

THE GEOMETRIC STRUCTURE AND MAGNETIC PROPERTIES OF Li ADSORBED ON MONOLAYER GRAPHENE

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We report the structural, electronic and magnetic properties of Li_n and single Li atom adsorbed on graphene supercell. The effect of the adsorption states for these atoms on 5×5 graphene supercell and with carbon vacancy on the value of the magnetic moment is studied. The total magnetic moments of supercells and local magnetic moments formed in the vicinity of vacancy carbon atoms are calculated. It was found that Li adsorbed on 5×5 graphene supercells with vacancies exhibit ferromagnetic spin ordering. Using the calculations of the adsorption energy in these structures, its dependence on the deformation of the graphene cell is investigated.

Keywords: graphene supercells, Li adsorbed graphene, Atomistix ToolKit software package, local spin density approximation

PACS: 31.15.E-, 71.15.Nc, 75.50.Gg, 81.05.ue

INTRODUCTION

Graphene has very high mechanical strength [1] and good thermal [2] and electrical conductivities at room temperature. These properties make it a potential candidate for applications in many fields such as electronics [3], sensors [4], and electrochemical storage systems [5,6] such as Li-ion batteries.

The vacancy defect can [7] improve energy barrier, and if a vacancy defect is big enough, lithium-ion migrating through the vacancy area from one layer to another is feasible. The possible applications of present study include rechargeable lithium-ion graphene battery and Li storage in carbon material. The interaction between graphene and Li will provide a theoretical basis for the future application of graphene in lithium ion battery [8]. Li adsorption on defective graphene has been reported using computational calculations [9,10]. Doping of graphene with electron-withdrawing elements [11] or electron-donating elements [12] changes the electronic structure of graphene which, in turn, may affect its electrochemical properties. Using density functional theory, interaction of up to two Li atoms with mono- and dual-doped graphene including P-doping is studied by Denis,[13] who concluded that Li adsorption on doped graphene offers a wide range of possibilities to fine tune the band gap in doped graphene systems. For elements like Si, adsorption of Li opens a band gap, for Al lithium restores the structure of the Dirac cones and the semimetallic character at the K-point, while for P it does not alter the gap at the K-point [13]. Thus, lithium dosage can be used to fine-tune the band gap in doped monodoped and dual graphene systems.

In this paper is developed by the first-principles calculations to explore the feature-rich properties of the Li-adsorbed graphene systems. The results of calculations of the properties of graphene also adsorbed by Li_n atoms and single Li atom are considered; the results of calculations of the adsorption energy are also presented. That is, all the calculated results are consistent with one another

under such mechanisms. Furthermore, they are responsible for the semiconductor-metal transitions after the Li_n atoms and single Li atom adsorptions and the creation of energy gaps in this case.

COMPUTATIONAL METHODS

To simulate the Li_n atoms and single Li atom adsorption on top of the graphene, we adopt the structures of 5×5 graphene supercell and 5×5 graphene supercell with vacancy. The electronic and magnetic properties of this structure are studied theoretically. The graphene properties were calculated using the density functional theory (DFT) method implemented using the Atomistix ToolKit. In addition, the adsorption energies and structural properties are investigated for the graphene supercell model.

First-principles calculations of graphene properties were carried out on the based on the spin-polarized density functional theory. The local spin density approximation in the Perdew–Zunger (PZ) parameterization was employed for the exchange–correlation functional. The kinetic cut-off energy is 150 Ry and the lattice constant of graphene $a=b=12.306\text{\AA}$, $c=6.709\text{\AA}$ is used. During the structure relaxation, all atoms are allowed to relax along the direction of graphene and all parameters are optimized with force and stress tolerances of 0.05eV/\AA and 0.05eV/\AA^3 , respectively. A $5 \times 5 \times 5$ k point was used for geometry optimization and total energy calculations.

DISCUSSION

The adsorption of several adatoms (Li,Na,K,Ca,Al,Ga, In,Ti,Fe,Co,Mn, etc.) on graphene is investigated [14-16]. In this research, we considered the adsorption of Li_n atoms and single Li atom on graphene at bridge sites and studied the resulting electronic and magnetic properties. We found unusual properties of graphene can be modified dramatically even at low Li_n and single Li adatom coverage. Notably, semimetallic graphene becomes metallized and attains finite spin polarization at the Fermi level.

