

Theoretical investigation on two-dimensional non-traditional carbon materials employing three-membered ring and four-membered ring as building blocks

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ABSTRACT

A series of two-dimensional non-traditional carbon materials employing three-membered ring or four-membered ring as building blocks were systematically investigated by theoretical calculations in searching of highly conductive metallic carbon materials. It was found all the studied two-dimensional systems have metallic nature. The three-membered ring derivatives are not kinetically stable, and present of trap-like bands. While the four-membered ring systems of C4-8 and its derivatives containing triple bonds are kinetically stable, which provide a new choice of synthesizing two-dimensional carbon materials with metallic nature towards the application in the all carbon electronic circuits.

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1. Introduction

Graphene, which is a single sheet composed of sp^2 -hybridized carbon with honeycomb structure, has drawn great attention owing to its outstanding electronic, optical, thermal and mechanical properties [1–5]. Especially, its unique and superior charge transport and electronic properties strongly stimulate scientists to find its application in the field of organic field effect transistor [6–8]. However, as a semi-metal material with fused six-membered ring, graphene has unsatisfied application in OFET due to the smaller on-off ratio [1]. Thus, much effort is paid to open its

bandgap to address this issue [9–19]. The outstanding progress in the research field of graphene has triggered many interests in exploring novel two-dimensional materials through both experiments and theoretical calculations [20–29]. For example, another important 2D carbon allotrope, graphdiyne, is successfully synthesized by Li et al. through bottom up approach [30]. This new carbon allotrope has been predicted to be a semiconductor with theoretical band gap of 0.46 eV and the calculated hole and electron mobility are 1.97×10^4 and $2.81 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively [31]. However, most of these 2D materials mainly employed six-membered rings as building units due to the good stability and lowest ring strain energy. Using the ring systems other than six-membered rings remains unexplored. Until recently, 2D sp^3 - or sp^2 -hybridized carbon allotropes based on five-membered ring system (known as “penta-graphene”) was investigated by theoretical calculation, and the former is proved to have an intrinsic quasi-direct band gap of 3.25 eV [32], while the later exhibits metallic [33,34] and ferromagnetic nature [35]. Synthetic effort has demonstrated the possible co-existence carbon materials with other phases [36]. However, searching novel 2D carbon allotropes based on three- or four-membered rings is not successful due to the

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possible poor stability and synthetic challenge although few theoretical calculations based on three- and four-membered ring system have already been conducted [22,37–46].

Considering the emergence of 2D carbon-based materials and their advantages, it is of extreme importance to systematically investigate the electronic structures and stabilities of 2D carbon allotropes based on three- and four-membered rings, which are connected by single and triple C–C bonds. Such theoretical predictions are highly desirable and instructive to search metallic carbon materials.

The simplest three- and four-membered ring organic molecules are cyclopropene and cyclobutadiene, and the electronic structures for cyclopropene radical and cyclobutadiene are very unique. Both cyclobutadiene and cyclopropene radical are anti-aromatic compounds. According to the Hückel molecular orbital (HMO) theory [47], the ground state for cyclobutadiene is open-shell triplet, which has two unpaired electrons with the same α spins. For cyclopropene radical, there are two degenerate molecular orbitals for one electron based on HMO theory. We have optimized the geometrical structures of cyclobutadiene and cyclopropene radical through DFT calculations (MP2/6-311+G**) [48–50], and the frequency analysis was followed to assure that the optimized structures were stable states. The calculated spin density for these two molecules is show in Fig. 1. The optimized structure for cyclobutadiene is planar, and the C–C bond length in cyclobutadiene ring is 1.446 Å, which is between the bond length of C–C and C=C. However, the optimized structure for cyclopropene radical is not planar (Fig. S1), and the spin is mainly localized on the sp^3 -hybridized carbon. Therefore there are two kinds of C–C bond in cyclopropene radical, one is the $C(sp^3)$ – $C(sp^2)$ bond with length of 1.467 Å, the other is $C(sp^2)$ – $C(sp^2)$ bond with shorter length of 1.326 Å. Based on the above calculation results, we are trying to connect the cyclobutadiene or the cyclopropene radical ring through C–C single bonds and triple bonds (structures are shown in Fig. 2) and investigate the electronic structures of the corresponded 2D materials.

