Journal of Atomic and Molecular Sciences

Global Science Press

ISSN 2075-1303

Electronic and optical properties of graphene adsorbed with methanol molecules: first-principles calculations

Received Nov. 22, 2017,
Accepted Dec. 29, 2017,

DOI: 10.4208/jams.112217.122917a

http://www.global-sci.org/jams/

Xiuwen Zhao[a], Mengyao Liu[a], Xiaotian Zhang[a], Yufeng Li[a], Xiaobo Yuan[a], and Junfeng Ren[a]*

Abstract. Properties of methanol molecules adsorbed on graphene are studied theoretically and various adsorption geometrical structures, density of states as well as the optical properties are obtained by means of first-principles calculations. Electronic characteristics and optical properties of graphene are sensitive to the molecule adsorptions. It is found that band gap appears when the methanol molecules are adsorbed. The dielectric function, refractive index, extinction coefficient, absorption coefficient and the reflectivity are changed. In the case of one methanol molecule adsorption, the peaks for the imaginary of the dielectric function and the adsorption coefficient shift to the high energy region, and new peaks appear in the visible range. The maximum value of extinction coefficient rises, and new peaks appear in the visible range when two methanol molecules are adsorbed.

1. Introduction

Graphene is found to be a magical two-dimensional material with a variety of remarkable functions since it was stripped from graphite in 2004 [1-3]. Graphene has set off a research boom in electronics, optics and biomedicine, et al [4-5]. Graphene is a single layer honeycomb lattice plane which is formed by sp^2 hybrid of carbon atoms, and it has zero band gap, the electronic energy band structure near the Fermi level shows linear dispersion relation [6-8]. Graphene has large specific surface area, outstanding thermal conductivity and perfect quantum tunnelling effect, et al. The rich and novel physical characteristics make graphene a shining star in nanoelectronics and optoelectronic devices [9-10]. What we should know is that some devices involving graphene require non-zero band gaps, that is, the nature of semiconductors. Zero band gap structure limits the development of graphene in the field of nanoelectronics and optoelectronic devices. Only to open the band gap of graphene can it be applied to various aspects. In recent years, the electronic and optical structures of graphene and their derivatives have been studied and significant modifications of graphene were noted [11-14]. There are various methods to adjust the band structure and open the band gap and modify the optical properties of graphene. One method is doping atoms such as N, B and N-B pairs with the condition that the atomic radii of N and B are close to C atoms, and in addition, after doping with these atoms, the electronic and optical properties of graphene will be significantly optimized [14-16]. By contrast, doped atoms usually have different electronic configurations than C atoms, and charge transfer occurs after atomic doping. Another method is adsorbing atoms or molecules, such as CO, NO, NO_2 and thiophene molecule et al. Since graphene has only one atomic layer thickness and is easily exposed to the outside world, the atoms and molecules adsorbed on the surface of graphene can change the structure of graphene by perturbing the π-electron network [17-20]. The topological disorders like ripples and Stone-Wales defects play an important role in optimizing the properties of graphene as well [21-22]. The interest in the study of graphene in photonic and optoelectronics is rising which is shown by its various applications, such as solar cells, lighting-emitting and touch screen et al., and optical properties of graphene have been extensively studied both theoretically and experimentally.

2. Theoretical methods

All our theoretical calculations are done through VASP (Vienna ab-initio Simulation Package) [23-24], PAW (projector-augmented-wave) pseudopotential is used to describe the interaction between ions and electrons [25-26], the GGA (generalized gradient approximation) in the form of PBE (Perdew-Burke-Ernzerh) is used to describe the exchange correlation energy function [27]. The cut-off energy is 400 eV in the process of the structural optimizations and calculations. A 7×7×1 Monkhorst-Pack grid is chosen when calculate the integral in Brillouin zone, and the energy convergence is set to less than 10^{-4}eV. In optimization calculation, the convergence accuracy of nuclear motion is less than 0.2 eV/Å. A 4×4×1 supercell (32 atoms) of pristine graphene is chosen. To avoid interlayer interference, the thickness of the vacuum layer is set to 15 Å. In order to investigate the relationship between the properties of graphene and the adsorption distance of methanol, the methanol molecules are fixed in the Z axis.

