

First-principle study of nanostructures of functionalized graphene

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Abstract. We present first-principle calculations of 2D nanostructures of graphene functionalized with hydrogen and fluorine, respectively, in chair conformation. The partial density of states, band structure, binding energy and transverse displacement of C atoms due to functionalization (buckling) have been calculated within the framework of density functional theory as implemented in the SIESTA code. The variation in band gap and binding energy per add atom have been plotted against the number of add atoms, as the number of add atoms are incremented one by one. In all, 37 nanostructures with 18C atoms, $3 \times 3 \times 1$ (i.e., the unit cell is repeated three times along x -axis and three times along y -axis) supercell, have been studied. The variation in C–C, C–H and C–F bond lengths and transverse displacement of C atoms (due to increase in add atoms) have been tabulated. A large amount of buckling is observed in the carbon lattice, 0.0053–0.7487 Å, due to hydrogenation and 0.0002–0.5379 Å, due to fluorination. As the number of add atoms (hydrogen or fluorine) is increased, a variation in the band gap is observed around the Fermi energy, resulting in change in behaviour of nanostructure from conductor to semiconductor/insulator. The binding energy per add atom increases with the increase in the number of add atoms. The nanostructures with 18C+18H and 18C+18F have maximum band gap of 4.98 eV and 3.64 eV, respectively, and binding energy per add atom –3.7562 eV and –3.3507 eV, respectively. Thus, these nanostructures are stable and are wide band-gap semiconductors, whereas the nanostructures with 18C+2H, 18C+4H, 18C+4F, 18C+8F, 18C+10F and 18C+10H atoms are small band-gap semiconductors with the band gap lying between 0.14 eV and 1.72 eV. Fluorine being more electronegative than hydrogen, the impact of electronegativity on band gap, binding energy and bond length is visible. It is also clear that it is possible to tune the electronic properties of functionalized graphene, which makes it a suitable material in microelectronics.

Keywords. Graphene; density functional theory; SIESTA; electronic density of states; band structure.

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1. Introduction

Graphene has emerged as a promising carbon-based material that was mechanically exfoliated from graphite in 2004 [1], 440 years after the invention of pencil. It represents a new

class of materials that are only one-atom thick and it has gained attention due to its unique electronic and magnetic properties [2–5]. It offers new inroads into low-dimensional properties and continues to provide fertile ground for many applications [2]. Carbon electronics with a possibility of ballistic transport has technologically emerged more promising for fabricating nanoscale devices.

As graphene is a two-dimensional and low-cost material, it is possible to reduce the size and cost and further improve the quality of electronic devices, and graphene is going to play a key role in the development of carbon technology. Although the absence of a band gap hinders its applications in microelectronic devices, a suitable band gap can be tailored by chemical functionalization of graphene, which results in the tuning of electronic and magnetic properties for vast applications in microelectronics. A few other aspects such as (a) graphene can be used for hydrogen storage, (b) graphene can be made magnetic for its potential use in spintronics, (c) low reflectance, high carrier mobility and high absorption of graphene can be used for fabricating optoelectronic devices and (d) its use in electrochemical devices and biosensors, are the other motivations for studying chemical functionalization of graphene [3].

Also, recent computational and experimental studies have shown that hydrogenation of pristine graphene results in a metal–semiconductor transition [6–16]. Hydrogenation of graphene has been found to be reversible [10]. The reverse engineering on graphene has great potential in the design of functional nanomaterials and fuel storage devices. Fully hydrogenated graphene, i.e., graphane, is a wide band-gap semiconductor. It is at least as stable as graphene functionalized with fluorine [6]. Because of its structure and low dimensionality, it provides fertile possibilities for fundamental science and technological applications.

The fluorination of graphene has attracted considerable attention because it increases the reactivity of sp^2 bonds and opens up a wide range of modifications. It enables tuning of band gaps and opens up possibilities as a dopant for usage in electronics. Many experiments have shown dramatic changes in the electronic and structural properties of graphene by increasing the percentage of fluorine. Recent theoretical research has also focussed on fluorinated graphene [17,18]. When chemical elements like hydrogen and fluorine are absorbed on the surface of graphene, they form covalent bonds with the carbon atoms. As a result, the planar crystal structure of graphene characterized by sp^2 bonds between the carbon atoms is transformed into a three-dimensional structure with sp^3 bonds.

