

Chemical functionalization of graphene via aryne cycloaddition: a theoretical study

Jing-xiang Zhao · Hong-xia Wang · Bo Gao ·
Xiao-guang Wang · Qing-hai Cai · Xuan-zhang Wang

Received: 18 September 2011 / Accepted: 9 November 2011 / Published online: 30 November 2011
© Springer-Verlag 2011

Abstract Chemical functionalization of graphene provides a promising route to improve its solubility in water and organic solvents as well as modify its electronic properties, thus significantly expanding its potential applications. In this article, by using density functional theory (DFT) methods, we have studied the effects of the chemical functionalization of graphenes via aryne cycloaddition on its properties. We found that the adsorption of an isolated aryne group on the graphene sheet is very weak with the adsorption energy of -0.204 eV, even though two new single C-C interactions are formed between the aryne group and the graphene. However, the interaction of graphene with the aryne group can be greatly strengthened by (i) substituting the H-atoms in aryne group with F-, Cl-, $-\text{NO}_2$ (electron-withdrawing capability), or CH_3 -group (electron-donating capability), and (ii) increasing the coverage of the adsorbed aryne groups on the graphene sheet. As expected, the strongest bonding is found on the graphene edges, in which the adsorbed aryne groups prefer to be far away from each other. Interestingly, chemical functionalization with aryne groups leads to an opening of the band gap of graphene, which is dependent on the coverage of the adsorbed aryne groups. The present work provides an insight into the modifications of graphene with aryne groups in experiment.

Electronic supplementary material The online version of this article (doi:10.1007/s00894-011-1309-8) contains supplementary material, which is available to authorized users.

J.-x. Zhao (✉) · H.-x. Wang · B. Gao · X.-g. Wang · Q.-h. Cai ·
X.-z. Wang
College of Chemistry and Chemical Engineering and Provincial
Key Lab for Advanced Functional Materials and Excite State,
Harbin Normal University,
Harbin 150025, People's Republic of China
e-mail: xjz_hmily@yahoo.com.cn

Keywords DFT · Functionalization · Graphene

Introduction

Since its discovery by Novoselov and co-workers in 2004 [1], free-standing graphene has attracted a great deal of attention. This can be expected, because the remarkable properties of graphene [2–12], such as atomically thin two-dimensional planar structure that consists of sp^2 -hybridized carbon atoms, high carrier mobility, high-integer quantum Hall effect at room temperature, spin transport, high elasticity, electromechanical modulation, and ferromagnetism, have made it a very promising candidate for use in solid-state sensors, energy storage materials, fuel cells, nanoelectronics, and spintronics.

However, two fundamental problems have imposed greatly to the use of graphene: (1) just as other newly discovered allotropes of carbon, such as fullerenes and carbon nanotubes, pure graphene sheets are hydrophobic and easily form irreversibly agglomerates due to their strong π - π stacking tendency [13]. This tendency has limited the further purification and processing of graphene materials; (2) it is well known that graphene is a semimetallic material and is absent of a band gap in its band structure [2–12], which limits its applications in electrical, optical, and magnetic areas. It is expected that chemical modification of graphene could not only enhance its solubility and processability in water and organic solvents, but also change its electronic properties as well as render many new properties to graphene, which greatly widen its application scopes [2–12, 14]. Thus, developing chemical methods to functionalize graphenes has become one of the most critical issues in exploring graphene technologies. For example, modifications in the electronic

properties of graphene have been reported by adsorption of a variety of functional groups, such as H [15], F [16], OH [17], COOH [18], and O [19], in which the hybridization state of carbon atoms is transformed from sp^2 into sp^3 and opens the band gap of graphene, even up to several electron volts [15]. On the other hand, attachment of nitrene [20], diazonium [21], and 1,3 dipolar molecule [22, 23] to graphene, is found to greatly improve its solubility in organic solvents, such as CCl_4 , CH_2Cl_2 , and THF [2b].

Very recently, Ma et al. demonstrated in experiment a simple and efficient approach to covalently functionalize pristine graphene sheets under mild reaction conditions by using aryne cycloaddition with easily accessible benzene precursors [24]. The resulting highly functionalized and thermally stable aryne-modified graphene sheets can be well dispersed in various solvents. Moreover, the authors pointed out that the electronic properties of graphene may be changed due to the functionalization with aryne groups [24].

Compared with the experimental advances, to our knowledge, no prior theoretical study has been reported for the functionalization of graphenes with aryne groups. In particular, the following questions are still unclear: (1) how does the coverage of adsorbed aryne group affect its interaction with graphene? (2) What are the effects of aryne group adsorption on electronic properties of graphene? To uncover the above questions, we report the first ab initio density functional theory (DFT) study of graphenes functionalized with aryne groups.