Only the interband transition is considered when we calculate the optical properties, so the dielectric function

[a] School of Physics and Electronics, Shandong Normal University, Jinan, 250014, China
*corresponding author. Email address: renjf@sdnu.edu.cn

may be inaccurate in the Drude region (low frequencies) [27]. The optical properties are general evaluated by the dielectric function which is the sum of real and imaginary parts, $\varepsilon(w) = \varepsilon_1(w) + i\varepsilon_2(w)$. The imaginary part is calculated by the summation of the empty band states using the following equation [29],

$$\varepsilon_2^{\alpha\beta}(w) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\epsilon_{ck} - \epsilon_{vk} - w) \times < u_{ck} + e_{\alpha q} | u_{vk} >< u_{ck} + e_{\beta q} | u_{vk} >^* \quad (1)$$

where the Ωrepresents the volume, v and c is the valence and conduction bands respectively, α and β indicate the Cartesian components, e_α and e_β are the vacuum dielectric constant, ϵ_{ck} and ϵ_{vk} refer to the energy of conduction and valence band respectively , u_{ck} is the cell periodic part of the orbitals at the k-point k. The real part of dielectric tensor is calculated by the Kramers-Kronig relation,

$$\varepsilon_1^{\alpha\beta}(w) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2^{\alpha\beta}(w')w'}{w'^2 - w^2 + i\eta} dw' , \quad (2)$$

where P denotes the principle value. According to the values of real and imaginary parts of dielectric function, the optical properties such as refractive index $n(w)$, the extinction coefficient $k(w)$, the absorption coefficient $\alpha(w)$ and the reflectivity $R(w)$ can be given by [30-31],

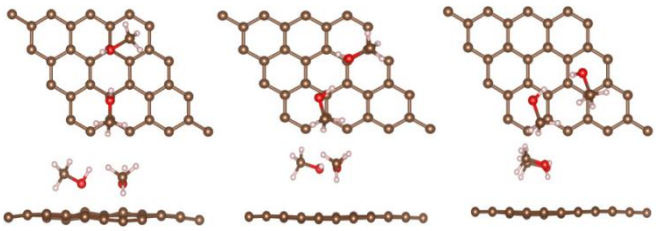
$$\alpha(w) = \frac{\sqrt{2}w}{c} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} - \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (3)$$

$$n(w) = \frac{1}{\sqrt{2}} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} + \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (4)$$

$$R(w) = \left| \frac{\sqrt{\varepsilon_1(w) + i\varepsilon_2(w)} - 1}{\sqrt{\varepsilon_1(w) + i\varepsilon_2(w)} + 1} \right|^2 , \quad (5)$$

$$k(w) = \frac{1}{\sqrt{2}} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} - \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (6)$$

3. Results and discussion

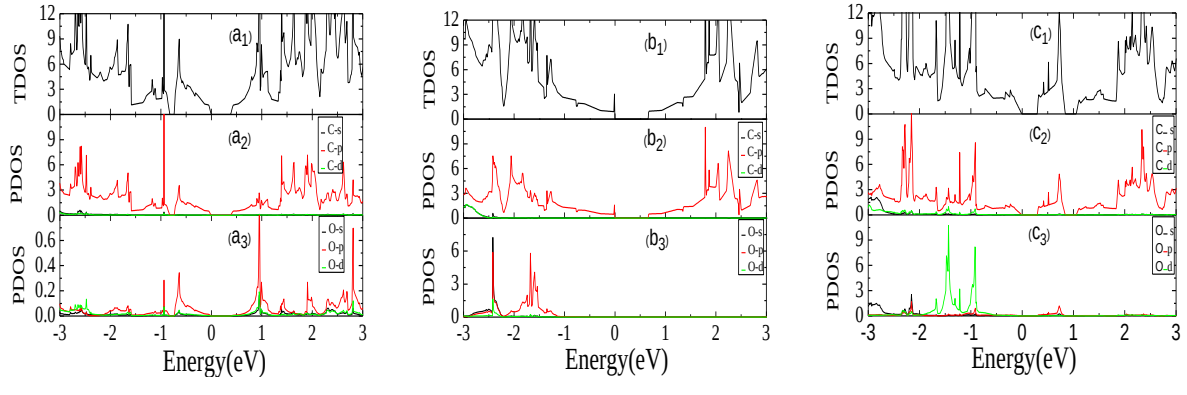


(a) (b) (c)

Figure 3.1: Top and side views of the relaxed structures with two methanol molecules adsorbed on graphene surface on (a) opposite position, (b) meta position, and (c) adjacent position. Red, white and brown spheres represent O, H and C atoms, respectively.