2. Computational methods

The first-principle calculations were carried based on density functional theory (DFT) within the generalized gradient approximation (GGA). These calculations were performed by Vienna *ab initio* simulation package (VASP) [51,52], which implement the projected augmented wave approach (PAW) [53]. The exchange correlation was calculated by the Perdew–Burke–Ernzerhof functional as revised for solids (PBEsol) [54]. The PBE-PAW

pseudopotentials with s^2p^2 orbitals were used for carbon ions. The energy cutoff was set as 500 eV. To avoid interactions between two layers, a 15 Å vacuum layer was inserted. These geometry structures were optimized until the force on every atom is smaller than 0.001 eV/Å. Γ -centered $9 \times 9 \times 3$ Monkhorst-Pack mesh k -points were used for static calculations, including density of states (DOS) and band structure. 60 k points were employed in two high symmetric k points in order to get accurate band structures and effective masses. The details to calculate the effective mass could be found at our recent works [55]. The phonon band structures and temperature-dependent free energies were obtained by Phonopy with the force constants generated based on finite displacement method [56,57]. Thermodynamic properties are calculated from phonon frequencies on a sampling mesh in the reciprocal space. $4 \times 4 \times 1$ supercells were used to estimate the force constant for C4-8, C4-16, C4-24, C3-12 and C3-24. While a $3 \times 3 \times 1$ supercell was used for C3-36 due to its large unit cell.

3. Results and discussion

All these six 2D materials have planar structure, and the optimized structures with unit cells are show in Fig. S2.

3.1. The optimized geometry of the studied 2D systems

The lattice constants (a or b) are increasing from 3.44 to 6.02 and 8.59 Å for C4-8, C4-16 and C4-24. The C–C bond length of the cyclobutadiene ring in these three materials is almost identical, with value of 1.465, 1.472 and 1.471 Å for C4-8, C4-16 and C4-24, which is slightly longer than the bond length for the parent cyclobutadiene calculated by DFT calculation. But the C=C bonds connected the cyclobutadiene rings show decreased bond lengths of 1.371, 1.344 and 1.345 Å, which indicates C4-8 with the combination of cyclobutene and cyclooctatetraene units is more stable (Fig. 3). Similar phenomenon has been also observed in C3-12, the C–C bond length in the cyclopropene ring is 1.421 Å, and the connected bond of the cyclopropene rings is 1.355 Å. The lattice constants for the C3-12, C3-24 and C3-36 are 5.19, 9.64 and 14.08 Å, respectively.

3.2. The ground states of the studied 2D systems

The spin-polarized calculations were performed for these six structures to confirm their ground state, however, no energy difference between spin-polarized and spin-unpolarized computations was observed, which suggests that all these six structures have a close shell ground state and there are no unpaired electrons or unsaturated dangling bonds in these monolayers.

3.3. The cohesive energy and temperature dependent free energy of the studied 2D systems

Moreover, the stability of these 2D materials was compared by calculating the cohesive energy (E_{coh}), which is defined as Eq (1).

$$E_{coh} = \frac{n \cdot E(C) - E(C_n)}{n} \quad (1)$$

Where $E(C)$ and $E(C_n)$ are the total energies of single carbon atom and the studied 2D monolayer (unit cell), and n is the number of carbon atoms in the repeat units of the studied 2D system. Based on our calculation, C4-8 shows the largest cohesive energy of 7.46 eV/atom among all the investigated 2D systems in this work (Table S1), which is 0.51 eV/atom lower than that of graphene (7.97 eV/atom) based on our calculation with the same theoretical level (the reported E_{coh}

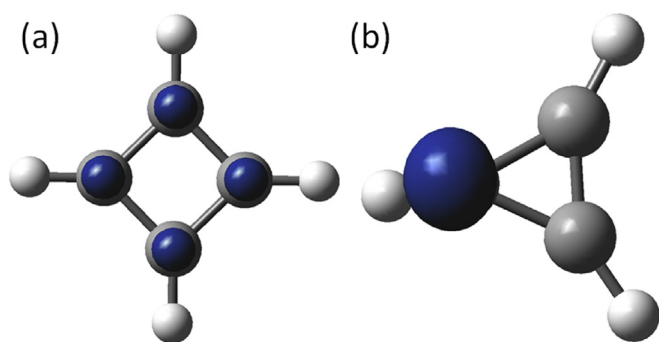


Fig. 1. The spin density distributions of cyclobutadiene (a) and cyclopropene radical (b) calculated by MP2 functional with 6-311+G** as the basis set. Blue surface represents α spin density (there is only α spin in cyclobutadiene and cyclopropene radical), drawn at 0.04 e/au³ level, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

