Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Physical Chemistry Chemical Physics

ARTICLE

Widely Tunable Band Gap of Graphdiyne: An Ab initio Study

Jahyun Koo[a,*], Minwoo Park[a,*], Seunghyun Hwang[a,*], Bing Huang[b], Byungryul Jang[a], Yongkyung Kwon[a], and Hoonkyung Lee[a]

Functionalization of graphdiyne, a two-dimensional atomic layer of sp–sp^2 hybrid carbon networks, was investigated through first-principles calculations. Hydrogen or halogen atoms preferentially adsorb on sp-bonded carbon atoms rather than on sp^2-bonded carbon atoms, forming sp^2- or sp^3-hybridizations. The energy band gap of graphdiyne is increased from ~0.5 eV to ~5.2 eV through the hydrogenation or halogenation. Unlike graphene, segregation of adsorbing atoms is energetically unfavourable. Our results show that hydrogenation or halogenation can be utilized for modifying the electronic properties of graphdiyne for applications to nano-electronics and -photonics.

1. Introduction

In recent years, graphene, a two-dimensional (2D) atomic layer of sp^2-bonded carbon atoms, has received considerable attention because of its unique electronic properties, such as the Dirac cone and high electron mobility (~10^5 m^2/Vs) [1-3]. Various methods have been devised for opening the band gap of graphene for applications for 2D nano-electronic device materials. Bilayer graphene under a vertically applied electric field has been found to have energy band gaps that are tunable up to ~0.32 eV when the electric field is increased to ~4 V/nm[4]. Hydrogenation and fluorination of graphene have been proposed, on a theoretical basis, as a more convenient method for tuning the band gap up to ~3.4 eV and ~2.7 eV, respectively[5-7]. Recent experimental studies confirmed that the band gap of graphene can be opened by hydrogenation[8] or fluorination[9], but with limitations. Hydrogen or fluorine atoms on graphene tend to aggregate with each other, thereby making it difficult to achieve band gap engineering of graphene[10-12].

Graphyne, a 2D carbon allotrope layer consisting of sp–sp^2 hybrid atoms[13], was predicted to have a coexistence of symmetric and asymmetric Dirac cones[14-16]. The asymmetric Dirac cone can allow electrons to flow in a preferred direction. It was demonstrated that the energy band gap of α-graphyne can be opened with an AB sublattice symmetry breaking of the honeycomb lattice[17]. γ-graphyne is known to have intrinsic band gaps[17], which presents the possibility of applications for new 2D device materials. The porous structure and large surface area may also allow for a variety of potential applications in energy storage, such as hydrogen and lithium-ion batteries[18-22]. It was found that no clustering of hydrogen or halogen atoms on graphyne occurs[23]. This implies that

adjustment of the electronic properties of graphyne can be achievable by adsorption of other elements without segregation to disturb the engineering. The band gap tuning by the hydrogenation or halogenation is ~3.4 eV[23] and ~4.3 eV[24], respectively.

Recently, graphdiyne, an atomic layer of sp- and sp^2-bonded carbon networks, was found to have possible applications for new 2D device materials[25] and lithium ion battery anodes[26-28]. Similar to graphyne, which consists of two adjacent sp-bonded carbon atoms and sp^2-bonded carbon atoms, graphdiyne consists of four adjacent sp-bonded carbon atoms and sp^2-bonded carbon atoms. There have been experimental efforts to synthesize graphdiyne films[28] and flakes[29]. Since the synthesis of graphdiyne is possible, in this paper, we performed a detailed study on geometrical and electronic properties of graphdiyne functionalized by hydrogenation or halogenation. The hydrogen or halogen atoms preferentially adsorb on the sp-bonded carbon atoms to form sp^2 or sp^3 bonds. This is in sharp contrast to the adsorption on graphene; only fluorine atoms are attached to graphene to form sp^3 hybridized bonds while chlorine, bromine, and iodine atoms do not form any hybrid bonds on graphene[30]. The local geometries of adsorbing atoms to graphdiyne are distinct: hydrogen atoms were found to have both in-plane and oblique-plane adsorption, fluorine to have both in-plane and oblique-plane adsorption, and chlorine and bromine to have only oblique-plane adsorption. The energy band gaps of the hydrogenated or halogenated graphdiyne as a function of the concentration of adsorbing atoms were also investigated. Findings show the band gaps are tunable up to ~5 eV with varying concentrations, much greater than band gap tuning of ~3.4 (~4.3) and ~2.7 (~3.5) eV by hydrogenation and fluorination of graphene[5-7] (graphyne[23,24]), respectively[5-7]. Our