Methods and models

We carried out all-electron ab initio DFT calculations using double numerical basis set with polarization function (the DNP basis set), which are implemented in the DMol³ package [25, 26]. The generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) functional [27] was chosen for the spin-restricted DFT calculations. Test calculation with a spin-unrestricted method gave the same results. The used GGA/PBE method has also been successfully employed to study graphene systems in previous theoretical studies, including their functionalization with various functional groups [28–34]. A tetragonal supercell with dimension $17.22 \times 17.22 \times 30 \text{ \AA}^3$ (7 periodic lengths of graphene layer in both a and b directions) was chosen as the benchmark model system, which consists of 98 carbon atoms. The size of this employed supercell is large enough to completely remove the image interactions. For geometry optimizations, the Brillouin zone was sampled by $3 \times 3 \times 1$ special k -points using the Monkhorst-Pack scheme [35], while a $15 \times 15 \times 1 k$ -points was used for calculating electronic properties. The adsorption energy (E_{ads}) is defined as $E_{\text{ads}} = [E_{\text{total}}(\text{graphene-}n\text{aryne}) -$

$E_{\text{total}}(\text{graphene}) - n E_{\text{total}}(\text{aryne})]/n$, where E_{total} is total energy of the system in bracket, and n stands for the number of adsorbed aryne groups. By this definition, $E_{\text{ads}} < 0$ corresponds to a stable adsorption configuration and indicates bonding.

Results and discussion

Adsorption of aryne group on graphene at low coverage

We started with a low coverage of aryne group (C_6H_4) on graphene. Figure 1a shows the most stable configuration of attaching a single C_6H_4 to graphene through [2+2] cycloaddition. It is found that adsorption of an individual C_6H_4 on graphene sheet is very weak ($E_{\text{ads}} = -0.204 \text{ eV}$), suggesting that the functionalization of pristine graphene with C_6H_4 group with a low coverage is difficult. This weak interaction of one C_6H_4 group with graphene is further testified by calculated charge transfer with the Hirshfeld method [36]: about 0.039 electrons are transferred from graphene to C_6H_4 . Furthermore, in the optimized structure (Fig. 1a), the bond lengths of the formed C-C bonds are $\sim 1.546 \text{ \AA}$. In addition, C_6H_4 adsorption induces a slight deformation to graphene: (1) the two adsorbed carbon atoms by C_6H_4 group are pulled outward from graphene sheet; (2) the C-C bond lengths in graphene involving the C_6H_4 -adsorbed carbon atoms (1.496, 1.496, and 1.594 \AA) are longer than those in pristine graphene (1.420 \AA). Clearly, these C-C bonds have been weakened, thus rendering their chemical reactivity be enhanced.

To gain more insights into this process of an individual C_6H_4 adsorption on graphene, we further calculated the minimum energy pathway (MEP) from separated C_6H_4 and graphene using the nudged elastic band (NEB) method [37, 38]. This method has been widely used to search for MEP and transition state of reaction on graphene surface [28, 39–43]. Here, physisorption of a C_6H_4 on graphene sheet was chosen as reactant state, while the most stable configuration of C_6H_4 on graphene (Fig. 1a) was product state. The calculated MEP (Fig. 2) indicates that C_6H_4 will overcome an energy barrier of $\sim 1.711 \text{ eV}$ before being adsorbed on graphene. Thus, sufficient initial energy is required to overcome this large energy barrier. For the obtained transition state, the nearest distance between adsorbed C_6H_4 and graphene is $\sim 2.101 \text{ \AA}$. Conversely, to remove C_6H_4 from graphene sheet, an energy barrier $\sim 1.915 \text{ eV}$ should be overcome, that is, once formed, the functionalized graphene with a single C_6H_4 is expected to be stable at room temperature.

In the experimental study of Ma et al. [24], the authors found that pristine graphene can be chemically modified with other substituted C_6H_4 functional groups, such as