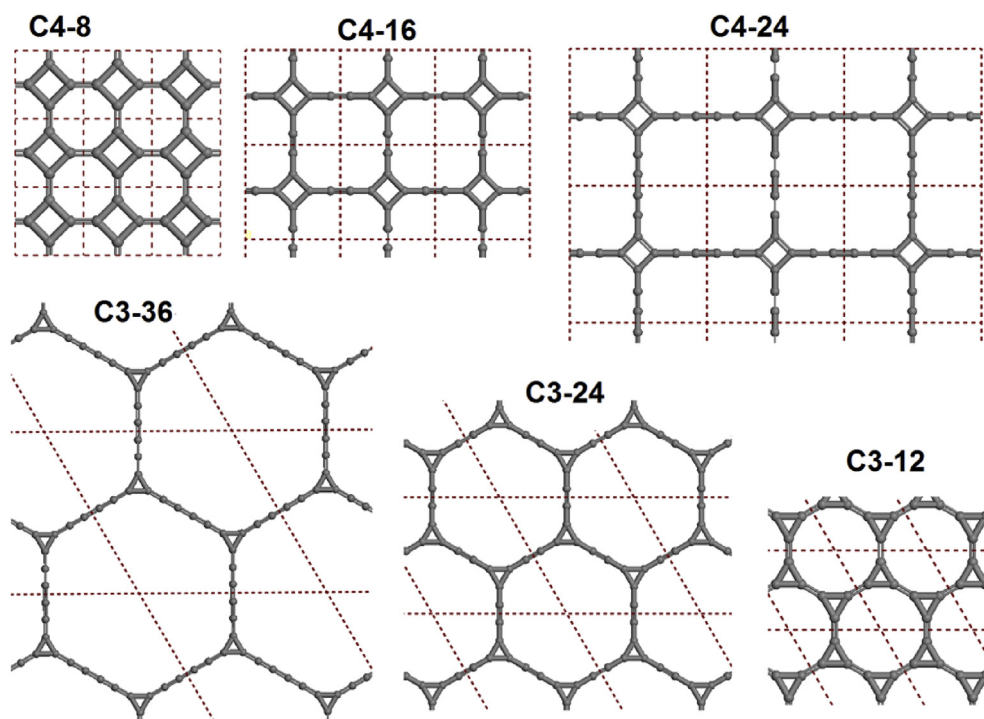


Fig. 2. Chemical structures of the 2D materials studied in this work composed of three- and four-membered rings.

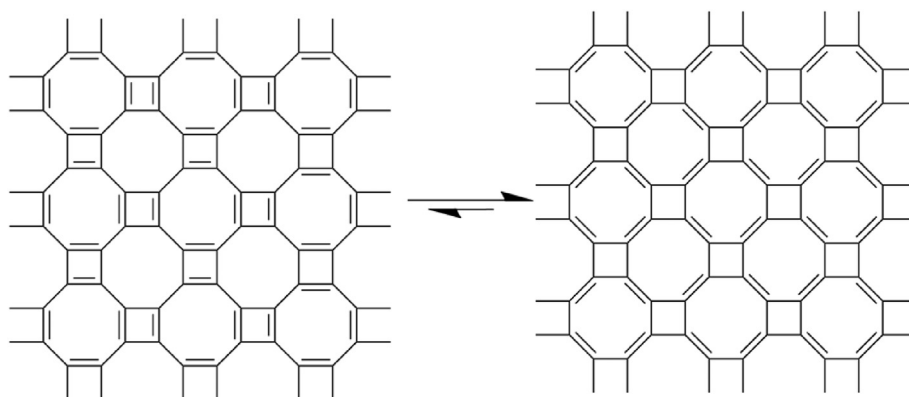


Fig. 3. The resonant structures for C4-8.

for graphene is 7.95 eV/atom in literature [27]). The E_{coh} for C4-16 and C4-24 is 7.15 eV/atom and 7.08 eV/atom, which is higher than that of C3-12 (7.01 eV/atom). Both C3-24 and C3-36 exhibit the same E_{coh} value of 6.94 eV/atom. Although the relative stabilities of these materials could not be compared directly by their cohesive energy, the rough comparison indicates that the studied four-membered ring system is more stable than the three-membered ring systems.

The temperature dependent free energy has also been calculated [40]. As shown in Fig. S3, C4-8 gives the best thermodynamic stability (below 730 K) in the studied carbon allotropes in this work. On the contrary, C3-36 shows the worst thermodynamic stability below 500 K compared with other 2D materials studied in this work, and the free energy of C3-36 becomes negative after 834 K.

3.4. The kinetic stability of the studied 2D systems

In order to further compare the stability of these carbon

allotropes, the kinetic stability of these 2D monolayers was investigated through phonon band structure. As shown in Fig. 4, no soft modes are observed in the studied C4-8, C4-16 and C4-24, which indicate these three structures are kinetically stable. The highest frequency of C4-8, C4-16 and C4-24 increases from 1759 cm^{-1} to 2189 and 2221 cm^{-1} with the introduction of one and two triple bonds, which is higher than that of graphene (1630 cm^{-1}) [58], silicene (580 cm^{-1}) [59] and MoS_2 monolayer (473 cm^{-1}) [60]. However, there are small imaginary frequencies existing in C3-12 and C3-36, which becomes larger in C3-24. The present of imaginary frequencies in these three structures with cyclopropene units suggests they are not kinetically stable. This is also consistent with the cohesive energy calculations as discussed above.