This journal is © The Royal Society of Chemistry 2013

Phys. Chem. Chem. Phys., 2013, **00**, 1-3 | 1

results provide evidence that the band gap of graphdiyne can be tailored for new 2D device applications.

2. Computational details

Our calculations, using density functional theory (DFT)[31], were done in the Vienna Ab-initio Simulation Package (VASP) with a projector-augmented-wave (PAW) method.[32] For the exchange correlation energy functional, the generalized gradient approximation (GGA) was employed in the Perdew–Burke–Ernzerhof scheme[33] and the kinetic energy cutoff was taken to be 400 eV. For calculations of hydrogen or halogen adsorption, our model of γ-graphdiyne was a 1×1 hexagonal cell. Geometry optimization of the hydrogenated graphdiyne was carried out until the Hellmann–Feynman force acting on each atom was smaller than 0.01 eV/Å. The first Brillouin zone integration was performed using the Monkhorst–Pack scheme.[34] 4×4 k-point sampling for the 1×1 graphdiyne cell was utilized, which falls within the expected accuracy based on our test calculations.

3. Results and discussion

To investigate geometrical properties of graphdiyne functionalized by halogen and hydrogen atoms, we chose γ-graphdiyne as a representative (though graphdiyne can exist in a variety of symmetries). γ-graphdiyne is known to be the most energetically stable phase because of lowest ratio of sp^2-bonded carbon atoms to sp-bonded carbon atoms[35]. Here we denote γ-graphdiyne as graphdiyne. For functionalizing graphdiyne, we chose hydrogen and halogen atoms, where the functionalizing atom is denoted by M. There are two attachment sites on graphdiyne, i.e., sp-bonded and sp^2-bonded carbon atom sites. These adatoms are preferred to be bound to sp-bonded carbon atoms rather than to sp^2-bonded ones and to form an alternative pair, as shown in Figure 1, where one atom is attached above the graphdiyne plane and the other below the plane. This is consistent with the preference for hydrogen or halogen attachments on graphyne.[23,24] However, local geometries of the adsorption are different from each other. Furthermore, iodine atoms lack any hybrid forms, while adsorbing on graphyne[24].

Figure 1 displays the optimized atomic geometries of the hydrogenated or halogenated graphdiynes at the x=0.66 concentration, with hydrogen or halogen atoms attached to the sp-bonded carbon atoms, defined by the composite of C_1M_x where C and M indicate the composites of the carbon atoms and the adsorbed atoms, respectively. H atoms attach to graphdiyne in two configurations: H in-plane adsorption, and H oblique-plane adsorption. The oblique-plane configuration has an energy lower than the in-plane configuration by 0.09 eV/H, as shown in Figures 1(a) and 1(b). Although an out-of-plane configuration was not present in hydrogenated graphdiyne, the results are consistent with the recent report[23] on hydrogenated graphyne. In the case of fluorinated graphdiyne, the oblique-plane configuration was observed, and found to be energetically lower than the in-plane configuration by 1.7 eV/F as shown in Figures 1(c) and 1(d). In contrast, an oblique-plane configuration in the cases of Cl and Br atoms was only found to exist (Figures 1(e) and 1(f)), which can be understood by steric effects in the triangular carbon lattice due to longer ionic radii of Cl and Br ions than those of H and F ions or other electronic effects due to change in the energy bands. The ionic radii of the

