. O atoms have formed an epoxy group as reported in available theoretical results [31, 32].

c. Formation, adsorption and interaction energies

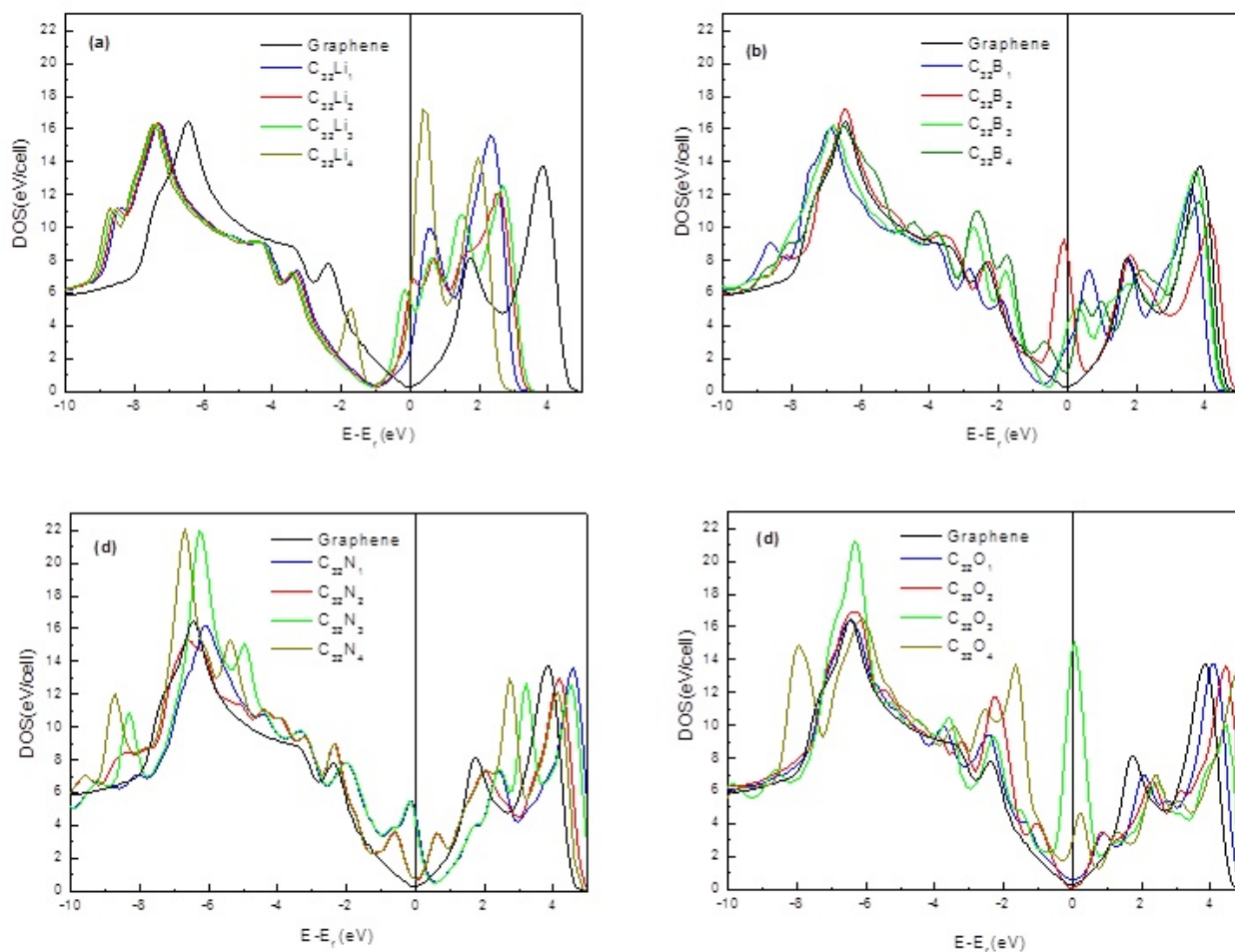


Figure 5. The total DOS of nX atoms on a graphene sheet compared to pure graphene (closed line). The Fermi energies of all systems are shifted to 0 eV.