The high-frequency phonons above 2000 cm^{-1} for C4-16, C4-24, C3-C24 and C3-C36 are clearly related to the stretching mode of $\text{C}\equiv\text{C}$ bonds linking the cyclobutadiene or cyclopropene units, which are quite similar with that of the characteristic one-phonon Raman lines between 2000 and 2300 cm^{-1} for graphyne derivatives [61].

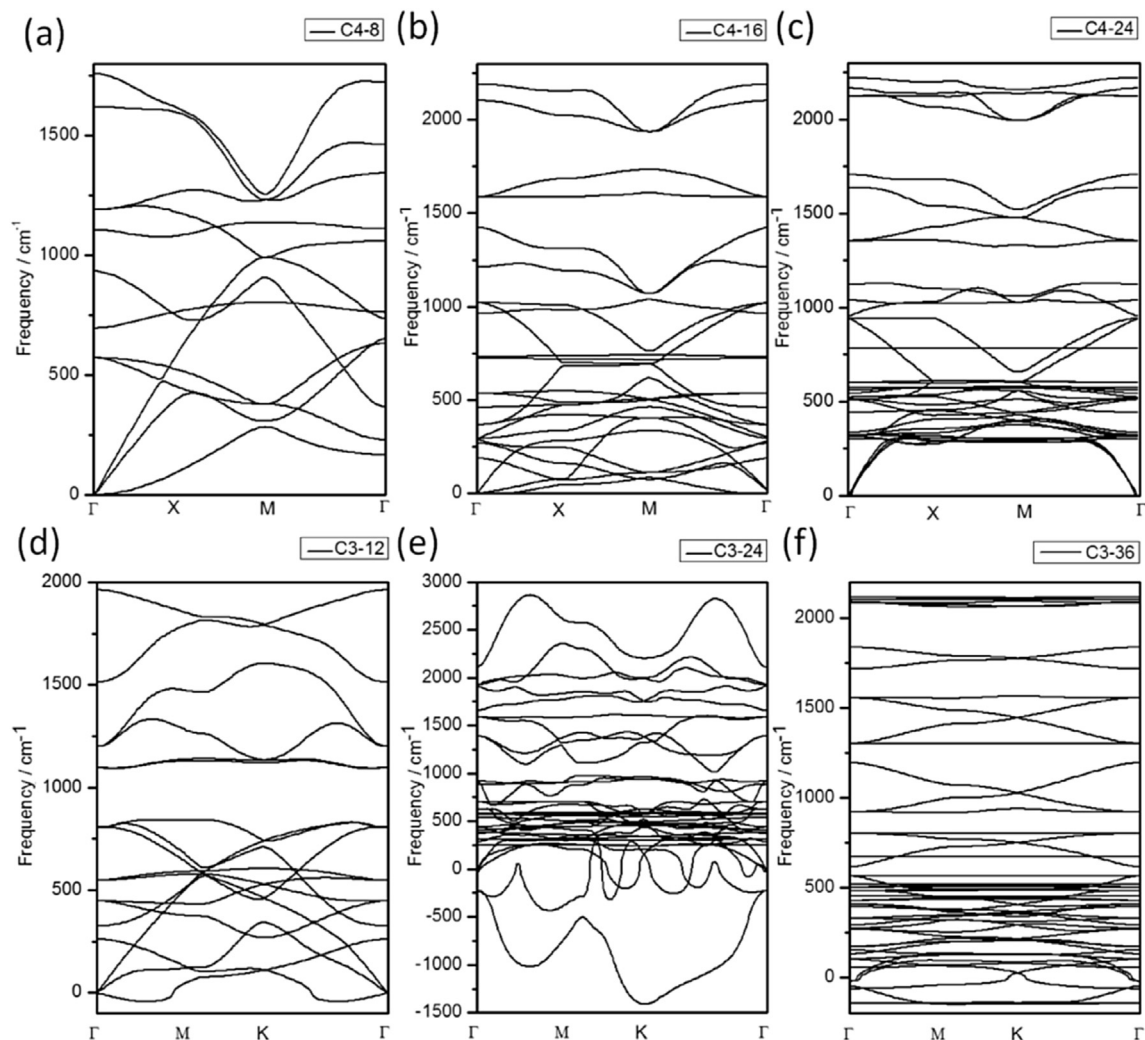


Fig. 4. Phonon dispersion curves along the selected directions within the Brillouin zone of C4-8 (a), C4-16 (b), C4-24 (c), C3-12 (d), C3-24 (e) and C3-36 (f).