Different adsorption configurations are considered in our calculations. Firstly, one methanol molecule is adsorbed on the graphene surface with the oxygen atom on the top site. Secondly, two methanol molecules are adsorbed on the graphene surface, which contains three configurations, i.e., the two methanol molecules are in opposite, adjacent, and meta positions, respectively. All these two methanol molecules are adsorbed with oxygen atoms on the top site. Fig. 3.1 shows the relaxed configurations when the adsorption distance is 1.6 Å with two methanol molecules adsorptions.

It is well known that pure graphene has a zero band gap. After one methanol molecule is adsorbed on the graphene surface, the electronic properties have been modified, and a band gap appears. In our present work, we calculate the electronic properties of two methanol molecules absorbed on the surface of graphene, which is shown in the Fig. 3.2. Fig. 3.2(a) represents the total electronic density of states (TDOS) and the partial DOS (PDOS) of the two methanol molecules which are in the opposite position, Fig. 3.2(b) and Fig. 3.2(c) represent the TDOS and PDOS of two methanol molecules which are in adjacent position and meta position, respectively. From the TDOS, we can obtain that the electronic properties of graphene are changed significantly. Band gap opens, the value of the band gap in these three cases are 0.40 eV, 0.65 eV and 0.28 eV, respectively. It is thus evident from the figure that the band gap is sensitive to the adsorption sites.



(a) (b) (c)

Figure 3.2: TDOS and PDOS of two methanol molecules adsorbed in graphene in (a) opposite position, (b) meta position, and (c) adjacent position, respectively.

Moreover, by calculating the PDOS, we can see clearly that the electronic states near the fermi level are mainly hybridized by the orbitals of C-p and O-p when the two methanol molecules are in the opposite and meta positions. For the case when the two molecules are in the adjacent position, the electronic states near the fermi level are mainly hybridized by the orbitals of C-p and O-d.

Fig.3.3 shows the optical properties of pristine graphene. From Fig. 3.3 (a) and (b), people can see that the real part of the dielectric function has values less than zero while the imaginary part is always greater than zero. The imaginary part of the dielectric function of pristine graphene consists of significant peaks at small energy (0-5 eV) and these peaks are attributed to $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ interband transitions, respectively, which is explained in the previous work [32]. Fig. 3.3(c) presents the refractive index and its maximum is 2.3, and the value of the refractive index tends to 1 gradually when the energy increases to 30 eV. The optical adsorption index of pure graphene is shown in Fig. 3.3(d), we can see that the adsorption index is zero when energy is near the zero and there are two peaks at about 4.4 eV and 14.7 eV, respectively, the results are agreement with previous works [14, 33]. The reflectivity is shown in Fig. 3.3(e), the maximum value is 0.37 and the reflectivity is almost zero and keeps this value constant when the energy reaches to 32 eV. From Fig. 3.3(f) we can see that the maximum value of the extinction index is 1.4 when the energy is 4.2 eV.

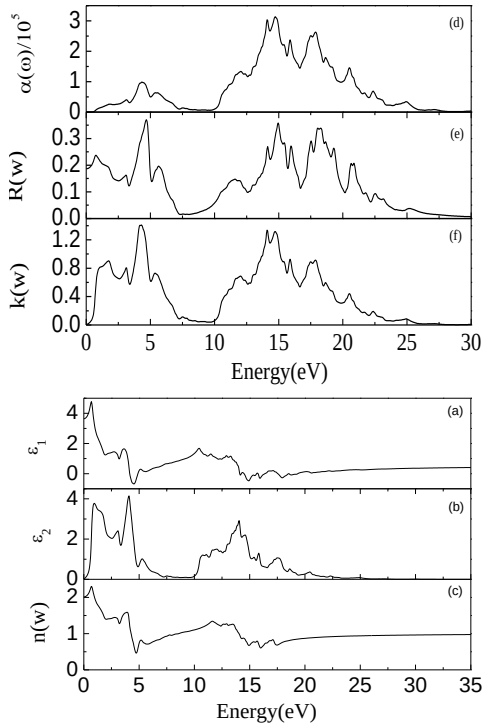


Figure 3.3: Optical properties of pristine graphene. (a) Real part of dielectric function, (b) imaginary part of dielectric function, (c) refractive index, (d) adsorption coefficient, (e) reflectivity, (f) extinction index.