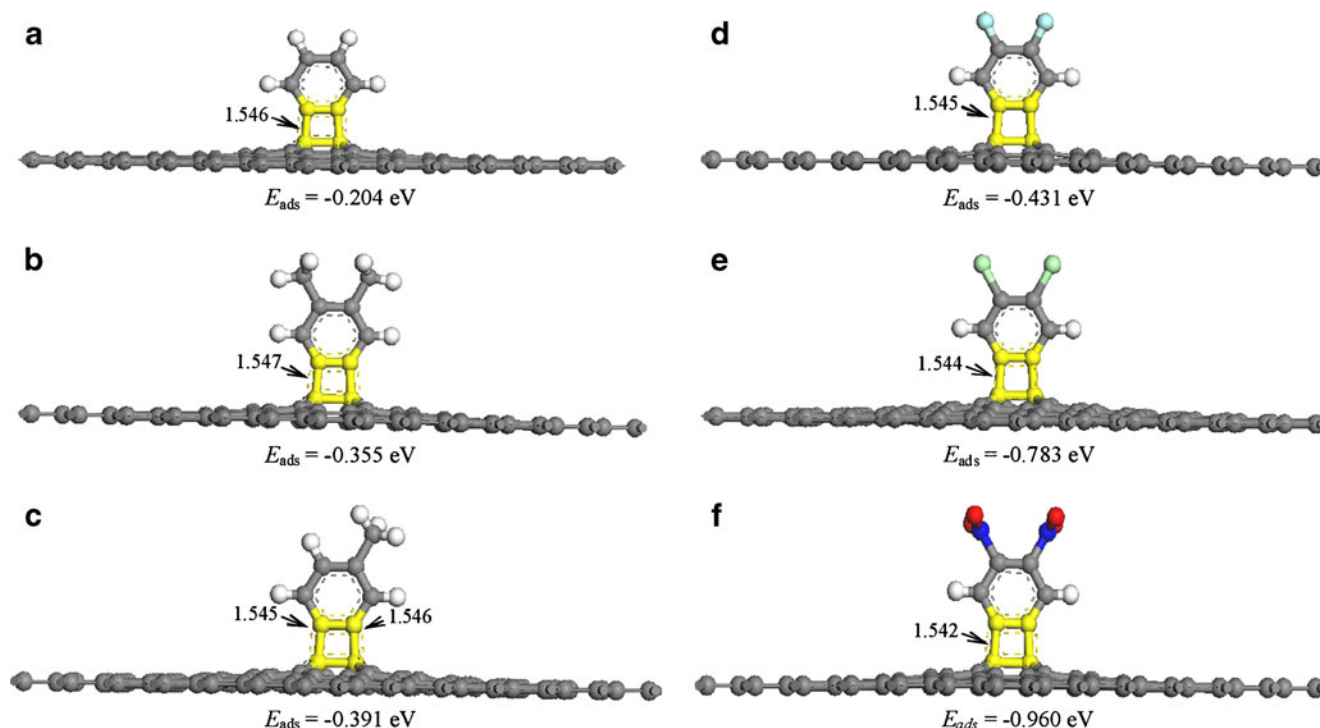


Fig. 1 The obtained stable adsorption configurations of the functionalized graphene sheet by an isolated (a) C_6H_4 , (b) $C_6H_2(CH_3)_2$, (c) $C_6H_3(CH_3)$, (d) $C_6H_2F_2$, (e) $C_6H_2Cl_2$, and (f) $C_6H_2(NO_2)_2$. The

binding region between arylene functional groups and graphene is highlighted in yellow. The bond distances are in angstroms

$C_6H_2F_2$, $C_6H_3(CH_3)$, and $C_6H_2(CH_3)_2$. Thus, we studied the adsorption of other arylene functional groups on graphene, including $C_6H_2F_2$, $C_6H_2Cl_2$, $C_6H_2(NO_2)_2$,

$C_6H_3(CH_3)$, and $C_6H_2(CH_3)_2$. The calculated adsorption energies and the shortest distances between graphene and these adsorbates are listed in Fig. 1b–f. It is found that all C_6H_4 functional groups can be adsorbed on graphene via [2+2] cycloaddition. The lengths of the newly formed C–C bonds range from 1.542 to 1.547 Å. The adsorption energies of these substituted C_6H_4 functional groups are larger than that of C_6H_4 group. The trend of change of adsorption energy can be understood on the basis of the relative electron-withdrawing or -donating capability of adsorbed molecular groups. Since about 0.039 electrons are transferred from graphene to C_6H_4 , the charge transfer from graphene to adsorbates should be increased when H-atoms in C_6H_4 are replaced with -F, -Cl, or -NO₂ groups with electron-withdrawing nature. Thus, the adsorption of arylene functional group on graphene is strengthened. In contrast, because CH₃- has electron-donating capability, the adsorption of $C_6H_3(CH_3)$ and $C_6H_2(CH_3)_2$ on graphene is weaker than that of $C_6H_2F_2$, $C_6H_2Cl_2$, $C_6H_2(NO_2)_2$.

One of the most important purposes of the functionalization of graphene is to modify its electronic properties. Thus, we explored the effects of the adsorption of a single C_6H_4 group on electronic properties of graphene. In Fig. 3, we depict the calculated electronic band structures for functionalized graphene as well as pristine graphene for comparison. It should be pointed out that GGA methods tend to underestimate the band gap of semiconductors. But

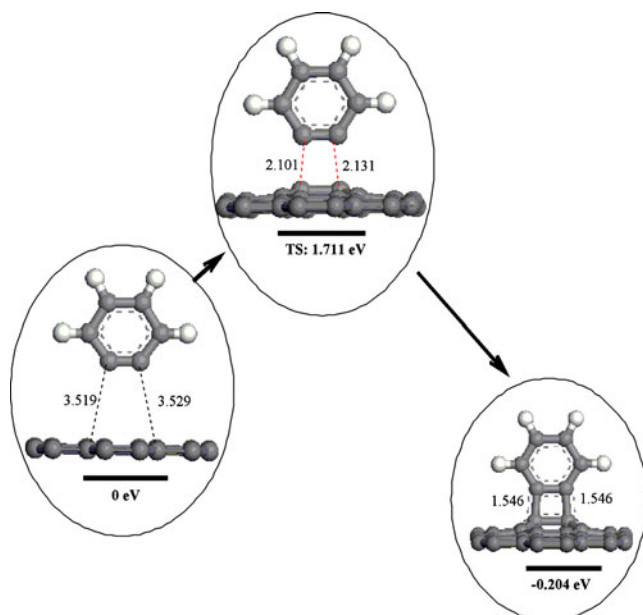


Fig. 2 The minimum energy path (MEP) for the functionalization of the graphene with a single C_6H_4 group (product state) from separated C_6H_4 group and graphene sheet (reactant state). The distances are in angstroms