3.5. The electronic structure of the studied 2D systems

Moreover, the electronic structures of all these carbon allotropes were calculated and shown in Fig. 5. The bands cross the Fermi energy level (0 eV) in C4-8, C4-16 and C4-24 indicate that all three 2D carbon monolayers have metallic nature. The corresponding density of states (DOS) which exhibit non-zero values at the Fermi levels also confirm this (Fig. S4), and further evident there are certain occupations in the delocalized π states for these four-membered ring systems. At the energy of -1 eV, in the vicinity of M-points or Γ -point, the energy depends almost linearly on the wave vector, which is quite similar with that of the doped graphenes [26]. These dispersions could bring about small effective masses (as shown in Table S2), and the smallest effective mass is only about one twentieth of free electron (m_0), which indicates C4 derivatives could be very good conductors.

For the C3-12 derivatives, small proportion of conduction band locates just below Fermi level, as shown in Fig. 5d–f. This indicates few charge carriers exist at 0 K, and presents half-metallic characters. A very flat conduction band appears near the Fermi level, which is more proper to consider it as an energy level rather than a band. Charge carriers at this band are hardly to move due to its heavier effective mass than free electrons. Especially for C3-24, the energy is almost constant (M- Γ) and leads to infinite effective mass,

which indicates that electrons cannot be transported. Therefore, this level is a trap-like or a recombination center, and C3-12 derivatives exhibit poor charge transport ability according to our calculation results.

4. Conclusion

To summarize, by systematic *ab-initio* calculations, we have investigated a series of 2D carbon allotropes composed of three- and four-membered ring systems. All the studied three- and four-membered ring systems exhibit close-shell structures. However, the 2D allotropes with three-membered ring are not kinetically stable based on calculating the phonon spectra and cohesive energy. In addition, few charge carriers and the present of trap-like bands in three-membered 2D sheet, makes it less possible to apply in organic electronics. On the contrary, the four-membered ring systems of C4-8 and its derivatives are kinetically stable. In addition, they show nearly linear dispersion in the electronic band diagram. Small effective masses are expected and verified with calculation, which suggests C4-8 and its derivatives should have good conductivities. These two advantages provide a new choice of synthesizing four-membered rings based 2D carbon materials with metallic nature towards the application in the all carbon electronic circuits.