H, F, Cl, Br, and I ions are 0.35, 1.33, 1.74, 1.96, and 2.20 Å, respectively.
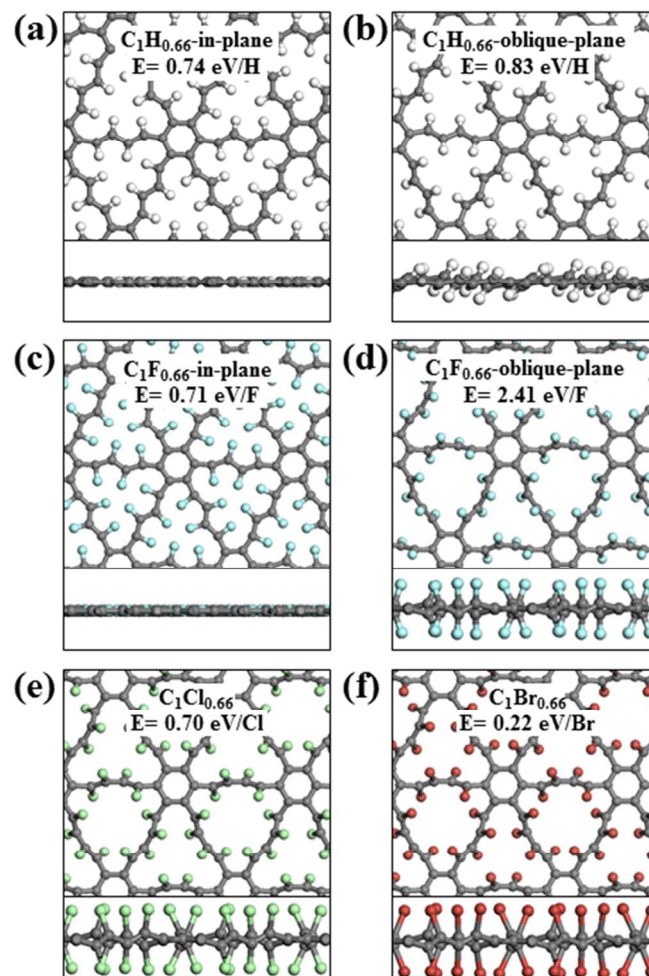
Fig. 1. Optimized atomic structures of hydrogen or halogen atoms adsorbed on graphdiyne with the composite of $C_1M_{0.66}$ when each sp-bonded carbon atom accommodates one hydrogen or halogen atom: (a) in-plane H adsorption and (b) oblique-plane H adsorption, (c) in-plane F adsorption and (d) oblique-plane F adsorption, (e) oblique-plane Cl adsorption chlorine atoms, and (f) oblique-plane Br adsorption. The grey-coloured, white-coloured, azure-coloured, green-coloured, and red-coloured spheres represent carbon atoms, hydrogen atoms, fluorine atoms, chlorine atoms, and bromine atoms, respectively.

Figure 2 shows the geometry of the local bonds of hydrogenated or halogenated graphdiynes. The bond length between the C–M atoms is found to increase as the atomic number of the halogen atoms increases: the calculated C–M bond lengths are 1.10, 1.38, 1.74, and 1.92 Å for the C–H, C–F, C–Cl, and C–Br, respectively, as presented in Table I. These lengths are associated with ionic radii of hydrogen or halogen atoms. The bond lengths of the nearest carbon-carbon atoms differ slightly with the position of attached M atoms, as presented in Table I.

We also considered adsorption of two atoms to each sp-bonded carbon atom of graphdiyne. We found that adsorption