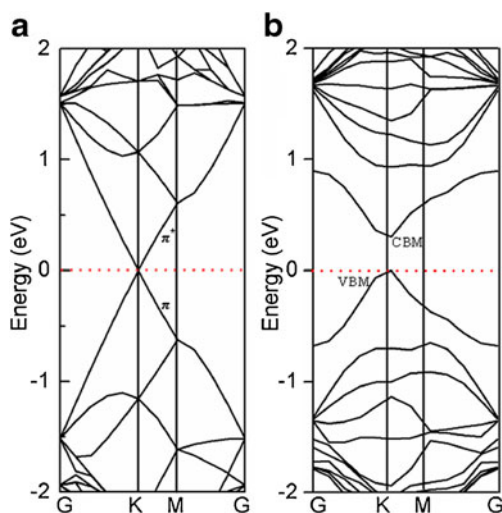


Fig. 3 Electronic band structure of a graphene sheet (a) before and (b) after the adsorption of a single C_6H_4 group. Red dashed lines denote the Fermi level. $G = (0, 0, 0)$, $K = (-1/3, 2/3, 0)$, and $M = (0, 1/2, 0)$ in the Brillouin zone. G represents the Γ point

this theoretical deficiency will not affect qualitative analysis of the trend of the changes in electronic properties due to functionalization. Our DFT calculation reproduces known results that pristine graphene is semimetallic. Upon adsorption of one C_6H_4 group, the π and π^* linear dispersion of pristine graphene in the proximity of the Dirac point (K) largely preserves, while there exists a band gap with ~ 0.299 eV between π and π^* states. Obviously, C_6H_4 group adsorption leads to an opening of band gap of graphene, rendering it semiconducting characteristic. Furthermore, we plot the highest occupied state (HOS) and lowest unoccupied state (LUS) at Γ point of functionalized graphene (Fig. 4). The results suggest that both the minimum of the conduction band edge (CBM) and the maximum of the valence edge (VBM) at the Γ point are mainly contributed by graphene as well as a few carbon atoms of C_6H_4 that form covalent bonds with graphene.

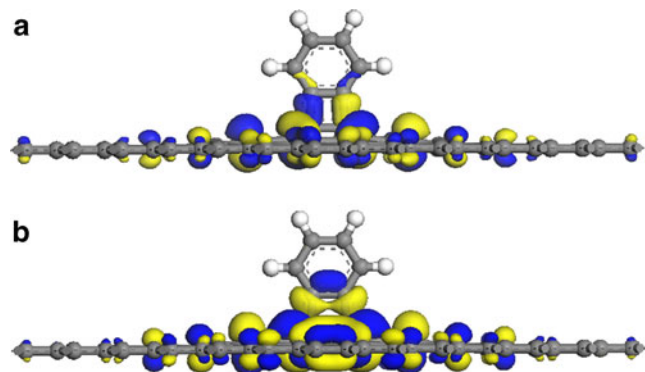


Fig. 4 Profiles of (a) HOS and (b) LUS at the Γ point for the functionalized graphene by a single C_6H_4 group. The isosurface value is 0.025 au

Adsorption of aryne group on graphene at high coverage

In addition to C_6H_4 attachment to graphene at a low coverage, the high coverage of C_6H_4 adsorption on graphene sheet is also investigated to provide a further comparison. First, we studied a second C_6H_4 adsorption on the basis of the results of a single C_6H_4 adsorption. Two kinds of initial models were considered: the second C_6H_4 is on (1) the same or (2) the other side of the first adsorbed C_6H_4 on graphene.

After full structural optimization for these initial configurations, the most stable adsorption configuration for a second C_6H_4 is located on the para-site of the first C_6H_4 , in which the two adsorbed C_6H_4 groups lie across graphene (Fig. 5a). The adsorption energy of this configuration is -0.730 per C_6H_4 group, which is much larger than that of one C_6H_4 group (-0.204 eV). About 0.045 electrons are transferred from graphene to C_6H_4 groups, which is slightly larger than that of one C_6H_4 group (0.039). Furthermore, a small energy barrier of ~ 0.100 eV is encountered before the second C_6H_4 is adsorbed on graphene as shown in Fig. 6, which is much smaller than that of the first C_6H_4 (1.711 eV). In light of the large adsorption energy and the small energy barrier, we expect that a second C_6H_4 adsorption on graphene is easier than that of the first C_6H_4 . This is understandable, because these C-C bonds around the first C_6H_4 have been “activated” and possess higher chemical reactivity toward adsorbates than other C-C bonds in graphene. This fact can be testified by calculated projected density of states (PDOSs) near the Fermi level of C_6H_4 -graphene complex (Fig. 7): the C-C bonds at the para-site of the first C_6H_4 have the sharpest