To investigate the stability of nX atoms upon adsorption on a graphene sheet, we have calculated the adsorption energy of X atoms referenced to their bulk energies. We have also determined the interaction energy between the cluster and the graphene sheet. The interaction of nX atoms with a graphene sheet is considered stable if the adsorption energy absolute value is larger than the X bulk binding energy. Moreover, the nX atoms form a bond with the graphene sheet if the interaction energy is negative ($E_{int} < 0$). The enthalpy ΔH_f , the adsorption energy E_{ads} and the interaction energy E_{int} are defined as follows:

$$\Delta H_f = \frac{(E_{gra-nX} - nE_X^{bulk} - E_C^{bulk})}{n} \quad (1)$$

where E_{gra-nX} is the total energy of graphene with nX atoms ($X = \text{Li}, \text{B}, \text{N}, \text{and O}$), E_X^{bulk} and E_C^{bulk} are the energy of X and C in bulk structure, respectively, n is the number of adsorbed atoms.

$$E_{ads} = \frac{(E_{gra-nX} - nE_X - E_{gra})}{n} \quad (2)$$

$$E_{int} = \frac{(E_{gra-nX} - E_{nX}^{SL} - E_{gra}^{SL})}{n} \quad (3)$$

where E_X is the total energy of an isolated X atom, and E_{gra} is the total energy of graphene sheet. The E_{nX}^{SL} and E_{gra}^{SL} are the sublattice energies of nX and graphene, respectively.

In Fig. 4, we have represented adsorption and interaction energies for nX atoms on a graphene sheet versus the number of adsorbed atoms. As it can be shown in Fig. 4(a), adsorption energies for any X concentration have negative values. It is interesting to notice that the absolute value increases with the number of adsorbed B and N atoms. However, adsorption energies of Li and O remain unchanged. With increasing adsorbed atoms, obtained results indicate that Li and O have preferred to be physisorbed. Clustering and molecular configurations are noticed for Li and O, respectively. These results are confirmed by configurations of Fig. 3. Moreover, adsorption energies of Li and B are greater than bulk binding energies of Li (-1.63 eV/Li) and B (-5.81 eV/B). For Li, obtained results are in good agreement with those of Dimakis et al. [33]. For O and N, adsorption energies are smaller than molecular binding energies of O (-2.60 eV/O) and N (-4.92 eV/N).

To investigate the interaction of adsorbed atoms and the graphene sheet, we have represented X -C interaction energies in Fig. 4(b). As shown, all interaction energies are