2 | *Phys. Chem. Chem. Phys.*, 2013, **00**, 1-3

This journal is © The Royal Society of Chemistry 2013

of hydrogen or fluorine atoms takes place at a concentration of x=1.33, where each sp-bonded carbon atom accommodates two hydrogen or fluorine atoms as shown in Figures 3(a) and 3(c), respectively. Adsorption processes of other halogen atoms are endothermic at this concentration; the repulsive interaction between the adsorbing atoms increases as the ionic radius of the atoms increases. In lower concentrations, the adsorption of Cl and Br atoms may be exothermic; adsorption of a single atom to each sp-bonded carbon atom is energetically favourable because of smaller repulsive interactions compared to those at higher concentrations. We also considered additional adsorption of one hydrogen or fluorine atom to each sp^2-bonded carbon atom of graphdiyne with the composite of $C_1M_{1.66}$ (Figures 3(b) and 3(d)). We found that alternating different side adsorption of the atoms on sp^2-bonded carbon atoms is favourable in energy, consistent with that of graphyne[23,24].
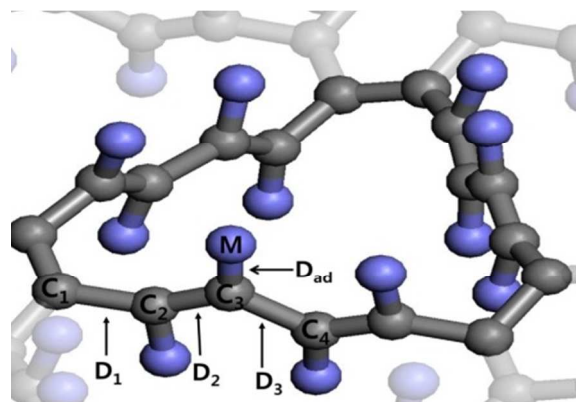

Fig. 2. Optimized atomic structure of hydrogen or halogen atoms adsorbed on sp-bonded carbon atoms of graphdiyne when pairs of halogens are attached to four adjacent sp-bonded carbon atoms. D_1, D_2, D_3, and D_{ad} indicate the C_1-C_2 bond length, the C_2-C_3 bond length, the C_3-C_4 bond length, and the C_3-M bond length, respectively.

Table I. The calculated bond lengths (D_1, D_2, D_3, and D_{ad}) for hydrogenated or halogenated graphdiyne. D_1, D_2, D_3, and D_{ad} are shown in Figure 2.

Composites	D_1(Å)	D_2(Å)	D_3(Å)	D_{ad}(Å)
$C_1H_{0.66}$	1.50	1.38	1.47	1.10
$C_1H_{1.33}$	1.53	1.53	1.54	1.10
$C_1H_{1.66}$	1.55	1.52	1.53	1.10
$C_1F_{0.66}$	1.51	1.36	1.49	1.36
$C_1F_{1.33}$	1.55	1.60	1.57	1.36
$C_1F_{1.66}$	1.61	1.57	1.56	1.36
$C_1Cl_{0.66}$	1.52	1.37	1.50	1.74
$C_1Br_{0.66}$	1.51	1.36	1.49	1.92

It was found that out-of-plane adsorption of hydrogen atoms to sp-bonded carbon atoms are preferred as shown in Figure 3(a), where out-of-plane is defined by the position of the center point between adsorbed H atoms on a sp-bonded atom. In contrast, oblique-plane adsorption of F atoms is energetically favourable as shown in Figure 3(c) because the repulsive interaction is minimized due to the increase of the distance between the fluorine atoms. The binding energies of the hydrogen and fluorine atoms are estimated to be 0.55 eV/H and 2.19 eV/F, respectively.
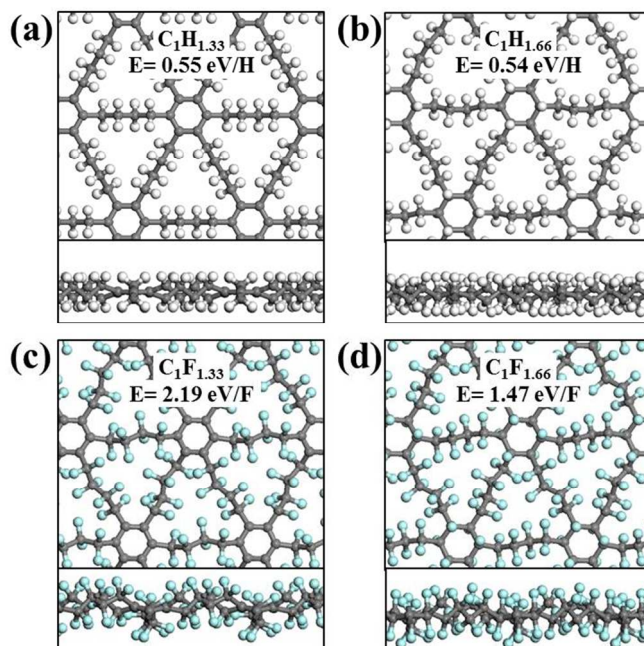
Fig. 3. Atomic structures of hydrogen and fluorine atoms adsorbed on graphdiyne: (a) $C_1H_{1.33}$, (b) $C_1H_{1.66}$, (c) $C_1F_{1.33}$, and (d) $C_1F_{1.66}$.