After adsorbed methanol molecules, all the optical properties change. The dielectric function of graphene adsorbed methanol molecules are shown in Fig.3.4. From the Fig. 3.4 (a)-(d), it can be seen that the maximum value of the real part of the dielectric function is 5.8. The peak is at the position of 10.3 eV and the valley is at 14.8 eV. Earlier valleys at 15.8 eV and 17.8 eV vanish when two methanol molecules are adsorbed on the graphene. Moreover, the dielectric function curve tends to be smooth when the energy increases to 23 eV. When two methanol molecules are adsorbed in the opposite, adjacent and meta positions, the maximum values are 4.0, 3.2, and 4.6, respectively, and all these curves tend to be constant eventually. The imaginary parts are depicted in Fig. 3.4 (e), (f), (g) and (h). The peak at 13.9 eV of pure graphene is shifted to the high-energy range when one methanol molecule is adsorbed. And new peaks appear in the visible range for these four adsorption cases. The highest peak is 4.7 when the energy is 0.7eV, and the peak is much smaller than that of pristine graphene when the energy is 15.3 eV. It is observed that the maximum value of the imaginary is 4.5, 2.9, and 5.1, when the two methanol molecules are adsorbed in opposite, adjacent and meta positions, respectively.

The plots for the adsorption coefficients of graphene adsorbed by methanol molecules are shown in Fig.3.5. From Fig. 3.5(a), it can be seen that the peaks of the adsorption coefficient appear at about 4.5 eV and 15.4 eV when one methanol molecule is adsorbed. A distinct movement of the peaks takes place compared with that of pure graphene, while the width of the peaks becomes narrow. Fig.3.5 (b), (c), and (d) represent the adsorption coefficient of two methanol molecules adsorbed in the opposite, meta and adjacent positions, respectively. The peaks of these cases are shown at about 4 eV and 14 eV, no apparent movements occur for these peaks compared with those of pure graphene.

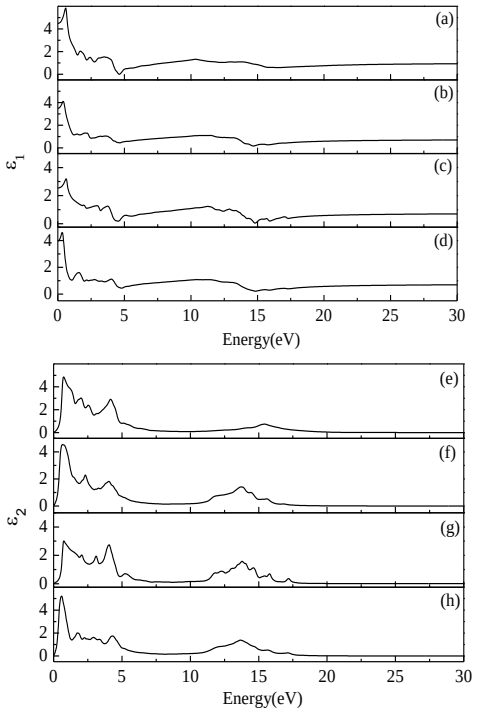


Figure 3.4: Real parts of dielectric function of graphene adsorbed by (a) One and two methanol molecules in (b) opposite position, (c) meta position, and (d) adjacent position, respectively. Corresponding imaginary parts are shown in (e), (f), (g), and (h).

Fig. 3.6 represents the refractive index of graphene adsorbed by methanol molecules. From Fig. 3.6 (a), we can see that the maximum value is 2.8 and it lies at 0.6 eV, the peaks lie in the range around 14 eV-20 eV in the pristine graphene vanish and the value tends to be 1. It can be seen from Fig. 3.6 (b) and (d) that the maximum values of the refractive index are 3.2 and 2.6 when two molecules are adsorbed in the opposite and adjacent positions, and the curves become smooth. For the case of Fig. 3.6(c), no noticeable change of the refractive index is observed comparing with that of pristine graphene. In other words, the value of the refractive index increases when one methanol molecule is adsorbed or two methanol molecules are adsorbed in opposite and adjacent positions. However, when two methanol molecules are adsorbed in meta position, the refractive index keeps almost unchanged.

The reflectivity index are shown in Fig.3.7. The maximum value of the reflectivity is 0.3 when the energy is 4.7 eV for the case when one molecule is adsorbed on the graphene surface, which is shown in Fig. 3.7(a). The peaks in the range of 14 eV-20 eV vanish compared with those of pristine graphene. For the three cases of two molecules adsorptions, which are shown in Fig. 3.7 (b), (c) and (d), the maximum values are 0.3, 0.25 and 0.2, respectively. The peaks of them become less obvious within the range of 14 eV-20 eV. In general, after adsorptions of methanol molecules, the reflectivity of graphene decreases in both low and high energy regions.