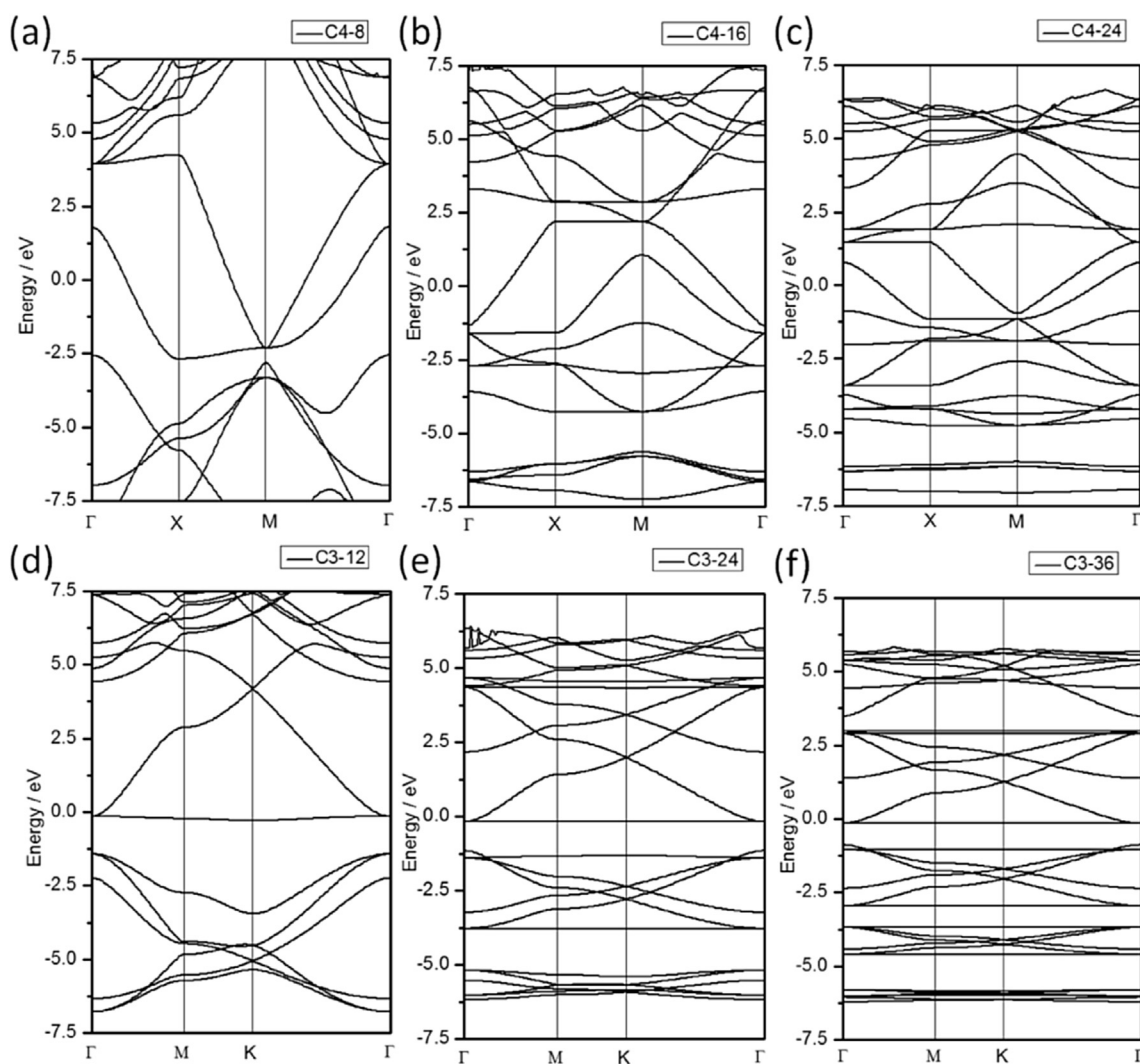


Fig. 5. Calculated electronic band structures of C4-8 (a), C4-16 (b), C4-24 (c), C3-12 (d), C3-24 (e) and C3-36 (f). The Fermi energy level was set at 0 eV.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2015.09.030>.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, et al., Electric field effect in atomically thin carbon films, *Science* 306 (5696) (2004) 666–669.
- [2] C. Soldano, A. Mahmood, E. Dujardin, Production, properties and potential of graphene, *Carbon* 48 (2010) 2127–2150.
- [3] H.A. Becerril, J. Mao, Z. Liu, R.M. Stoltenberg, Z. Bao, Y. Chen, Evaluation of solution-processed reduced graphene oxide films as transparent conductors, *ACS Nano* 2 (3) (2008) 463–470.
- [4] S.K. Pal, Versatile photoluminescence from graphene and its derivatives, *Carbon* 88 (2015) 86–112.
- [5] C.N.R. Rao, A.K. Sood, K.S. Subrahmanyam, A. Govindaraj, Graphene: the new two-dimensional nanomaterial, *Angew. Chem. Int. Ed.* 48 (42) (2009) 7752–7777.
- [6] F. Schwierz, Graphene transistors, *Nat. Nanotechnol.* 5 (7) (2010) 487–496.
- [7] Y.-M. Lin, C. Dimitrakopoulos, K.A. Jenkins, D.B. Farmer, H.-Y. Chiu, A. Grill, et al., 100-GHz transistors from wafer-scale epitaxial graphene, *Science* 327 (5966) (2010) 662.
- [8] Y.-M. Lin, A. Valdes-Garcia, S.-J. Han, D.B. Farmer, I. Meric, Y. Sun, et al., Wafer-scale graphene integrated circuits, *Science* 332 (6035) (2011) 1294–1297.
- [9] F. Xia, D.B. Farmer, Y.-m Lin, P. Avouris, Graphene field-effect transistors with high on/off current ratio and large transport band gap at room temperature, *Nano Lett.* 10 (2) (2010) 715–718.
- [10] S.Y. Zhou, G.H. Gweon, A.V. Fedorov, P.N. First, W.A. de Heer, D.H. Lee, et al., Substrate-induced band gap opening in epitaxial graphene, *Nat. Mater.* 6 (10) (2007) 770–775.
- [11] V.M. Pereira, A.H. Castro Neto, N.M.R. Peres, Tight-binding approach to uniaxial strain in graphene, *Phys. Rev. B* 80 (4) (2009), 045401.
- [12] Z. Chen, Y.-M. Lin, M.J. Rooks, P. Avouris, Graphene nano-ribbon electronics, *Phys. E* 40 (2) (2007) 228–232.
- [13] M.Y. Han, B. Özyilmaz, Y. Zhang, P. Kim, Energy band-gap engineering of graphene nanoribbons, *Phys. Rev. Lett.* 98 (20) (2007) 206805.
- [14] E. McCann, Asymmetry gap in the electronic band structure of bilayer graphene, *Phys. Rev. B* 74 (16) (2006), 161403.
- [15] E.V. Castro, K.S. Novoselov, S.V. Morozov, N.M.R. Peres, J.M.B.L. dos Santos, J. Nilsson, et al., Biased bilayer graphene: semiconductor with a gap tunable by the electric field effect, *Phys. Rev. Lett.* 99 (21) (2007), 216802.
- [16] H. Min, B. Sahu, S.K. Banerjee, A.H. MacDonald, *Ab initio* theory of gate induced gaps in graphene bilayers, *Phys. Rev. B* 75 (15) (2007), 155115.