We analyzed the electronic structures of functionalized graphdiyne with different concentrations of adsorbing atoms. The calculated band gap of pristine graphdiyne is 0.49 eV, which is in good agreement with the values of ~0.48−0.53 eV in previous studes[36-38]. The calculated energy band gaps of graphdiyne functionalized by adsorption of H, F, Cl, and Br atoms at the x=0.66 concentration are 0.66, 2.14, 2.05, and 1.86 eV, respectively. The band gaps increase as the concentration increases and depend on which the atoms are adsorbed as shown in Figures 4(a)−4(d) because of the difference in the adsorption geometry. We also confirmed that the flat-like bands come from the localized states near the sp-bonded carbon atoms adsorbing hydrogen or halogen atoms.
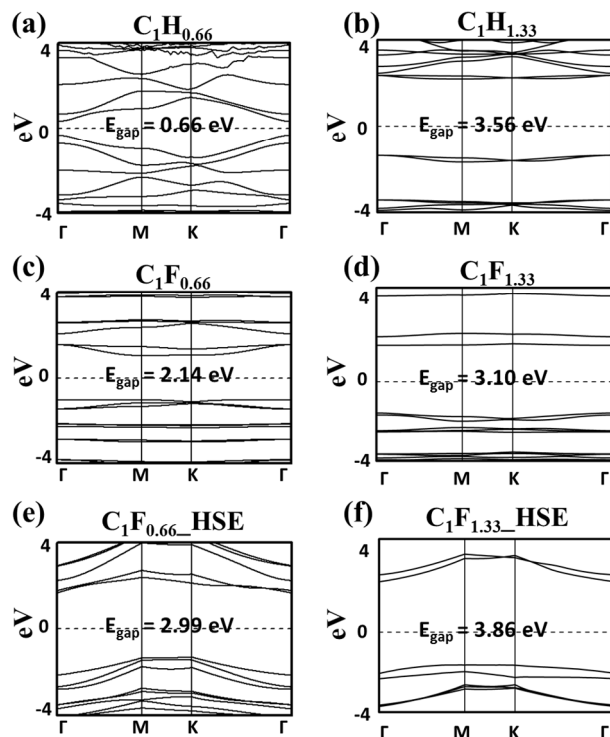
This journal is © The Royal Society of Chemistry 2013

Phys. Chem. Chem. Phys., 2013, **00**, 1-3 | **3**

The degree of band gap tuning is ~1.2 eV as the type of atoms changes from hydrogen to halogen as shown in Table II. The band gap tuning does not depend much on the type of halogen atoms; only hydrogen atoms affect the band gap tuning. When each sp-bonded carbon atom adsorbs two hydrogen or fluorine atoms, the band gaps for $C_1H_{1.66}$ and $C_1F_{1.66}$ are 5.11 eV and 4.50 eV, as shown in Table II, respectively. These results show that the band gap of graphdiyne is widely tunable by hydrogenation and halogenation by ~4.6 eV, which is greater than the value ~3.4 eV of graphene[5-7] or ~4.3 eV of graphyne[23,24]. The conduction and valence bands of graphdiyne consist of the vertically-aligned orbitals (p_z) of the sp- and sp^2-bonded carbon atoms. The density of states of the p_z orbitals near the Fermi level are decreased as the hydrogen or halogen concentration increases while the density of states of the sp^3-bonded carbons are increased. Generally, sp^3-bonded carbon structures have a large energy gap of a few eV, e.g., ~5.5 eV for diamond. Thus the band gaps increase as the concentration increases.

