

Band gap modulation of graphyne: A density functional theory study

ROYA MAJIDI

Department of Physics, Faculty of Science, Shahid Rajaee

Teacher Training University, Tehran, 16785 – 136, I R. Iran

Email: royamajidi@gmail.com, r.majidi@srttu.edu

ABSTRACT. Modifying the electronic properties of graphyne via doping, organic molecule adsorption, and chemical functionalization was reviewed. The electronic band structure and density of states were studied by using density functional theory. The α -graphyne was considered due to its analogous to graphene. The results indicate α -graphyne is a semimetal with zero band gap. It was shown that doping, adsorbing organic molecule, and chemical functionalization can open a band gap in α -graphyne. The size of the band gap was dependent on the concentration of impurity, adsorbed TCNE or CCl_2 molecules. The mentioned methods provide the possibility of opening an energy band gap in α -graphyne as required for fabricating high-performance nanoelectronic devices based on graphyne.

Keywords: α -graphyne, doping, organic molecule adsorption, functionalization, electronic properties

1. INTRODUCTION

Carbon's hybridization states (sp , sp^2 , and sp^3) can lead to form various carbon allotropes such as diamond (sp^3), graphite (sp^2), fullerene (sp^2), carbon nanotube (sp^2), and graphene (sp^2) [1]. Among these carbon based nanomaterials, a two dimensional hexagonal network of carbon atoms known as graphene has become the focus of many studies since its first successful synthesis in 2004 [2]. The high conductivity of the graphene is the most important property of graphene. The cause of the novel electronic properties of graphene is its peculiar band structure that features so-called Dirac cones [3, 4]. At a Dirac point, the conduction and valence bands meet in

a single point at the Fermi level. It means graphene is a semiconductor with zero band gap known as a semimetal [1, 5]. Beyond these well known allotropes, new members named as graphyne was predicted and added to the carbon family in recent years [6, 7]. Graphyne, a single atomic layer of carbon sheet, was obtained by replacing some of carbon bonds in graphene with acetylenic linkages [7]. The resulting networks include sp -hybridized carbon atoms together with sp^2 -hybridized carbon atoms. Three various types of graphyne (α , β , γ) were built by inserting carbon triple bond into carbon single bonds in graphene. The presence of acetylenic groups in these structures introduces a rich variety of electrical, optical, and mechanical properties [6, 8]. One of the most exciting features of graphynes is related to its unusual electronic properties. It was reported that some graphynes have gapless band structure with unusual Dirac-like electronic excitations [9, 10]. It means the Dirac cone like feature is not a unique characteristic of graphene [10] and does not depend on the hexagonal symmetry of carbon sheets. The interesting electronic properties of graphene and graphyne promise the use of these materials in nanoelectronic devices.

It should be mentioned that the lack of an energy gap is one of the biggest challenges for use of graphene and graphyne in nanoelectronic devices. Because of these requisites, several physical and chemical methods including doping with impurity, applying electric and magnetic fields, chemical functionalization, and organic molecules adsorption, etc. were proposed to open a band gap in graphene [11-31]. As an example, the possibility of modifying the electronic properties of graphene and graphyne was reported by doping with B and N atoms [20, 21]. It was also reported that the electronic properties of graphene was modified and the energy band gap was opened by adsorption of different functional groups such as H , F , OH , $COOH$, O , acryne and carbene groups [22-26]. In addition, it was found that a single graphene layer, when deposited on substrates such as silicon dioxide or silicon carbide, loses its semimetallic characteristic due to strong chemical interaction with the underlying substrate [13, 15-17]. Moreover, charge transfer doping by organic molecules is a promising way to create a band gap in graphene [18, 19, 27]. As an example, it was shown that surface modification of graphene by organic molecule such as tetracyanoethylene ($TCNE$) is an effective method to control the electronic structure of graphene [18, 19]. Furthermore, it was found that the Dirac cones in the electronic structures of monolayer graphene are very stable against external stress and electric field [28-30]. While the electric field changes significantly the electronic properties of bilayer graphene [31].