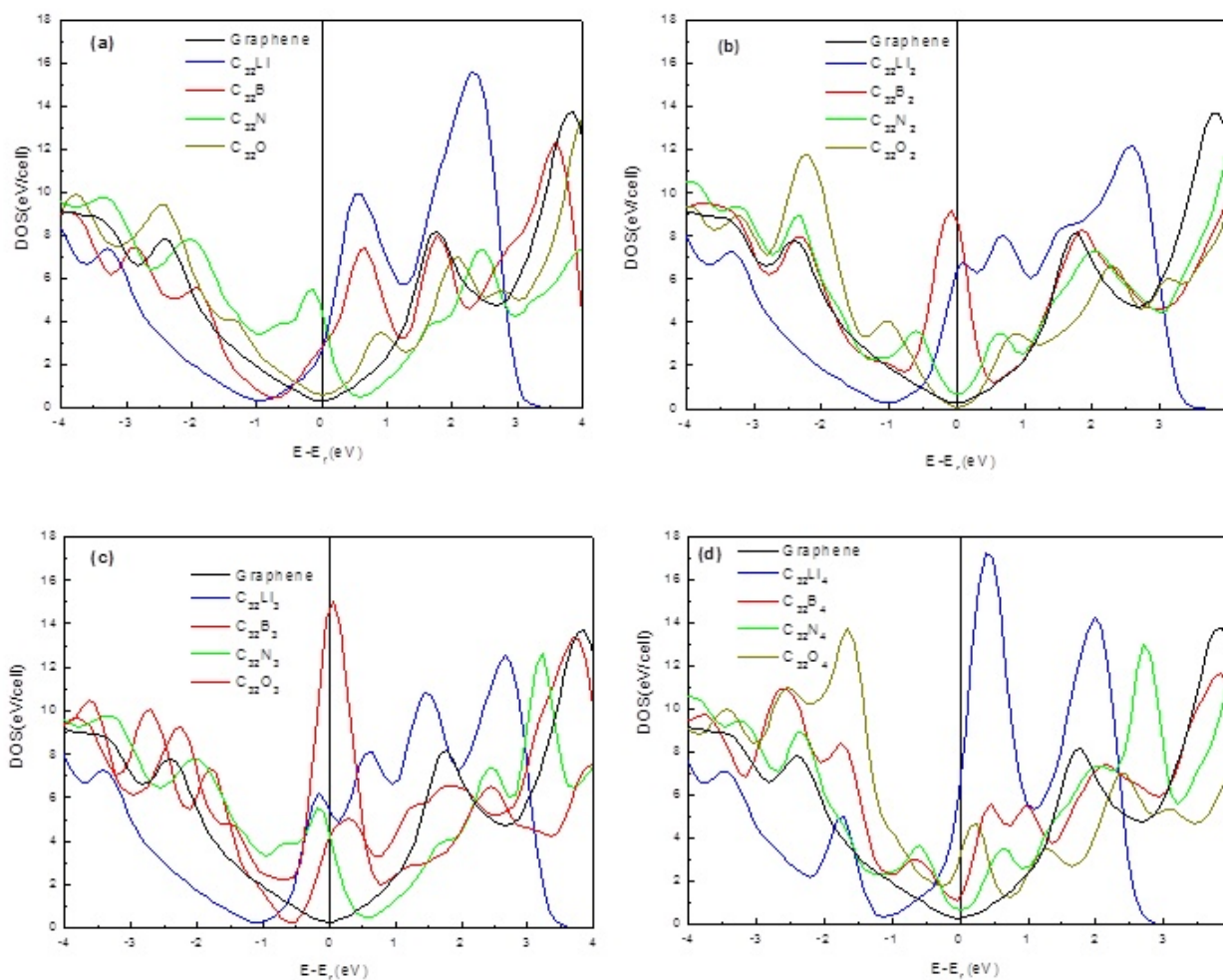


Figure 6. The comparison of the total DOS between the $nX-C$ systems for different concentrations.

attractive except for two and four N atoms. In these cases, interaction energies are repulsive. In addition, the Li-C bond is weaker when compared to other bounds. More details about formation energies and X-X interaction energies are given in Table 1. As indicated, all formation energies are negative indicating the stability of present systems. Also, all energies are low then the formation energy of monolayer of graphene which is about -0.55 eV/at. Thus, systems with adsorbed X atoms are more stable than the clean graphene and the stability increases with increasing number of X atoms.

For the X-X interaction, the Li-Li interaction is closer to the Li-C one. However, the Li cluster interacts weakly with the graphene sheet without any distortions (see Fig. 3). It can be deduced that the Li cluster is physisorbed on the graphene sheet, as concluded above. In contrast, the B-B interaction is weaker than the B-C one, which explains the strong distortion of the graphene sheet. This fact also leads to the formation of B clusters. Concerning N and O, N-N and O-O interactions are stronger than N-C and O-C ones, respectively. The N-N interaction for 2N and 4N atoms adsorbed on the graphene sheet is greater than the binding energy of N_2 (4.92 eV/at). This confirms the occurrence

of the molecular configuration of N and O on the graphene sheet. The detailed description of N and O adsorption is given below.

For 3N adsorbed on the graphene sheet, the N-N interaction is closer to the binding energy of N_2 . This indicates that one N atom is bounded to one C atom. Remaining two atoms have formed a molecule which interacts weakly with graphene. For 4N adsorbed atoms, the N-N interaction energy is close to the N-N one of 2N adsorbed atoms. Consequently, one N_2 molecule is freely formed on the graphene sheet. For two O adsorbed atoms, the O-O interaction energy is close to zero, indicating equilibrium between the attractive and the repulsive interaction. These two atoms have formed an attractive interaction with C atoms (epoxy group), as shown in the Fig. 4(b). However, interaction energies of 3O and 4O have close values and are comparable to the O_2 binding energy (2.6 eV/at). These results confirm the formation of O_2 and O_3 (ozone) molecules, as shown in the Fig. 3.

3.2 Structural and energetic properties

In this section, we examine the effects of the nX atoms on electronic properties of the graphene system. The Fig. 5

Table 1. The $X-X$ interaction energy of adsorbed atoms on graphene, E_{int} (in eV/at), and the formation energy, ΔH_f (in eV/at), of $C_{32}X_n$.