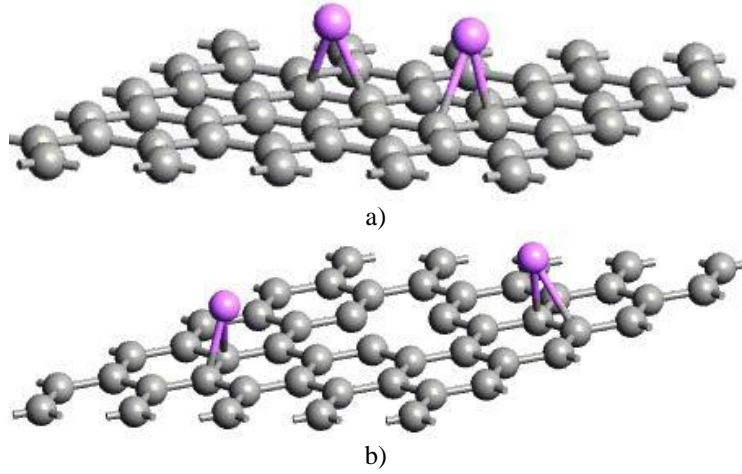


Fig. 1: The adsorption states for Li_α atoms on a) 5×5 graphene supercell, b) 5×5 graphene supercell with carbon monovacancies.

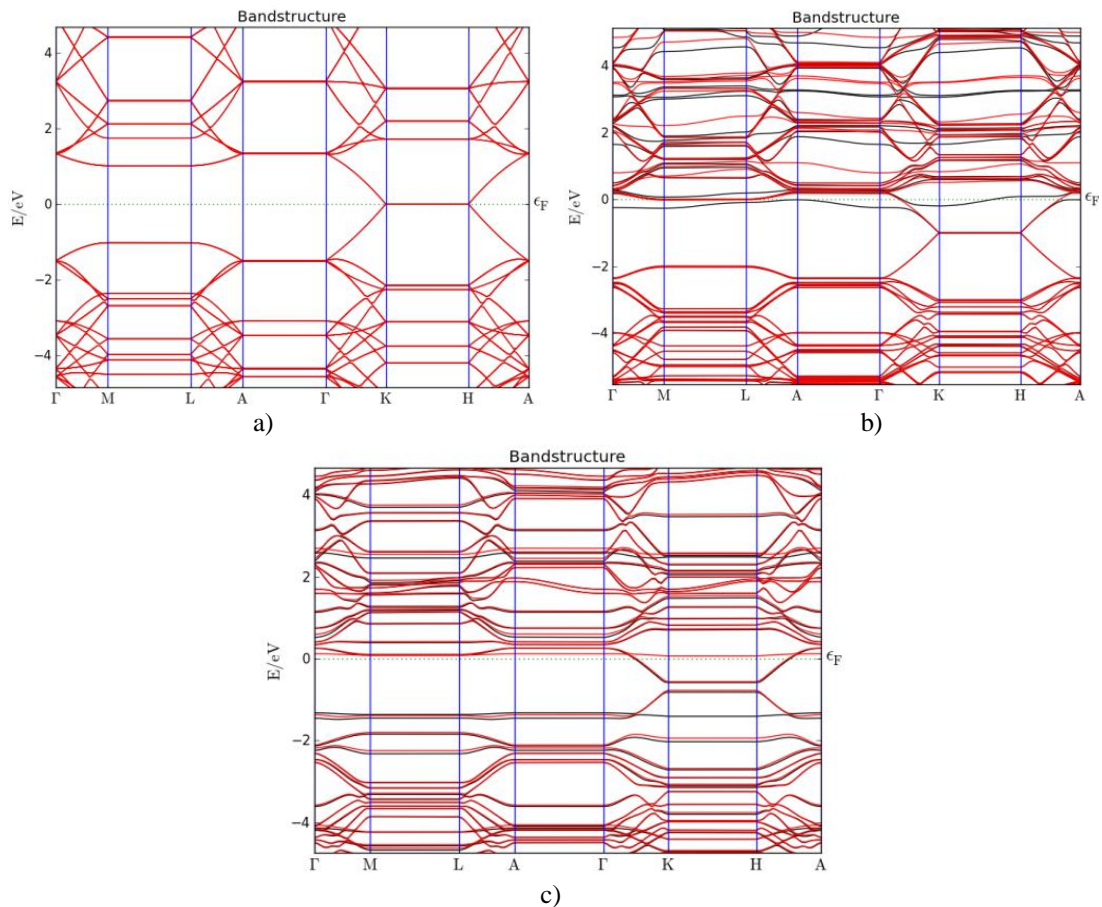


Fig. 2. Band structure of the a) 5×5 graphene supercell, b) Li_α adsorbed on 5×5 graphene supercell c) Li_α adsorbed on 5×5 graphene supercell with vacancy.