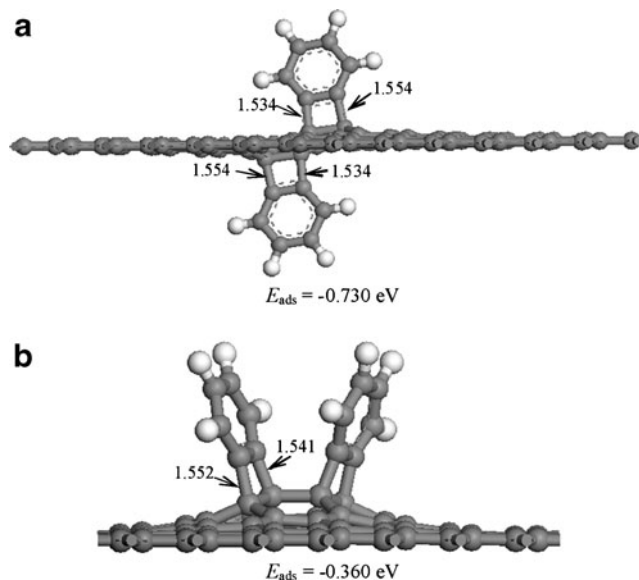
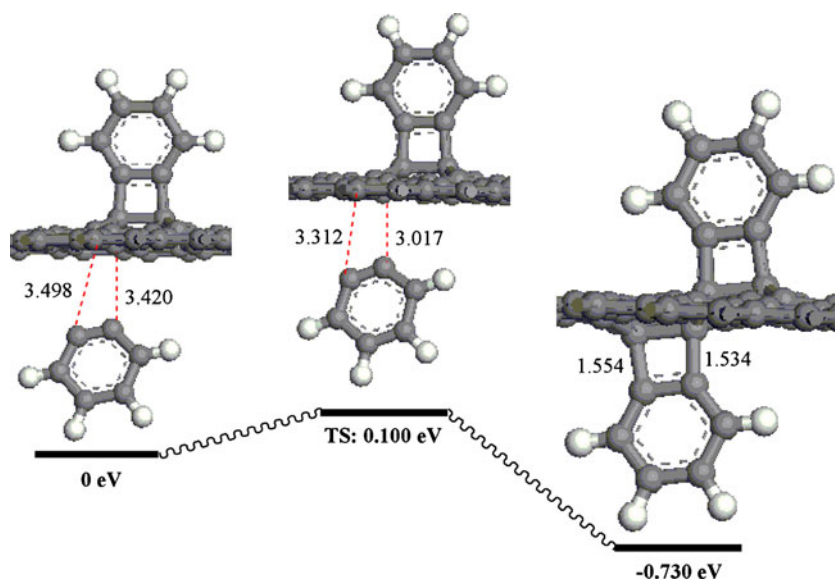


Fig. 5 The optimized structures of a second C_6H_4 group on the graphene sheet. Various adsorption sites are examined. The bond distances are in angstroms

Fig. 6 The minimum energy path (MEP) for the functionalization of the graphene of a second C_6H_4 group. The distances are in angstroms



peak. In addition, the other metastable configuration is also obtained as shown in Fig. 5b, whose adsorption energy is -0.360 eV. For this metastable configuration, its steric repulsion between adsorbed C_6H_4 groups on the same side of graphene, may be responsible for its adsorption energy being lower than that of the double-side adsorption (Fig. 5a).

The next question is: what will happen if more than C_6H_4 groups are attached to graphene? To answer this question, we

performed further calculations to study the adsorption of four and six C_6H_4 groups on a graphene on the basis of two C_6H_4 groups adsorption. The most stable configurations for four and six C_6H_4 adsorptions are given in Fig. 8. The calculated adsorption energies for four and six C_6H_4 groups are -0.834 and -0.881 eV, respectively, which are much larger than that of at low coverage (-0.204 eV). This shows that pristine graphene can be functionalized by C_6H_4 groups with a high coverage. When more than six C_6H_4 groups are bound with graphene, the obtained complex is unstable due to the large steric repulsion among these C_6H_4 groups. Hence, up to six C_6H_4 groups can be adsorbed on a pristine graphene

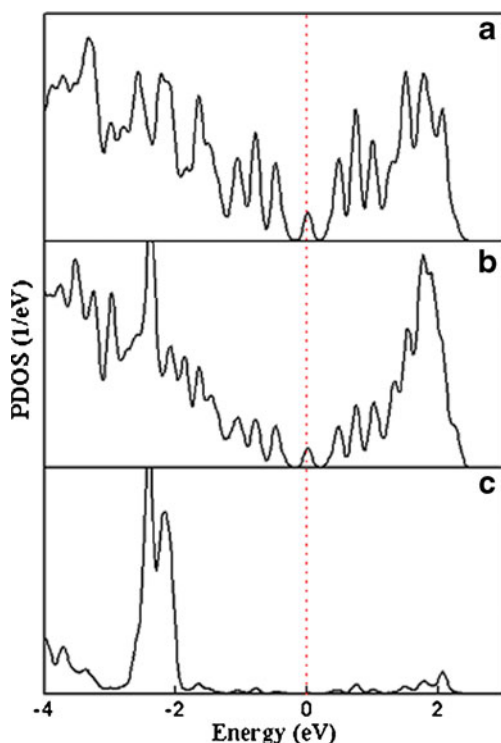


Fig. 7 The projected PDOS of (a) the para-site carbon, (b) other site carbon, and (c) C_6H_4 group. Red dashed lines denote the Fermi level