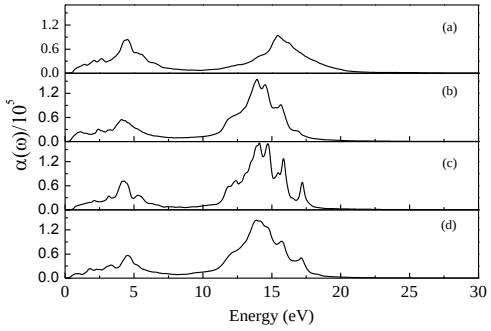


Figure 3.5: adsorption coefficient of the graphene adsorbed by (a) one methanol molecule and two methanol molecules in (b) opposite position, (c) meta position, and (d) adjacent position, respectively.

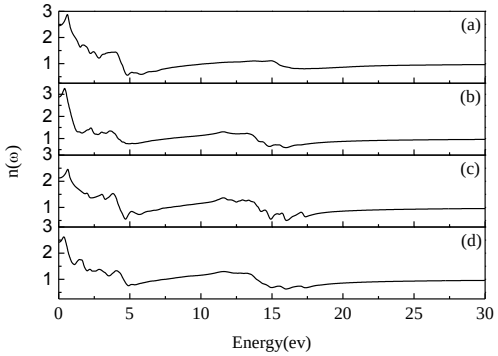


Figure 3.6: Refractive index of graphene adsorbed by (a) One methanol molecule and two methanol molecules in (b) opposite position, (c) meta position, and (d) adjacent position, respectively.

The extinction coefficient of graphene for the four different adsorption configurations are given in Fig. 3.8. The different changes of these curves can be identified. Overall, the maximum value of the extinction coefficient declines in Fig. 3.8 (a), (c) and (d). For the case of two methanol molecules adsorbed in opposite position, the maximum value rises. For the case of one methanol molecule adsorbed in graphene, the peaks in the range of 10 eV-25 eV almost disappear. Furthermore, the maximum values are located at about 4 eV for Fig. 3.8 (a) and (c). However, the maximum values are located at about 0.7 eV for (b) and (d). In addition, peaks appear in the visible range.

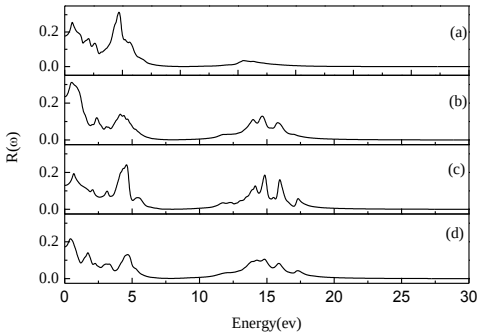


Figure 3.7: The reflectivity index of graphene adsorbed by (a) one methanol molecule and two methanol molecules in (b) opposite position, (c) meta position, and (d) adjacent position, respectively.

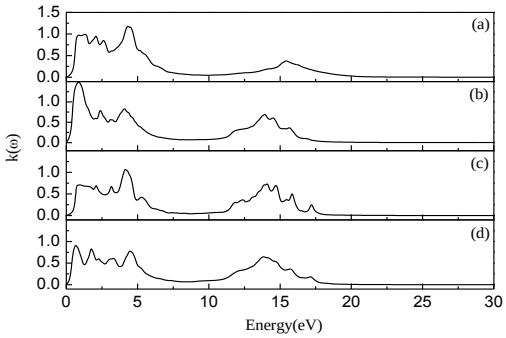


Figure 8: The extinction coefficients of graphene adsorbed by (a) one methanol molecule and two methanol molecules in (b) opposite position, (c) meta position, and (d) adjacent position, respectively.

4. Conclusions

In summary, the structural, electronic and optical properties of graphene adsorbed by methanol molecules are studied through first-principles calculations. Band gap appears after methanol molecules are adsorbed and the values of band gap are different for different adsorption configurations. In addition, we demonstrate the effect of methanol adsorptions on optical properties of graphene. For the real and imaginary parts of dielectric function, the maximum values change after the adsorptions, and the values of the real part tend to be constant eventually. Besides, new peaks appear in the visible range, and the peak of the imaginary and the adsorption coefficient shift to the high-energy range when one methanol molecule is adsorbed. The values of refractive index increase when one methanol molecule is adsorbed and two methanol

molecules are adsorbed in opposite and adjacent positions. However, the refractive index keeps almost unchanged when two methanol molecules are adsorbed in meta position. The reflectivity of graphene decreases in both low and high energy regions after the adsorption of methanol molecules. The maximum value of extinction coefficient rises, and peaks appear in the visible range when two methanol molecules are adsorbed in opposite position. All these calculations can be used to optimize the optical properties of graphene, and help to understand the optical properties of optoelectronic materials involving graphene.