- [17] K.F. Mak, C.H. Lui, J. Shan, T.F. Heinz, Observation of an electric-field-induced band gap in bilayer graphene by infrared spectroscopy, *Phys. Rev. Lett.* 102 (25) (2009), 256405.
- [18] J.B. Oostinga, H.B. Heersche, X. Liu, A.F. Morpurgo, L.M.K. Vandersypen, Gate-induced insulating state in bilayer graphene devices, *Nat. Mater.* 7 (2) (2008) 151–157.
- [19] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, Controlling the electronic structure of bilayer graphene, *Science* 313 (5789) (2006) 951–954.
- [20] R.H. Baughman, H. Eckhardt, M. Kertesz, Structure-property predictions for new planar forms of carbon: Layered phases containing sp^2 and sp atoms, *J. Chem. Phys.* 87 (11) (1987) 6687–6699.
- [21] N. Narita, S. Nagai, S. Suzuki, K. Nakao, Optimized geometries and electronic structures of graphyne and its family, *Phys. Rev. B* 58 (16) (1998) 11009–11014.
- [22] A.N. Enyashin, A.L. Ivanovskii, Graphene allotropes, *Status Solidi B* 248 (8) (2011) 1879–1883.
- [23] J. Zhou, K. Lv, Q. Wang, X.S. Chen, Q. Sun, P. Jena, Electronic structures and bonding of graphyne sheet and its BN analog, *J. Chem. Phys.* 134 (17) (2011), 174701.
- [24] D. Malko, C. Neiss, F. Vines, A. Goerling, Competition for graphene: graphynes with direction-dependent dirac cones, *Phys. Rev. Lett.* 108 (8) (2012), 086804.
- [25] M. Zhao, W. Dong, A. Wang, Two-dimensional carbon topological insulators superior to graphene, *Sci. Rep.* 3 (2013) 3532.
- [26] Y.-C. Zhou, H.-L. Zhang, W.-Q. Deng, A 3N rule for the electronic properties of doped graphene, *Nanotechnology* 24 (22) (2013), 225705.
- [27] Y. Li, Y. Liao, Z. Chen, Be_2C Monolayer with quasi-planar hexacoordinate carbons: a global minimum structure, *Angew. Chem. Int. Ed.* 53 (28) (2014) 7248–7252.
- [28] J. Dai, X.C. Zeng, Titanium trisulfide monolayer: theoretical prediction of a new direct-gap semiconductor with high and anisotropic carrier mobility, *Angew. Chem. Int. Ed.* 54 (10) (2015) 7572–7576.
- [29] S. Zhang, Z. Yan, Y. Li, Z. Chen, H. Zeng, Atomically thin arsenene and antimonene: semimetal-semiconductor and indirect-direct band-gap transitions, *Angew. Chem. Int. Ed.* 54 (10) (2015) 3112–3115.
- [30] G. Li, Y. Li, H. Liu, Y. Guo, Y. Li, D. Zhu, Architecture of graphdiyne nanoscale films, *Chem. Commun.* 46 (19) (2010) 3256–3258.
- [31] M. Long, L. Tang, D. Wang, Y. Li, Z. Shuai, Electronic structure and carrier mobility in graphdiyne sheet and nanoribbons: theoretical predictions, *ACS Nano* 5 (4) (2011) 2593–2600.
- [32] S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe, P. Jena, Penta-graphene: a new carbon allotrope, *P. Natl. Acad. Sci. U. S. A.* 112 (8) (2015) 2372–2377.
- [33] C. Su, H. Jiang, J. Feng, Two-dimensional carbon allotrope with strong electronic anisotropy, *Phys. Rev. B* 87 (7) (2013), 075453.
- [34] V.H. Crespi, L.X. Benedict, M.L. Cohen, S.G. Louie, Prediction of a pure-carbon planar covalent metal, *Phys. Rev. B* 53 (20) (1996) R13303–R13305.
- [35] M. Maruyama, S. Okada, Two-dimensional sp^2 carbon network of fused pentagons: all carbon ferromagnetic sheet, *Appl. Phys. Express* 6 (9) (2013), 095101–4.
- [36] T.C. Fitzgibbons, M. Guthrie, Xu E-s, V.H. Crespi, S.K. Davidowski, G.D. Cody, et al., Benzene-derived carbon nanofibers, *Nat. Mater.* 14 (1) (2015) 43–47.
- [37] K.M. Merz, R. Hoffmann, A.T. Balaban, 3,4-Connected carbon nets: through-space and through-bond interactions in the solid state, *J. Am. Chem. Soc.* 109 (22) (1987) 6742–6751.