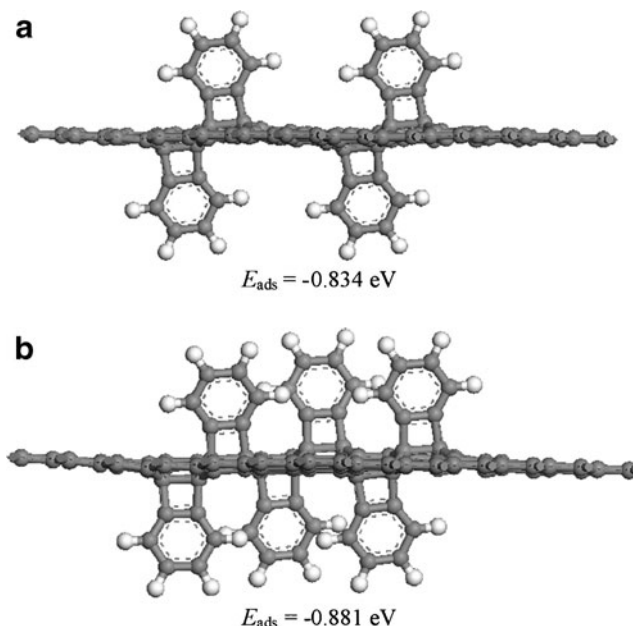


Fig. 8 The optimized structures of (a) four and (b) six C_6H_4 groups on the graphene sheet

consisting of 98 carbon atoms. This is in good agreement with Ma's experimental study [24]: the degree of functionalization is approximately one functional group per 16 carbon atoms.

Since the functionalization of C_6H_4 at a low coverage can effectively open a band gap of graphene, how do electronic properties of graphene modify upon adsorption of more C_6H_4 groups? As shown in Fig. 9, we found that 1) after the covalent functionalization with two or four C_6H_4 groups, the π and π^* state dispersions of pristine graphene at the Dirac point preserve, while there is a large perturbation upon six C_6H_4 groups adsorption on graphene sheet; 2) band gaps of graphenes after adsorption of two, four, and six C_6H_4 groups are opened in various ways: the band gap is 0.327, 0.925, and 0.190 eV for two, four, and six C_6H_4 groups adsorption, respectively. Obviously, the alteration of electronic properties of functionalized graphene is determined by the coverage of adsorbed C_6H_4 groups.

Adsorption of aryne group on graphene nanoribbon

Due to the two-dimensional nature of graphene sheet, the edge regions play an important role in electronic structures

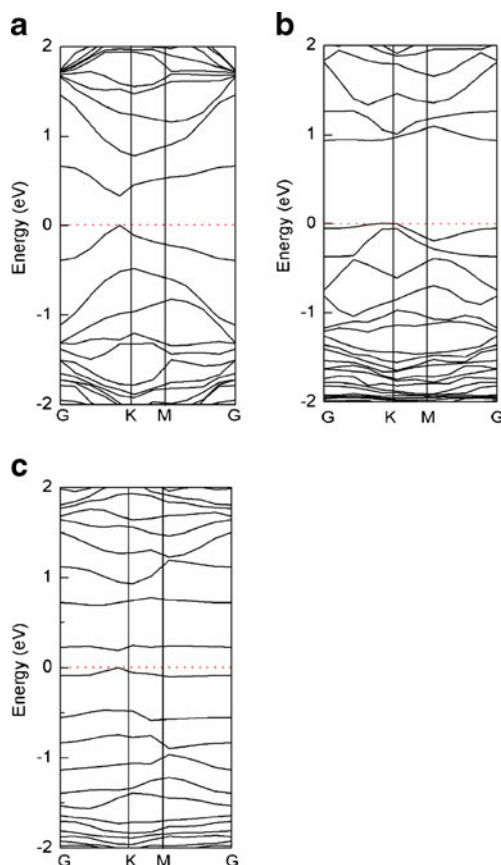


Fig. 9 Electronic band structure of the functionalized graphene sheet by (a) two, (b) four, and (c) six C_6H_4 groups. Red dashed lines denote the Fermi level

of molecules. In this section, we studied C_6H_4 adsorption on a graphene nanoribbon and was compared with that of on graphene plane. A graphene nanoribbon with armchair edge, which displays lower reactivity than zigzag edge [2 h], was used. The edges of the armchair graphene nanoribbon were saturated with hydrogen atoms. The C_6H_4 group was initially considered to be adsorbed on the top (Fig. 10a) or seat site