In the present work, we have reviewed the possibility of opening a band gap by various methods such as doping, organic molecule adsorption, and chemical functionalization.

2. Methods

The calculations were done in the framework of density functional theory (DFT) as implemented in the OpenMX 3.6 package [32]. The generalized gradient

approximation (*GGA*) was used with the Perdew-Burke-Ernzerhof (*PBE*) functional for the exchange-correlation potential [33]. The long range van der Waals interactions were included by the *DFT-D2* approach proposed by Grimme [34]. The electron wave function was expanded in plane waves with cutoff of 100-150 Ry. The cutoff energy was chosen such that a proper convergence of total energy is achieved. All atomic coordinates were fully relaxed using the convergence threshold of $0.01 \text{ eV}/\text{\AA}$ in force. For calculations of the electronic band structures, 41 *k*-points were chosen along each high symmetry line in the first Brillouin-Zone.

3. Results and Discussion

3.1 Monolayer α -graphyne

First, the electronic properties of an intrinsic α -graphyne sheet were studied. The 2×2 supercell with 32 carbon atoms was considered to simulate graphyne sheet (Fig. 1). In this figure, the unit cell of α -graphyne which consists of 8 carbon atoms was defined by the primitive lattice vectors:

$$\bar{a}_1 = a \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) \quad (1)$$

and

$$\bar{a}_2 = a \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \quad (2)$$

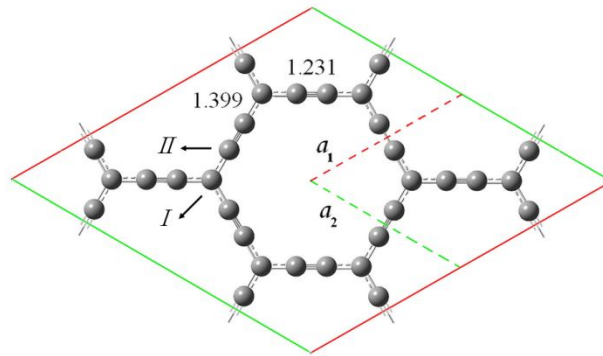


Figure 1. Atomic structure of a supercell of α -graphyne.

The electronic band structures and density of states (*DOS*) of α -graphyne are shown in Fig. 2. Here, the valence and conduction bands cross each other at the single point at the Fermi level. (The Fermi level is at 0 eV). The *DOS* of α -graphyne is zero at the Fermi level (Fig. 2). Therefore, our results [35] emphasize that the α -graphyne is a semimetal as reported in the previous studies [9, 10].

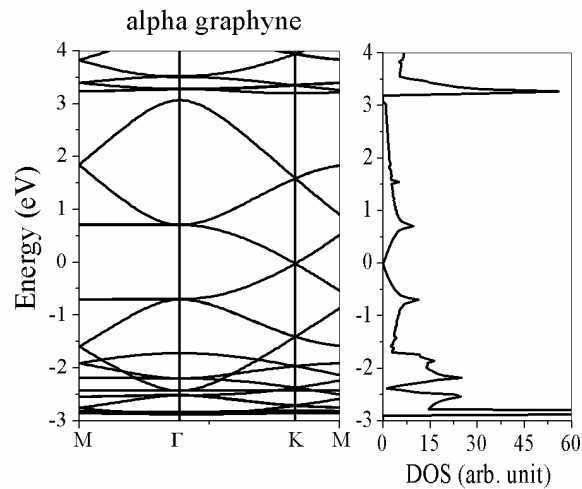


Figure 2. Electronic band structure and *DOS* of monolayer α -graphyne [35].

3.2 Doped monolayer α -graphyne

The α -graphyne doped with impurity was modeled by replacing one of *C* atoms with one impurity atom (*B*, *N*, or *O*). It means 3.1% impurity was introduced in graphyne. We have considered two different doping sites labeled by *I* and *II* in Fig. 1.