- [38] E. Konstantinova, S.O. Dantas, P.M.V.B. Barone, Electronic and elastic properties of two-dimensional carbon planes, *Phys. Rev. B* 74 (3) (2006), 035417.
- [39] M.A. Hudspeth, B.W. Whitman, V. Barone, J.E. Peralta, Electronic properties of the biphenylene sheet and its one-dimensional derivatives, *ACS Nano* 4 (8) (2010) 4565–4570.
- [40] Y. Liu, G. Wang, Q. Huang, L. Guo, X. Chen, Structural and electronic properties of T graphene: a two-dimensional carbon allotrope with tetrarings, *Phys. Rev. Lett.* 108 (22) (2012) 225505.
- [41] J. Nisar, X. Jiang, B. Pathak, J. Zhao, T.W. Kang, R. Ahuja, Semiconducting allotrope of graphene, *Nanotechnology* 23 (38) (2012) 385704.
- [42] G. Brunetto, P.A.S. Autreto, L.D. Machado, B.I. Santos, R.P.B. dos Santos, D.S. Galvao, Nonzero gap two-dimensional carbon allotrope from porous graphene, *J. Phys. Chem. C* 116 (23) (2012) 12810–12813.
- [43] H. Lu, S.-D. Li, Two-dimensional carbon allotropes from graphene to graphyne, *J. Mater. Chem. C* 1 (23) (2013) 3677–3680.
- [44] L.-C. Xu, R.-Z. Wang, M.-S. Miao, X.-L. Wei, Y.-P. Chen, H. Yan, et al., Two dimensional dirac carbon allotropes from graphene, *Nanoscale* 6 (2) (2014) 1113–1118.
- [45] X.-Q. Wang, H.-D. Li, J.-T. Wang, Prediction of a new two-dimensional metallic carbon allotrope, *Phys. Chem. Chem. Phys.* 15 (6) (2013) 2024–2030.
- [46] Q. Song, B. Wang, K. Deng, X. Feng, M. Wagner, J.D. Gale, et al., Graphenylene, a unique two-dimensional carbon network with nonlocalized cyclohexatriene units, *J. Mater. Chem. C* 1 (1) (2013) 38–41.
- [47] E. Hückel, Quantentheoretische Beiträge zum benzolproblem, *Physik* 70 (3–4) (1931) 204–286.
- [48] M. Head-Gordon, J.A. Pople, M.J. Frisch, MP2 energy evaluation by direct methods, *Chem. Phys. Lett.* 153 (6) (1988) 503–506.
- [49] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (2) (1988) 785–789.
- [50] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (7) (1993) 5648–5652.
- [51] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp. Mater. Sci.* 6 (1) (1996) 15–50.
- [52] G. Kresse, J. Hafner, Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements, *J. Phys.-Condens. Mat.* 6 (40) (1994) 8245–8257.
- [53] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (24) (1994) 17953–17979.
- [54] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, et al., Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* 100 (13) (2008), 136406.
- [55] Y.-C. Zhou, F. Huang, Y.-B. Cheng, A. Gray-Weale, *Phys. Chem. Chem. Phys.* 17 (35) (2015) 22604–22615.
- [56] L. Chaput, A. Togo, I. Tanaka, G. Hug, Phonon-phonon interactions in transition metals, *Phys. Rev. B* 84 (9) (2011), 094302.
- [57] K. Parlinski, Z.Q. Li, Y. Kawazoe, First-principles determination of the soft mode in cubic ZrO_2 , *Phys. Rev. Lett.* 78 (21) (1997) 4063–4066.
- [58] J.-A. Yan, W.Y. Ruan, M.Y. Chou, Phonon dispersions and vibrational properties of monolayer, bilayer, and trilayer graphene: density-functional perturbation theory, *Phys. Rev. B* 77 (12) (2008) 125401.
- [59] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, S. Ciraci, Two- and one-dimensional honeycomb structures of silicon and germanium, *Phys. Rev. Lett.* 102 (23) (2009), 236804.
- [60] A. Molina-Sánchez, L. Wirtz, Phonons in single-layer and few-layer MoS_2 and WS_2 , *Phys. Rev. B* 84 (15) (2011), 155413.
- [61] V.N. Popov, P. Lambin, Theoretical Raman fingerprints of α -, β -, and γ -graphyne, *Phys. Rev. B* 88 (7) (2013), 075427.