Let us, consider the electronic properties of a graphene supercell consisting of 50 carbon atoms. For illustration, Fig.1 presents the electronic band structure of graphene supercell consisting of 50 carbon atoms (Fig.1a), Li_α adsorbed on graphene supercell (Fig.1b) and Li_α adsorbed on graphene supercell with vacancy (Fig.1c).

The band structure of adsorbed on graphene supercells near the Fermi level was determined based spin-polarized calculations. An analysis of the band spectra presents that Li_α adsorbed on graphene

supercell with vacancy more efficient than Li_α adsorbed on graphene supercell for opening the energy gap. Defective graphene is associated with the presence of band gaps and thus, Li adsorptions can be used to tune these gaps [17].

We have studied magnetic moment in the adsorption states for Li_α atoms and single Li atom on 5×5 graphene supercell and with carbon vacancy. In this case the Mulliken population analysis gives the magnetic moments are received different values, as described in Table 1. The total magnetic moment of

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the graphene supercell by adsorption Li_{α} atoms is $0.703\mu_B$. Here the main contribution belongs to two Li atoms, which the local magnetic moments are acquired $0.266\mu_B$ (Li_{50}) and $0.355\mu_B$ (Li_{51}). The magnetic moment of Li_{α} atoms adsorbed onto the graphene supercell with a carbon vacancy is $0.962\mu_B$, and the local magnetic moment around the vacancy is $0.78\mu_B$ (C_{25}). In the case of the adsorption of a single Li atom on graphene supercell with a carbon vacancy the total magnetic moment is $0.996\mu_B$, and the local magnetic moment around the vacancy is $0.817\mu_B$ (C_{14}).

We have calculated the adsorption energy at bridge sites, which is defined as follows: $E_{ads}=E_{Li/Gr} - E_{Li} - E_{Gr}$, where E_{ads} is the adsorption energy, $E_{Li/Gr}$ is the total energy of the whole system including the Li and graphene, E_{Li} is the total energy of adsorbed atom, and E_{Gr} is the total energy of graphene. In order to represent the structure distortion after the adsorption,

we determine the height difference $\Delta h = z_{max} - z_{min}$ in the graphene, where z_{max} and z_{min} is the maxima and minima value of the z coordinate of the carbon atoms in graphene. The adsorption geometry is received of the atoms positions after relaxation. The bond length d_{LiC} is the distance between the lithium and the carbon atom nearest it in graphene. We have calculated the distance between the adsorbed Li_{α} atoms and C atom in graphene supercell. Here the nearest $Li_{51}-C_{35}$ and $Li_{50}-C_{24}$ bond length are 2.157\AA , 2.26\AA , respectively. Also the distance between the adsorbed Li_{α} atoms and C atom in graphene supercell with vacancy is calculated. Here the nearest $Li_{49}-C_{15}$ and $Li_{50}-C_{33}$ bond length are 2.16\AA , 2.175\AA , accordingly. The adsorption energy, defined in the above equation, is listed in Table 2. Here, the negative (positive) adsorption energy indicates that it is an exothermic (endothermic) process.

Table 1.

The value of magnetic moment

Graphene	total magnetic moments	magnetic moments around vacancy
Li_{α} adsorbed on 5×5 graphene	$0.703\mu_B$	$0.266\mu_B$ (Li_{50}), $0.355\mu_B$ (Li_{51})
Li_{α} adsorbed on 5×5 graphene with vacancy	$0.962\mu_B$	$0.78\mu_B$ (C_{25})
Li adsorbed 5×5 graphene	$0\mu_B$	---
Li adsorbed 5×5 graphene with vacancy	$0.996\mu_B$	$0.769\mu_B$ (C_{24})

Table 2.

Adsorption energy and bond length

Method	E_{ad} (eV)	d_{LiC} (\AA)	Δh (\AA)	Literary data
Li_{α} adsorbed on 5×5 graphene	0.73	2.157 ($Li_{51}-C_{35}$), 2.26 ($Li_{50}-C_{24}$)	0.13, 0.272	0.773 [15]
Li_{α} adsorbed on 5×5 graphene with vacancy	-1.17	2.188 ($Li_{49}-C_{15}$), 2.21 ($Li_{50}-C_{33}$)	0.028 0.026	-1.079eV [18]
Li adsorbed on 5×5 graphene	-0.72	1.81 ($Li_{50}-C_{14}$)	0.405	0.773 [15]
Li adsorbed on 5×5 graphene with vacancy	-1.83	2.126 ($Li_{49}-C_{24}$)	0.606	-