Since the DFT tends to underestimate band gaps because of its missing many-body effects, the band gap tuning in experiment is expected to be larger than theoretically estimated value. Noting that hybrid functional can significantly improve the energy gaps of solids beyond the PBE calculations[39], we performed HSE06[40] calculations on hydrogenated or halogenated graphdiynes. The band gaps with the HSE are increased compared with those with the PBE as shown in Table II or Figure 5(a). The PBE wave functions near the Fermi level depend on the k-points though the PBE energy eigenvalues are independent of the k-points. This leads that exact exchange energy depends on the k-points. Therefore the band dispersions obtained from the HSE and PBE calculations are different as shown in Figure 4. The positions of the valence band maximum and the conduction band mimimum are presented in Table II.

Table III. The band gaps and positions of the valence band maximum (VBM) and conduction band minimum (CBM) of the hydrogenated or halogenated graphdiynes from the PBE and HSE calculations.

Composites	PBE			HSE		
	VBM	CBM	Band gap (eV)	VBM	CBM	Band gap (eV)
$C_1H_{0.66}$	Γ	Γ	0.66	Γ	Γ	1.10
$C_1H_{1.33}$	Γ	M	3.56	Γ	M	2.63
$C_1H_{1.66}$	Γ	Γ	5.11	Γ	Γ	3.04
$C_1F_{0.66}$	M	M	2.14	K	Γ	2.99
$C_1F_{1.33}$	Γ	Γ	3.10	M	Γ	3.86
$C_1F_{1.66}$	Γ	Γ	4.50	Γ	Γ	5.20
$C_1Cl_{0.66}$	M	M	2.05	K	K- Γ	3.19
$C_1Br_{0.66}$	Γ	M	1.86	K	K- Γ	3.30

Fig. 4. The calculated band structure of hydrogenated or halogenated graphdiynes: (a) $C_1H_{0.66}$, (b) $C_1H_{1.33}$, (c) $C_1F_{0.66}$, (d) $C_1F_{1.33}$, (e) $C_1F_{0.66}$-HSE, and (f) $C_1F_{1.33}$-HSE. The Fermi energy (the dotted line) is set as zero.

A study of the effects on the band structure due to the adsorption of halogen atoms at varying concentrations was conducted. The binding energy of the halogen atoms on graphdiyne was calculated as a function of the concentration, x. The calculated binding energy of the halogen atoms is defined as $E_{bind}^x(M) = (E_C + N \cdot E_M - E_{C-M}^x)/N$ where N is the number of attached M atoms per cell for a given x, E_{C-M}^x is the total energy of the hydrogenated or halogenated graphdiynes with a x concentration of M atoms, E_C is the total energy of the pristine graphdiyne, and E_M is the total energy (per M atom) of an isolated M_2 molecule in a vacuum. At the x=0.33 concentration, the calculated binding energies are 0.83, 2.41, 0.70, and 0.22 eV/atom for H, F, Cl, and Br atoms, respectively. Iodine atoms were not found to be stable at any concentration; the adsorption process is endothermic. We have found that the changes in binding energies are decreased as the concentration varies as shown in Figure 5(b), indicating that the interaction between adsorbing atoms is repulsive. We note that the distance between halogen atoms is greater than ~2.5 Å at x=1.66. This leads us to conclude that the clustering of the

halogen atoms is not energetically preferable, making band gap tuning possible.
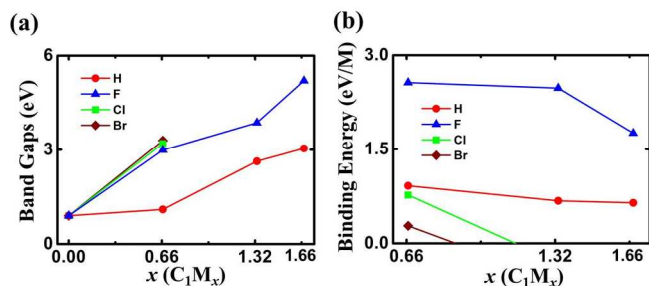
Fig. 5. (a) The calculated HSE band gap and (b) the calculated PBE binding energy of hydrogen or halogen atoms on graphdiyne as a function of the concentration x.