One *B* atom that substitutes one *C* atom lacks one electron to complete the bonding with its all neighbors. It means *B* impurity creates additional holes in the valence band. As shown in Fig. 3, linear dispersion near Dirac cone is not destroyed. The Fermi level was shifted significantly due to electron acceptor character of *B* atom and an energy band gap was introduced around the Dirac point. As a result of *B* doping, an unoccupied acceptor level is created close to the top edge of the valence band. Hence, *B* doping changes the behavior of α -graphyne from semimetal to *p*-type semiconductor [35].

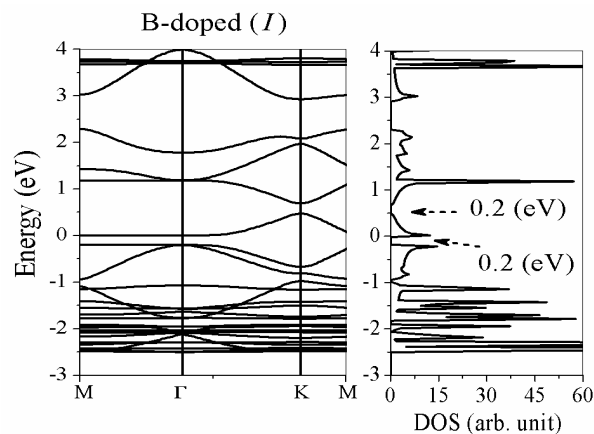


Figure 3. Electronic band structure and *DOS* of *B*-doped α -graphyne [35].

The N or O atoms may also enter to the α -graphyne by replacing one C atom. These impurities that enhance the carrier density by contributing additional electrons to the conduction band are called donor. On account of having these extra electrons for the purpose of conduction, the N -doped and O -doped graphyne become n -type semiconductors. In the n -type semiconductor, the donor levels, located closely below the lower edge of the conduction band, are the top occupied levels. In Fig. 4 and Fig. 5, the electronic band structures and DOS s of N -doped and O -doped graphynes with impurity atom in site I are presented,

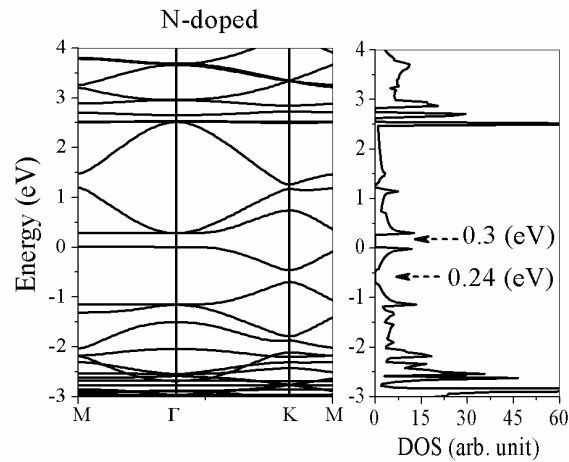


Figure 4. Electronic band structure and DOS of N -doped α -graphyne [35].

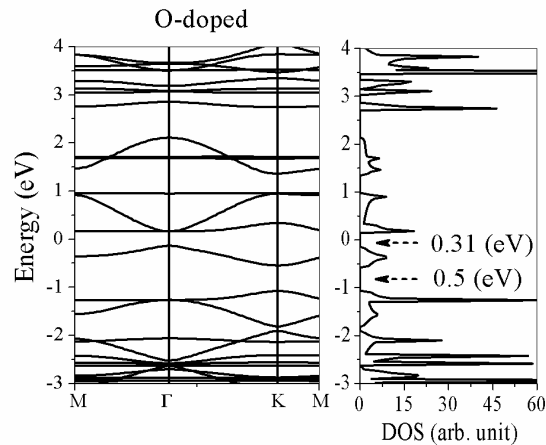


Figure 5. Electronic band structure and DOS of O -doped α -graphyne [35].