X	Li		B		N		O	
	E_{int}	ΔH_f	E_{int}	ΔH_f	E_{int}	ΔH_f	E_{int}	ΔH_f
$C_{32}X_1$	-0.00	-0.558	0.0	-0.571	0.0	-0.644	0.0	-0.645
$C_{32}X_2$	-0.57	-0.573	-1.56	-0.682	-7.26	-0.874	-0.003	-0.765
$C_{32}X_3$	-0.67	-0.603	-3.25	-0.880	-5.26	-1.124	-2.80	-0.900
$C_{32}X_4$	-0.74	-0.658	-3.51	-1.062	-7.56	-1.369	-3.08	-1.046

shows the DOS of $n\text{Li-C}$, $n\text{B-C}$, $n\text{N-C}$, and $n\text{O-C}$ ($n = 1 - 4$). For comparison, the total DOS of pristine graphene is also represented. As shown in all curves, graphene is a zero-bandgap material. However, nX atoms adsorbed on graphene change completely the electronic character of the system. DOSs near the Fermi level are significantly altered involving a charge transfer between the cluster and pristine graphene. The zero-bandgap character has disappeared in all cases.

In $n\text{Li}$ graphene systems, the total DOS represented in Fig. 5(a) shows that the $n\text{Li}$ adsorption leads to an upshift of the Fermi level into the conduction band due to a charge transfer from Li to graphene without any significant disruption of the π electronic system or graphene corrugation. All of these structures turn to a metallic character. These results are similar to those obtained by G. Yang et al. [29].

In the case of $n\text{B}$ graphene systems, all total DOS represented in Fig. 5(b) have the same behavior of Li-systems. Beyond the two atoms, the zero-bandgap character has disappeared and B-systems become metallic.

In the case of $n\text{N}$ graphene systems, the total DOS represented in Fig. 5(c) shows that the curves of N and 3N are similar. This is due to the formation of the N_2 molecule. The Dirac cone is shifted toward a higher binding energy with respect to pristine graphene which has the Dirac point at the Fermi energy, E_f . The conduction band appears below E_f . The zero-bandgap character has disappeared and systems become metallic. The DOS of 2N and 4N atoms are similar and more electronic states are fulfilled. The form of the DOS at the Fermi level suggests that the adsorption of 2N and 4N has pseudo-finite bandgap (semiconducting character).

For $n\text{O}$, the total DOS represented in Fig. 5(d) show that the curves of O and 2O adsorbed on graphene are similar. In these cases, finite energy gap arises at K point which leads to the change of the electronic states from a zero bandgap to a finite one. This result is confirmed by experiments [27]. The systems with O_2 or O_3 molecules have a metallic character as found experimentally [34] for O_2 adsorbed on the doped-graphene. It is important to notice the high conductivity character of 3O when compared to the 4O one.

To study the behavior of the atom cluster adsorbed on the graphene sheet, density of states for different concentrations are shown in Fig. 6. The results show that for all atoms and for each concentration, curves upshift in the conduction

band where the metallic character is pronounced except for the case of one and two oxygen. In these cases, the curves are very distinct. As shown, the adsorption of one O atom leads to a pseudo gap formation, whereas the adsorption of 2O atoms leads to an insulating character.

4. Conclusion

We have performed density functional theory calculations to investigate the structural and electronic properties of Li, B, N, and O atoms adsorbed on a graphene sheet. The results have shown an interesting behavior of clustering or molecule formation on a graphene sheet. To confirm these trends, relaxed geometries, adsorption and interaction energies, and electronic structures were calculated.

In the case of a single atom, Li and B atoms have preferred to be physisorbed without deforming the graphene sheet. However, the N and O atoms have preferred to be chemisorbed inducing a deformation of the graphene sheet. By increasing the number of X atoms, Li has preferred to be physisorbed with a cluster formation with a number greater than three. B has preferred to be chemisorbed with the clustering configuration. For N and O, a strong tendency to form a molecular structure on graphene was observed. It is important to note that the adsorption of B, N, and O atoms modifies the planar form of graphene.

DOS calculations for all adsorbed atoms have shown that the zero-bandgap character was disappeared in all cases. The adsorption of Li and B atoms has induced the loss of the zero-bandgap character which a metallic character appearance. However, the adsorption of 2N and 4N leads to an insulating (semiconducting) character. In addition, systems with O_2 or O_3 molecules have shown a metallic character. It is important to notice the high conductivity character of 3O when compared to the 4O one. The adsorption of one O atom has led to a pseudo gap formation, whereas the adsorption of 2O atoms has led to an insulating behavior.

Conflict of interest statement:

The authors declare that they have no conflict of interest.

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