Acknowledgements

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 11674197). Thanks to the supporting of Taishan Scholar Project of Shandong Province.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 306 (2014) 666.
[2] Y. Zhang, J. Small and P. Kim, Phys. Rev. Lett., 94 (2005) 176803.
[3] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, Nature, 442 (2006) 282.
[4] J. T. Robinson, S. M. Tabakman, Y. Liang, H. Wang, H. S. Casalongue, D. Vinh and H. Dai J. Am. Chem. Soc. 133 (2011) 6825.
[5] R. Kurapati, K. Kostarelos, M. Prato and A. Bianco, Adv. Mater., 29 (2016) 6052.
[6] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, Rev. Mod. Phys., 81 (2009) 109.
[7] D. S. L. Abergel, V. Apalkov, J. Berashevich, K. Ziegler and T. Chakraborty, Adv. Phys., 59 (2010) 261.
[8] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, Angew. Chem. Int. Edit., 48 (2009) 7752.
[9] F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari, Nat.Photonics, 4 (2010) 611.
[10] L. Kou, F. Hu, B. Yan, T. Frauenheim and C. Chen, Nanoscale, 6 (2014) 7474.
[11] D. Jana, C. L. Sun, L. C. Chen and K. H. Chen, Prog. Mater. Sci., 58 (2013) 565.
[12] D. Jana, L. C. Chen, C. W. Chen and K. H. Chen, Diam. Relat. Mater., 18 (2009) 1002.
[13] D. Jana, L. C. Chen, C. W. Chen and S. Chattopadhyay, Carbon, 45 (2007) 1482.
[14] P. Nath, S. Chowdhury, D. Sanyal and D. Jana, Carbon, 73 (2014) 275.
[15] X. K. Kong, C. L. Chen and Q. W. Chen, Chem. Soc. Rev., 43 (2014) 2841.
[16] J. Gebhardt, R. J. Koch, W. Zhao, O. Höfert, K. Gotterbarm, S. Mammadov, C. Papp, A. Görling, H. P. Steinrück and Th. Seyller, Phys. Rev. B, 87 (2013) 155437.
[17] Z. Xie, X. Zuo, G. P. Zhang, Z. L. Li and C. K. Wang, Chem. Phys. Lett., 657 (2016) 18.
[18] X. B. Yuan, M. S. Yang, Y. L. Tian, L. L. Cai and J. F. Ren, Synthetic. Met., 226 (2017) 46.
[19] A. S. Rad, Appl. Surf. Sci., 357 (2015) 1217.
[20] Y. L. Tian, J. F. Ren, W. W. Yue, M. N. Chen, G. C. Hu and X. B. Yuan, Chem. Phys. Lett., 685 (2017) 344.
[21] J. Ma, D. Alfè, A. Michaelides and E. Wang, Phys. Rev. B, 80 (2009) 033407.
[22] S. Chowdhury, S. Baidya, D. Nafday and S. Halder, Physica E, 61 (2014) 191.
[23] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson and K. S. Novoselov, Nat. Mater., 6 (2007), 652.
[24] G. Kresse and J. Hafner, Phys. Rev. B, 47, (1993) 558.
[25] G. Kresse and J. Furthmüller, Comp. Mater. Sci., 6 (1996) 15.
[26] P. E. Blöchl, Phys. Rev. B, 50 (1994)17953.
[27] G. Kresse and D. Joubert, Phys. Rev. B, 59 (1999)1758.
[28] H. Ehrenreich and H. R. Philipp, Phys. Rev., 128 (1962) 1622.
[29] M. Gajdoš, K. Hummer, G. Kresse and J. Furthmüller, Phys. Rev. B, 73 (2006) 045112.
[30] S. Saha, T. P. Sinha and A. Mookerjee, Phys. Rev. B, 62 (2000), 8828.
[31] B. Luo, X.Wang, E. Tian, G .Li and L. Li, J. Mater. Chem. C, 3 (2015) 8625.
[32] A. G. Marinopoulos, L. Reining, A. Rubio and V. Olevano, Phys. Rev. B, 69 (2004) 245419.
[33] W. Li, G. Cheng, Y. Liang, B. Tian, X. Liang and L. Peng, Carbon, 99 (2016) 348.