3.3 BN doped bilayer α -graphyne

In a bilayer graphene, the two graphene layers are arranged with carbon atoms in one layer located on top of the center of a hexagon in the other layer according to the

usual Bernal AB -stacking. This arrangement is commonly found in nature [36], and previous calculations were shown that it is the most energetically favorable configuration [37]. Similarly, a bilayer graphyne with two graphyne layers placed on top of the center of each other were considered (Fig. 6). The BN -doped bilayers were modeled by replacing one of the carbon atoms of the first layer by a B atom and putting a N atom instead one of the carbon atoms of the second layer. It means 3.1% B in the first layer and 3.1% N in the second layer were doped [39].

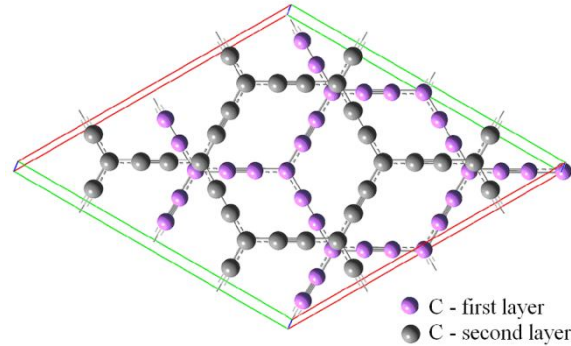


Figure 6. Atomic structure of bilayer α -graphyne [39].

The electronic band structure and DOS of the bilayer α -graphyne are presented in Fig. 7. As shown, two nearly parallel valence bands (π_1 and π_2 levels) are presented below two nearly parallel conduction bands (π_1^* and π_2^* levels). Similar to the monolayer α -graphyne, the lowest conduction band and highest valence band cross each other at the K point and the DOS is zero at the Fermi energy. Interestingly, the bilayer α -graphyne is also a semimetal with no energy gap and zero DOS [38, 39].

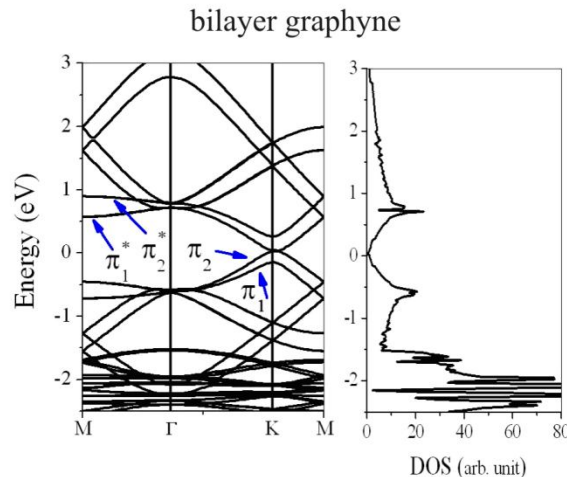


Figure 7. Electronic band structure and DOS of bilayer α -graphene [38, 39].

To clarify the effect of *BN* doping on the electronic properties of the bilayer graphyne, the electronic band structure and *DOS* of bilayer graphyne doped with 3.1% *B* and 3.1% *N* impurities are presented in Fig. 8. Because of the presence of *B* and *N* impurities, one unoccupied level and one occupied level are created close to the Fermi energy, respectively. A small band gap opens in the presence of these impurities and *BN*-doped bilayer graphyne is a semiconductor [39].