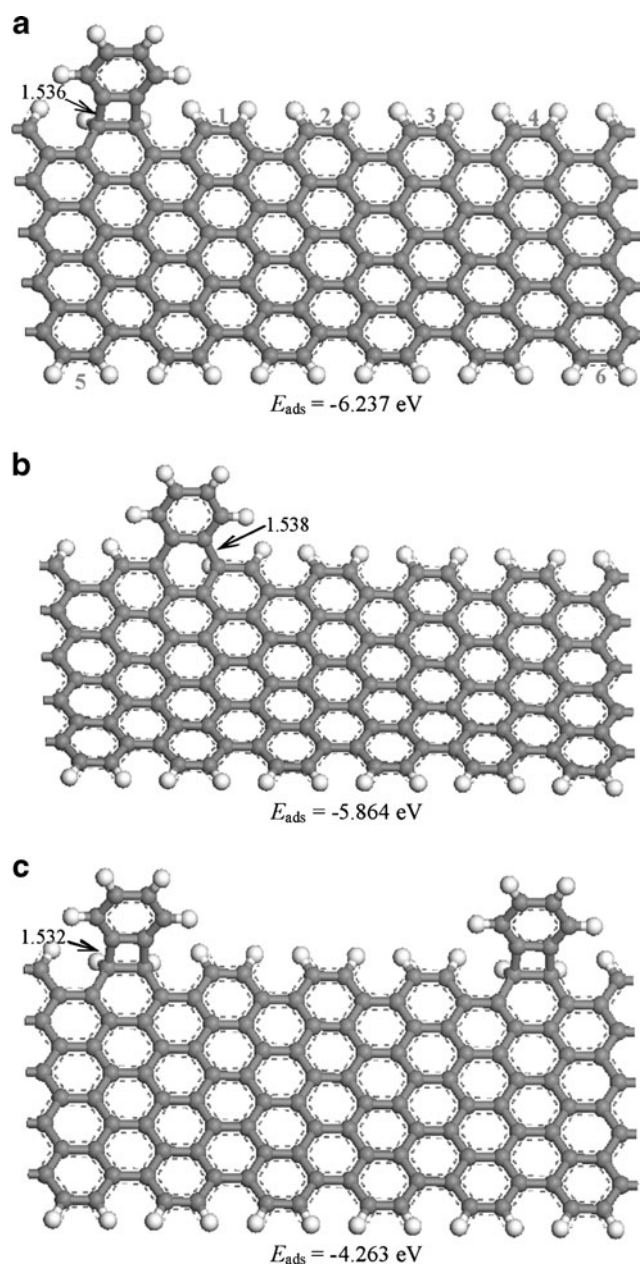


Fig. 10 The optimized structures of (a) an individual C_6H_4 group adsorbed on the top site in the armchair graphene nanoribbon, in which the number in red denotes the potential adsorption sites for a second C_6H_4 group, (b) an individual C_6H_4 group adsorbed on the seat site in the armchair graphene nanoribbon, and (c) the most stable configuration of two C_6H_4 groups attached to the armchair graphene nanoribbon. The distances are in angstroms

(Fig. 10b) in an armchair edge. The results indicate that the former ($E_{\text{ads}}=-6.237$ eV) is more energetically favorable than the latter ($E_{\text{ads}}=-5.864$ eV), which are much larger than that of graphene plane ($E_{\text{ads}}=-0.204$ eV). It is obvious that the edges of graphene nanoribbon exhibit much higher activity than graphene plane.

Attaching a second C_6H_4 group to edge site of graphene nanoribbon is also different from that to graphene sheet. After the structural optimization for different adsorption sites (Fig. 10a), the most stable configuration is given in Fig. 10c. The second C_6H_4 group is shown to be far away from the first one and they locate on the same side of graphene edge. The average adsorption energy of this configuration is -4.263 eV, being smaller than that of a single C_6H_4 group (-6.237 eV). Given the tendency that zigzag edge displays higher reactivity than armchair, it can be expected that C_6H_4 attachments to zigzag edges are stronger those of armchair edges. In addition, adsorption of C_6H_4 groups on armchair graphene nanoribbon renders its band gap be increased by 0.027 eV (for one C_6H_4 group) and 0.190 eV (for two C_6H_4 group), respectively, as displayed in Fig. S1 of Supporting information.

Conclusions

By exploring the chemical functionalization of graphene with arylene groups (C_6H_4) using DFT calculations, we found that C_6H_4 group with a low coverage is weakly adsorbed on graphene sheet. However, the interaction of graphene with C_6H_4 group at high coverage is considerably stronger because of the “activation” of some C-C bonds near the adsorbed C_6H_4 group upon adsorption of one C_6H_4 group, i.e., these C-C bonds possess higher reactivity toward incoming adsorbates than other sites of graphene. Furthermore, it was found that graphene nanoribbon has much higher reactivity toward C_6H_4 groups. The most important is that the band structures of graphene systems near the Fermi level are greatly disturbed after covalent functionalization of C_6H_4 groups. This leads to an opening of band gaps of graphenes to different degrees. Our calculations offer a better understanding of the experimental results that graphene sheets can be effectively functionalized with arylene groups at a high degree.

Acknowledgments This work is supported by the China Postdoctoral Science Foundation (20110491119), Heilongjiang Postdoctoral Science Foundation (LBH-Z10049), Committee of Education of Heilongjiang Province (11541095), the Natural Science Foundation of Heilongjiang Province (ZD200820–01, B200814), the Key Project of Chinese Ministry of Education (NO.210060), and the Scientific Research Foundation for Doctor of Harbin Normal University (08XKYL38). The authors would like to show great gratitude to the reviewers for raising invaluable comments and suggestions.