According to recent molecular dynamics studies[41-43] on hydrogen functionalized graphyne and graphdiyne, the structures are stable with high strength and stiffness. The Young's modulus and fracture stress of the hydrogenated graphdiyne (C_1H_1) are ~300 and ~22 GPa, respectively, comparable to ~600 and ~35 GPa of the hydrogenated graphene (C_1H_1), respectively. The values are also much greater than ~30 and ~0.05 GPa of high-strength concrete, respectively. Thus we believe that the functionalized graphdiyne with hydrogen or halogen atoms we proposed here are expected to be stable.

Conclusions

In conclusion, we have conducted the total energy calculations of hydrogenated or halogenated graphdiyne to investigate its geometry and band gaps. The feature of the functionalized graphdiyne is distinct from hydrogenated graphene. The band gaps were found to be broadly tunable by ~5 eV through a change in the hydrogen or halogen concentration. This band gap tuning is much greater than that (~3 eV) of graphene. Furthermore, unlike in graphene, a clustering of halogen atoms on graphdiyne was not preferred. Therefore, it is feasible to tune the band gap for specific applications. Our results suggest that graphdiyne can be more advantageous than graphene when tailoring energy band gaps for applications in nano-electronics and nano-photonics. In addition, hydrogenated or halogenated graphdiynes might be used for carbon dioxide separation because of their porous texture[44].

Acknowledgements

Notes and references

[a] School of Physics, Konkuk University, Seoul 143-701, Korea.
[b] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830 USA.

*These authors equally contributed to this work.

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*, 2004, **306**, 666-669.

2   Y. Zhang, Y.-W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201-204.

3   A. Hirsh, *Nat. Mater.*, 2010, **9**, 868-871.

4   Y. Liang, L. Yang, *Phys. Rev. B*, 2012, **86**, 205423.

5   P. Cudazzo, C. Attaccalite, I. V. Tokatly and A. Rubio, *Phys. Rev. Lett.*, 2010, **104**, 226804.

6   W. Wei and T. Jacob, *Phys. Rev. B*, 2013, **87**, 115431.

7   O. Leenaerts, H. Peelaers, A. D. Hernández-Nieves, B. Partoens and F. M. Peeters, *Phys. Rev. B*, 2010, **82**, 195436.

8   R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann and L. Hornekær, *Nat. Mater.*, 2010, **9**, 315-319.

9   K.-J. Jeon, Z. Lee, E. Pollak, L. Moreschini, A. Bostwick, C.-M. Park, R. Mendelsberg, V. Radmilovic, R. Kostecki, T. J. Richardson and E. Rotenberg, *ACS Nano*, 2011, **5**, 1042-1046.