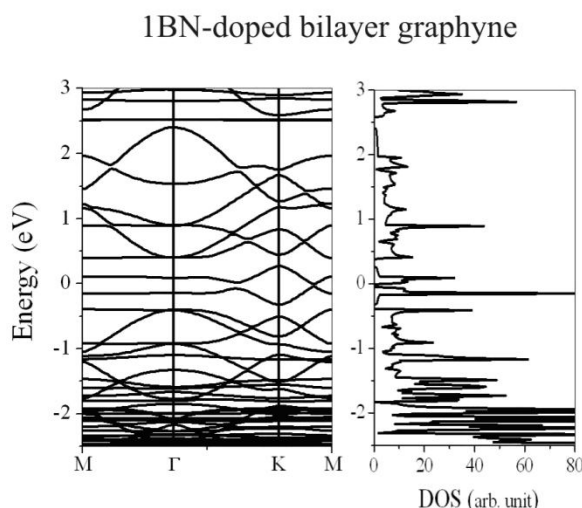


Figure 8. Electronic band structure and *DOS* of *BN*-doped bilayer α -graphyne [39].

3.4 Adsorption of organic molecule

The effect of organic molecules such as *TCNE* on the electronic properties of α -graphyne was studied [40, 41]. Atomic structures of α -graphyne in the presence of 1 and 9 *TCNE* molecules are shown in Fig. 9. To clarify the effect of *TCNE* molecule on the electronic property of graphyne, the electronic band structures and *DOS* of α -graphyne in the presence of one *TCNE* molecule per supercell are presented in Fig. 10. It was shown that a band gap is opened and α -graphyne becomes a semiconductor with *TCNE* adsorption. The band gap was enhanced by increasing the number of adsorbed *TCNE* molecules [40, 41].

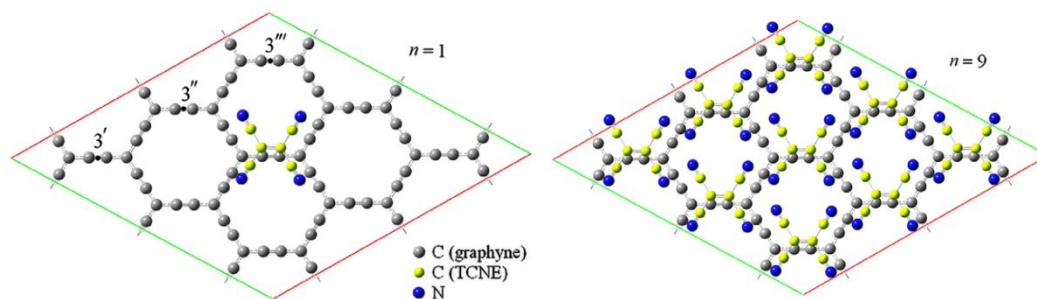


Figure 9. Atomic structures of α -graphyne in the presence of 1 and 9 TCNE molecules [40].

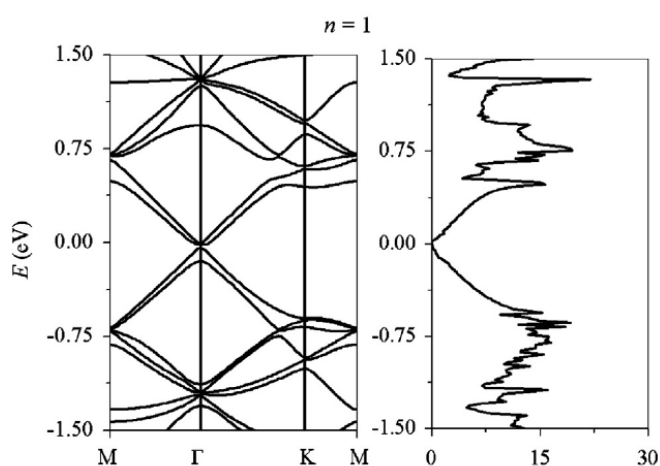


Figure 10. Electronic band structures and *DOS* of α -graphyne in the presence of 1 TCNE molecule [40].