References

- Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) *Science* 306:666–669
- Geim AK (2009) *Science* 324:1530–1534
- Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A (2009) *Angew Chem Int Ed* 42:7752–7777
- Rao CNR, Biswas K, Subrahmanyam KS, Govindaraj A (2009) *J Mater Chem* 19:2457
- Neto AHC, Guinea F, Peres NMR, Novoselov KS, Geim AK (2009) *Rev Mod Phys* 81:109–162
- Taghioskouei M (2009) *Mater Today* 12:34–37
- Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS (2010) *Adv Mater* 22:3906–3924
- Allen MJ, Tung VC, Kaner RB (2010) *Chem Rev* 110:132–145
- Loh KP, Bao Q, Ang PK, Yang J (2010) *J Mater Chem* 20:2277–2289
- Terrones M, Botello-Méndez AR, Campos-Delgado J, López-Urías F, Vega-Cantú YI, Rodríguez-Macías FJ, Elías AL, Muñoz-Sandoval E, Cano-Márquez AG, Charlier J-C, Terrones H (2010) *Nanotoday* 5:351–372
- Abergel DSL, Apalkov V, Berashevich J, Ziegler K, Chakraborty T (2010) *Adv Phys* 59:261–282
- Choi W, Lahiri L, Seelaboyina R, Kang YS (2010) *Crit Rev Solid State Mater Sc* 35:52–71
- Li D, Muller MB, Gilje S, Kaner RB, Wallace GG (2008) *Nat Nanotechnol* 3:101–105
- Boukhvalov DW, Katsnelson MI (2009) *J Phys: Condes Mat* 21:344205
- Elias DC, Nair RR, Mohiuddin TMG, Morozov SV, Blake P, Halsall MP, Ferrari AC, Boukhvalov DW, Katsnelson MI, Geim AK, Novoselov KS (2009) *Science* 323:610–613
- Nair RR, Ren W, Jalil R, Riaz I, Kravets VG, Britnell L, Blake P, Schedin F, Mayorov AS, Yuan S, Katsnelson MI, Cheng HM, Strupinski W, Bulusheva LG, Novoselov KS, Geim AK (2010) *Small* 6:2877–2884
- Wang L, Sun YY, Lee K, West D, Chen ZF, Zhao JJ, Zhang SB (2010) *Phys Rev B* 82:161406
- Al-Aqtash N, Vasiliev I (2009) *J Phys Chem C* 113:12970–12975
- Xu Z, Xue K (2010) *Nanotechnol* 21:045704–045707
- Strom TA, Dillon EP, Hamilton CE, Barron AR (2010) *Chem Comm* 46:4097–4099
- Lomeda JR, Doyle CD, Kosynkin DV, Hwang WF, Tour JM (2008) *J Am Chem Soc* 130:16201–16206
- Georgakilas V, Bourlinos AB, Zboril R, Steriotis TA, Theodore A, Dallas P, Stubos AK, Trapalis C (2010) *Chem Comm* 46:1766–1768
- Quintana M, Spyrou K, Grzelczak M, Browne WR, Rudolf P, Prato M (2010) *ACS Nano* 4:3527–3633
- Zhong X, Jin J, Li S, Niu Z, Hu W, Li R, Ma J (2010) *Chem Comm* 46:7340–7342
- Delley B (1990) *J Chem Phys* 92:508–517
- Delley B (2000) *J Chem Phys* 113:7756–7764
- Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865–3868
- Wu X, Zeng XC (2009) *Nano Lett* 9:250–256
- Jiang D, Sumpter BG, Dai S (2006) How Do Aryl Groups Attach to a Graphene Sheet? *J Phys Chem B* 110:23628–23632
- Choi WI, Jhi SH, Kim K, Kim YH (2010) *Phys Rev B* 81:085441
- Manna AK, Pati SK (2009) *Chem Asian J* 4:855–860
- Dai J, Yuan J, Giannozzi P (2009) *Appl Phys Lett* 95:232105–232108
- Dai J, Yuan J, Giannozzi P (2010) *Phys Rev B* 81(7):165414

34. Suggs K, Reuven D, Wang XQ (2011) *J Phys Chem C* 115:3313–3317
35. Monkhorst HJ, Pack JD (1976) *Phys Rev B* 13:5188–5192
36. Hirshfeld FL (1977) *Theor Chim Acta* 44:129–138
37. Henkelman G, Jónsson H (2000) *J Chem Phys* 113:9978
38. Olsen RA, Kroes GJ, Henkelman G, Jónsson H (2004) *J Chem Phys* 121:9776–9792
39. Li Y, Zhou Z, Yu G, Chen W, Chen Z (2010) *J Phys Chem C* 114:6250–6254
40. Li Y, Zhou Z, Shen P, Chen Z (2010) *Chem Comm* 46:3672–3674
41. Song EH, Wen Z, Jiang Q (2011) *J Phys Chem C* 115:3678–3683
42. Ao ZM, Peeters FM (2010) *Appl Phys Lett* 96:253106–253109
43. Ao ZM, Peeters FM (2010) *J Phys Chem C* 114:14503–14509