RESULT

We performed first-principle calculations based on DFT to investigate adsorption of Li_{α} and Li atoms on graphene supercell and with vacancy. These investigations are performed by using local spin density approximation method by employing the ATK program package. In particular, the adsorption energy and magnetic moments for graphene supercells adsorbed by Li_{α} and Li atoms differ from each other. The main contribution of the magnetic moment of the

graphene supercell in the adsorption states for Li_{α} atoms belongs to two Li atoms. However, the carbon vacancy existence of Li_{α} atoms adsorbed onto the graphene supercell, the value of the magnetic moment is increased as $0.962\mu_B$. In the presence of carbon vacancy for the adsorption of a single Li atom on graphene supercell the magnetic moment is acquired $0.996\mu_B$. In general the adsorption energy decreases in its absolute value with increasing atomic number for the adsorption of Li atoms on graphene supercell with vacancy.

- [1] C. Lee, X. Wei, J. W. Kysar, J. Hone. *Science*, 2008, 321, 385.
- [2] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau. *Nano Lett.*, 2008, 8, 902.
- [3] Y. Li, Z. Zhou, P. Shen, Z. Chen. *ACS Nano*, 2009, 3, 1952.
- [4] F. Schedin, A. Geim, S. Morozov, E. Hill, P. Blake, M. Katsnelson, K. Novoselov. *Nat. Mater.*, 2007, 9, 652.
- [5] W. Lv, D.-M. Tang, Y.-B. He, C.-H. You, Z.-Q. Shi, X.-C. Chen, C.-M. Chen, P.-X. Hou, C. Liu, Q.-H. Yang. *ACS Nano*, 2009, 3, 3730.
- [6] B. Z. Jang, C. Liu, D. Neff, Z. Yu, M. C. Wang, W. Xiong, A. Zhamu. *Nano Lett.*, 2011, 11, 3785.
- [7] Yan-Zi Yu and Jian-Gang Guo, Li-Jun Zhou. Theoretical investigation on the adsorption and diffusion of lithium-ion on and between graphene layers with size and defect effects *Adsorption Science & Technology* 2016, Vol. 34(2–3) 212–226. DOI:10.1177/0263617415623429.
- [8] Xiaoshuang Dai, Tao Shen, Yue Feng, Bin Yang & Hongchen Liu. First-principles investigation of the structure and electronic properties of graphene toward Li adsorption, *Molecular Simulation*, Published online: 01 Dec 2020, <https://doi.org/10.1080/08927022.2020.1846037>.
- [9] Y. Okamoto. Density Functional Theory Calculations of Lithium Adsorption and Insertion to Defect-Free and Defective Graphene. *J. Phys. Chem. C* 2016, 120, 14009–14014.
- [10] K. Shiota, T. Kawai. Li atom adsorption on graphene with various defects for large-capacity Li ion batteries: First-principles calculations. *Jpn. J. Appl. Phys.* 2017, 56, 06GE11.
- [11] N.T.T. Tran, D.K. Nguyen, O.E. Glukhova, M. F. Lin. *Sci. Rep.* 2017, 7, 17858, *Scientific Reports* volume 7, Article number: 17858, 2017.
- [12] B. Rani, K. Dharamvir. A first principle study of adsorption of two proximate nitrogen atoms on graphene, *Int. J. Quantum Chem.* 2014, 114, 1619, <https://doi.org/10.1002/qua.24741>.
- [13] P.A. Denis. Lithium adsorption on heteroatom mono and dual doped graphene, *Chemical Physics Letters* 2017, v. 672; p. 70-79, <http://dx.doi.org/10.1016/j.cplett.2017.01.036>.
- [14] H. Sevinçli, M. Topsakal, E. Durgun and S. Ciraci. *Phys. Rev.* 2008, B 77, 195434.
- [15] K. T. Chan, J. B. Neaton and M. L. Cohen. *Phys. Rev.* 2008, B 77, 235430.
- [16] C. Ataca, E. Aktürk and S. Ciraci. *Phys. Rev.* 2009, B 79, 041406(R).
- [17] N. Dimakis, I. Salas, L. Gonzalez, Om and et al. Li and Na Adsorption on Graphene and Graphene Oxide Examined by Density Functional Theory, *Quantum Theory of Atoms in Molecules, and Electron Localization Function, Molecules* 2019, 24, 754, doi:10.3390/molecules24040754.
- [18] J.H. Lee, S.G. Kang, H.S. Moon, H. Park, I.T. Kim, S.G. Lee. 2015. *Appl Surf Sci.* 351:193.

Received:19.01.2022