3.5 Functionalization

Atomic structure of α -graphyne with one CCl_2 molecule is shown in Fig. 11. The electronic band structures and *DOS* of α -graphyne with CCl_2 molecule was studied to clarify the possibility of using functionalization for band gap opening in α -graphyne. As an example, the electronic band structure and *DOS* of functionalized α -graphyne with a single CCl_2 molecule were shown in Fig. 12. Upon CCl_2 adsorption, energy band gap was opened between the valence and conduction band edges. Hence, α -graphyne functionalized with a single CCl_2 molecule show semiconducting properties. Here, the hybridization state of C atoms with CCl_2 molecules attached to them was transformed from sp^2 into sp^3 and opened the band gap in α -graphyne. It was also found that the size of the band gap was dependent on concentration of CCl_2 molecule [42].

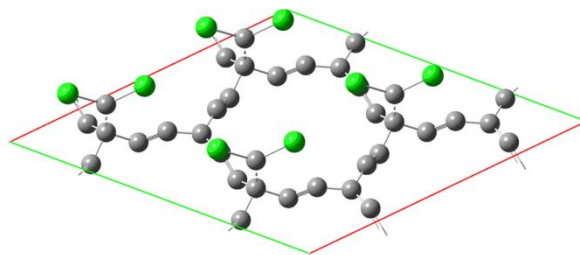


Figure 11. Atomic structures of functionalized α -graphyne with four CCl_2 molecules [42].

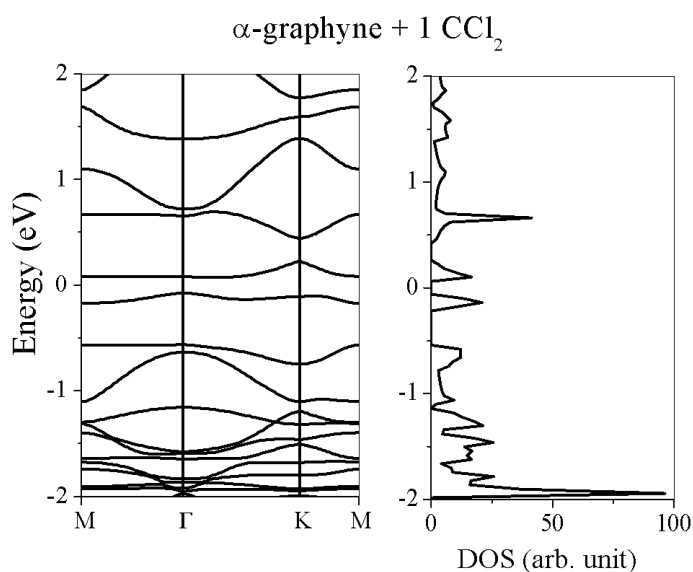


Figure 12. Electronic band structures and DOS of α -graphyne with one CCl_2 molecules [42].

4. Conclusions

We have reviewed different possible methods for modifying the electronic properties of α -graphyne. Opening band gap in α -graphyne with doping, adsorption of organic molecule, and chemical functionalization was investigated. The energy band gap and DOS were calculated by DFT . It was found that monolayer and bilayer α -graphyne sheets are semimetals. They show semiconducting properties when doped (with B , N , or O), functionalized with CCl_2 , or $TCNE$ molecule adsorbed on them. The results provide proper ways to open and control the energy band gap in α -graphyne.