10   H. Xiang, E. Kan, S.-H. Wei, M.-H. Whangbo and J. Yang, *Nano Lett.*, 2009, **9**, 4025-4030.

11   S. S. Han, H. Jung, D. H. Jung, S.-H. Choi and N. Park, *Phys. Rev. B*, 2012, **85**, 155408.

12   Y. Li and R. T. Yang, *J. Am. Chem. Soc.*, 2006, **128**, 8136-8137.

13   R. H. Baughman, H. Eckhardt and M. Kertesz, *J. Chem. Phys.*, 1987, **87**, 6687-6699.

14   D. Malko, C. Neiss, F. Viñes and A. Görling, *Phys. Rev. Lett.*, 2012, **108**, 086804.

15   O. Leenaerts, B. Partoens and F. M. Peeters, *Appl. Phys. Lett.*, 2013, **103**, 013105.

16   N. Narita, S. Nagai, S. Suzuki and K. Nakao, *Phys. Rev. B*, 1998, **58**, 11009-11014.

17   B. G. Kim and H. J. Choi, *J. Phys. Rev. B*, 2012, **86**, 115435.

18   H. J. Hwang, Y. Kwon and H. Lee, *J. Phys. Chem. C*, 2012, **116**, 20220-20224.

19   Y. Guo, K. Jiang, B. Xu, Y. Xia, J. Yin and Z. Liu, *J. Phys. Chem. C*, 2012, **116**, 13837-13841.

20   C. Li, J. Li, F. Wu, S.-S. Li, J.-B. Xia and L.-W. Wang, *J. Phys. Chem. C*, 2011, **115**, 23221-23225.

21   H. J. Hwang, J. Koo, M. Park, N. Park, Y. Kwon and H. Lee, *J. Phys. Chem. C*, 2013, **117**, 6919-6923.

22   H. Zhang, M. Zhao, X. He, Z. Wang, X. Zhang and X. Liu, *J. Phys. Chem. C*, 2011, **115**, 8845-8850.

23   J. Koo, H. J. Hwang, B. Huang, H. Lee, H. Lee, M. Park, Y. Kwon, S.-H. Wei and H. Lee, *J. Phys. Chem. C*, 2013, **117**, 11960-11967.

39   J. Koo, B. Huang, H. Lee, G. Kim, J. Nam, Y. Kwon and H. Lee, *J. Phys. Chem. C*, 2014, **118**, 2463-2468.

24   G. M. Psofogiannakis and G. E. Froudakis, *J. Phys. Chem. C*, 2012, **116**, 19211-19214.

25   C. Sun and D. J. Searles, *J. Phys. Chem. C*, 2012, **116**, 26222-26226.

26   H. Zhang, Y. Xia, H. Bu, X. Wang, M. Zhang, Y. Luo and M. Zhao, *J. Appl. Phys.*, 2013, **113**, 044309.

This journal is © The Royal Society of Chemistry 2013

Phys. Chem. Chem. Phys., 2013, **00**, 1-3 | **5**

27 B. Jang, J. Koo, M. Park, H. Lee, J. Nam, Y. Kwon, and H. Lee, *Appl. Phys. Lett.*, 2013, **103**, 263904.

28 G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256-3258.

29 M. M. Haley, S. C. Brand, and J. J. Pak, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 836-838.

30 F. Karlický, R. Zbořil, and M. Otyepkab, *J. Chem. Phys.*, 2012, **137**, 034709.

31 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A1138.

32 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.

33 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

34 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.

35 H. Shin, S. Kang, J. Koo, H. Lee, J. Kim and Y. Kwon, accepted for publication in *J. Chem. Phys.*.

36 G. Luo, X. Qian, H. Liu, R. Qin, J. Zhou, L. Li, Z. Gao, E. Wang, W.-N. Mei, J. Lu, Y. Li and S. Nagase, *Phys. Rev. B,* 2011, **84**, 075439.

37 L. D. Pan, L. Z. Zhang, B. Q. Song, S. X. Du and H.-J. Gao, *Appl. Phys. Lett.*, 2011, **98**, 173102.

38 J. Kang, F. Wu and J. Li, *J. Phys.: Condens. Matter*, 2012, **24**, 165301.

39 J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207-8215.

40 F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, G, Kresse, *Phys. Rev. B,* 2007, **76**, 115109.

41 Y.-Y. Zhang, Q.-X. Pei, C.-M. Wang, Y. Cheng, and Y.W. Zhang, *J. Appl. Phys.* 2013, **114**, 073504.

42 Q. X. Pei, Y. W. Zhang and V. B. Shenoy, *Carbon*, 2010, **48**, 898-904.

43. Y. Yang and X. Xu, *Computational Mat. Sci.*, 2012, **61**, 83-88.

44 J. Schrier *ACS Appl. Mater. Interfaces*, 2012, **4**, 3745-3752.