REFERENCES

- [1] M.S. Dresselhaus, G. Dresselhaus, and P. Avouris, Carbon Nanotubes: Synthesis, Structure, Properties, and Applications, Springer-Verlag Berlin Heidelberg (2001).
- [2] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, and A.A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, *Science* 306 (2004) 666.
- [3] A.K. Geim, and K.S. Novoselov, The Rise of Graphene, *Nat. Mater.* 6 (2007) 183.
- [4] A.K. Geim, Graphene Status and Prospects, *Science* 324 (2009) 1530.
- [5] S. Jalili, and R. Majidi, The Effect of Gas Adsorption on Carbon Nanotubes Properties, *J. Comput. Theor. Nanosci.* 3 (2006) 664.
- [6] A.L. Ivanovskii, Graphynes and Graphdiynes, *Progress in Solid State Chemistry*, 41 (2013) 1.
- [7] R.H. Baughman, H. Eckhardt, and M. Kertesz, Structure-Property Predictions for New Planar Forms of Carbon: Layered Phases Coating sp^2 and sp Atoms, *J. Chem. Phys.* 87 (1987) 6687.
- [8] S.W. Cranford, and M.J. Buehler, Mechanical Properties of Graphyne, *Carbon* 49 (2011) 4111.
- [9] B.G. Kim, and H.J. Choi, Graphyne: Hexagonal Network of Carbon with Versatile Dirac Cones, *Phys. Rev. B* 86 (2012) 115435.
- [10] D. Malko, C. Neiss, F. Viñes, and A. Görling, Completion for Graphene: Graphynes with Direction-Dependent Dirac Cones, *Phys. Rev. Lett.* 108 (2012) 086804.
- [11] D. Haberer, D.V. Vyalikh, S. Taioli, B. Dora, M. Farjam, J. Fink, D. Marchenko, T. Pichler, K. Ziegler, S. Simonucci, M.S. Dresselhaus, M. Knupfer, B. Büchner, and A. Grüneis, Tunable Band Gap in Hydrogenated Quasi-Free-Standing Graphene, *Nano Lett.* 10 (2010) 3360.
- [12] J. Nilsson, and A.C. Neto, Impurities in a Biased Graphene Bilayer, *Phys. Rev. Lett.* 98 (2007) 126801.
- [13] T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, Controlling the Electronic Structure of Bilayer Graphene, *Science* 313 (2006) 951.
- [14] B.R. Matis, J.S. Burgess, F. Bulat, A.L. Friedman, B.H. Houston, and J.W. Baldwin, Surface Doping and Band Gap Tunability in Hydrogenated Graphene, *ACS Nano* 6 (2012) 17.

- [15] P. Shemella, and S.K. Nayak, Electronic Structure and Band-Gap Modulation of Graphene via Substrate Surface Chemistry, *Appl. Phys. Lett.* 94 (2009) 032101.
- [16] K. Novoselov, Graphene: Mind the Gap, *Nature Matter* 6 (2007) 720.
- [17] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, Chemically Derived, Ultrasooth Graphene Nanoribbon Semiconductors, *Science* 319 (2008) 1229.
- [18] Y.H. Lu, W. Chen, Y.P. Feng, and P.M. He, Tuning the Electronic Structure of Graphene by an Organic Molecule, *J. Phys. Chem. B* 113 (2009) 2.
- [19] M. Chi, and Y-P, Zhao, First principle study of the interaction and charge transfer between graphene and organic molecules, *Comp. Mat. Sci.* 56 (2012) 79.
- [20] X. Wang, X. Li, L. Zhang, Y. Yoon, P.K. Weber, H. Wang, J. Guo, and H. Dai, N-Doping of Graphene Through Electrothermal Reactions with Ammonia, *Science* (2009) 768.
- [21] T.B. Martins, R.H. Miwa, A.J.R. da Silva, and A. Fazzio, Electronic and Transport Properties of Boron-Doped Graphene Nanoribbons, *Phys. Rev. Lett.* 98 (2007) 196803(1-4).
- [22] D.C. Elias, R.R. Nair, T.M.G. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall, A.C. Ferrari, D.W. Boukhvalov, M.I. Katsnelson, A.K. Geim, and K.S. Novoselov, Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane, *Science* 323 (2009) 610.
- [23] R.R. Nair, W. Ren, R. Jalil, I. Riaz, V.G. Kravets, L. Britnell, V.G. Kravets, L. Britnell, P. Blake, F. Schedin, A.V. Mayorov, S. Yuan, M.I. Katsnelson, H.M. Cheng, W. Strupinski, L.G. Bulusheva, K.S. Novoselov, and A.K. Geim, Fluorographene: A Two-Dimensional Counterpart of Teflon, *Small* 6 (2010) 2877.
- [24] L. Wang, Y.Y. Sun, K. Lee, D. West, Z.F. Chen, J.J. Zhao, and S.B. Zhang, Stability of Graphene Oxide Phases from First-Principles Calculations, *Phys. Rev. B* 82 (2010) 161406.
- [25] Z. Xu, and K. Xue, Engineering Graphene by Oxidation: A First-Principles Study, *Nanotechnol.* 21 (2010) 045704.
- [26] J-X. Zhao, H-X. Wang, B. Gao, X-G. Wang, Q-H. Cai, and X-Z. Wang, Chemical Functionalization of Graphene via Aryne Cycloaddition: A Theoretical Study, *J. Mol. Model.* 18 (2012) 2868.
- [27] T.H. Wang, Y.F. Zhu, and Q. Jiang, Bandgap Opening of Bilayer Graphene by Dual Doping from Organic Molecule and Substrate, *J. Phys. Chem. C* 117 (2013) 12873.

- [28] M. Farjam, and R. Rafii-Tabar, Bandgap Opening of Bilayer Graphene by Dual Doping from Organic Molecule and Substrate, *Phys. Rev. B.* 80 (2009) 167401 (1-3).
- [29] M. Mohr, K. Papageelis, J. Maultzsch, and C. Thomsen, Two-Dimensional Electronic and Vibrational Band Structure of Uniaxially Strained Graphene from *ab initio* Calculations, *Phys. Rev. B* 80 (2009) 205410 (1-4).
- [30] S.M. Choi, S.H. Jhi, and Y.W. Son, Effects of Strain on Electronic Properties of Graphene, *Phys. Rev. B* 81 (2010) 081407 (1-4).
- [31] R. Majidi, and K. Ghafoori Tabrizi, Electronic Properties of Defect-Free and Defective Bilayer Graphene in an Electric Field, *Fuller. Nanotub. Car. N.* 19 (2011) 532.
- [32] T. Ozaki, H. Kino, J. Yu, M.J, Han, N. Kobayashi, and M. Ohfuti, et al. (2011) User's manual of OpenMX version 3.6. <http://www.openmx-square.org>.
- [33] J.P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [34] S. Grimme, Band Gap Modulation of Graphyne via Chemical Functionalization: A Density Functional Theory Study, *J. Comput. Chem.* 27 (2006) 1787.
- [35] R. Majidi, Effect of Doping on the Electronic Properties of Graphyne, *Nano* 8 (2013) 1350060.
- [36] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, and A.K. Geim, The Electronic Properties of Graphene, *Rev. Mod. Phys.* 81 (2009) 109.
- [37] S.B. Trickey, F. Muller-Plathe, G.H.F. Diercksen, and J.C. Boettger, Interplanar Binding and Lattice Relaxation in a Graphite Dilayer, *Phys. Rev. B* 45 (1992) 4460.
- [38] R. Majidi, and A.R. Karami, Electronic Properties of Bilayer and Trilayer Graphyne in the Presence of Electric Field, *Struct. Chem.* 25 (2014) 853.
- [39] R. Majidi, and A.R. Karami, A Biosensor for Hydrogen Peroxide Detection based on Electronic Properties of Carbon Nanotubes, *Mol. Phys.* 111 (2013) 3194.
- [40] R. Majidi, A.R. Karami, Band Gap Opening in α -Graphyne by Adsorption of Organic Molecule, *Physica E* 63 (2014) 264.
- [41] R. Majidi, and A.R. Karami, Band Gap Modulation of Graphene and Graphyne via Tetracyanoethylene Adsorption, *Studia. UBB. Chemia.* 1 (2016) 177.
- [42] R. Majidi, Band Gap Modulation of Graphyne via Chemical Functionalization: A Density Functional Theory Study, *Can. J. Chem.* 94 (2016) 229.