In this paper we have undertaken an *ab initio* computational study of 2D nanostructures of graphene functionalized with hydrogen as well as with fluorine, modelled in chair conformation, to look for possible systematics in their influence on band structure, bond lengths and buckling (transverse displacement of C atoms) on functionalization. Our calculations are based on the method of numeric localized atomic orbitals and pseudopotentials using density functional theory (DFT) [19,20] as implemented in the SIESTA code. We have scanned the complete spectrum of variation in band gap, binding energy per add atom, bond lengths and transverse displacement of C atoms due functionalization of 2D nanostructure of graphene, functionalized with H and F, increasing add atom in steps of 1 up to 18. We have also observed the impact of electronegativity of add atom in the functionalization on these properties. Some of the other studies have focussed mainly on 100% and 50% functionalized cases of hydrogenation, for which we have compared our results and comparison was possible only for bond lengths. As has been

mentioned in recent papers [16,17], 100% functionalization has not been achieved so far. Therefore, more thorough investigation into the variation in electronic and structural properties due to functionalization is desirable. Our study is more detailed and exhaustive as we present more useful results which are illustrated graphically and discuss the effect of electronegativity of add atom.

Through first-principle total energy calculations, Sofo *et al* [6] predicted for the first time, in 2007, that graphene could be fully hydrogenated to form a stable hydrocarbon, the so-called graphane. This theoretical prediction was translated into reality by Elias *et al* [8], who demonstrated experimentally that a single layer of graphene could be hydrogenated to graphane. Some of the other computational studies of functionalized (hydrogenated) graphene are by Boukhvalov *et al* [7], Flores *et al* [9] and Chandrachud *et al* [11]. A detailed comparison of our results with these studies has been made (see §3 and table 1).

We have studied the 37 nanostructures of functionalized graphene with 18C atoms in $3 \times 3 \times 1$ supercell. The number of add atoms (H or F) are incremented in a step of one from 1 to 18 in chair conformation. Figures 1a–1d show the optimized structures for pristine graphene (18C) and hydrogenated graphene in chair conformation with 50% (18C+9H), 75% (18C+14H) and 100% (18C+18H) of H atoms, respectively. Figures 2a–2c show optimized structures for fluorinated graphene in chair conformation with 50% (18C+9F), 75% (18C+14F) and 100% (18C+18F) of F atoms, respectively. Our study is more systematic and thorough as compared to other computational studies mentioned above as we have incremented add atoms one by one in chair conformation. In this way, it is possible to study the tuning of band gap and other properties such as variation in formation energy, bond lengths, bond angles, buckling and HUMO–LUMO of functionalized graphene more thoroughly.

2. Simulation details

Simulations presented are based on the method of numerical localized atomic orbitals, pseudopotentials and density functional theory (DFT) [19,20]. We have used Troullier Martin, norm conserving, relativistic pseudopotentials [21,22] in fully separable Kleinman and Bylander form for carbon, hydrogen and fluorine. The exchange and correlation energies are treated within the generalized gradient approximation (GGA) according to the Perdew, Burke and Ernzerhof (PBE) parametrization. The pseudopotentials used were tested for properties of molecules such as CH₄ provide us converged parameters for the present study. Throughout geometry optimization, double zeta polarization (DZP) basis set with a confinement energy of 0.01 Ry were used. $11 \times 11 \times 1$ Monkhorst–Pack of k points was used for sampling Brillouin zone. The spacing of the real space grid used to calculate the Hartree, exchange and correlation contribution to the total energy and Hamiltonian was 250 Ry. Minimization of energy was carried out by giving sufficient number of SCF iterations using standard conjugate-gradients technique. Interactions between adjacent layers is eliminated by creating a vacuum between two layers with a large spacing of 20 Å.

The binding energy (BE) per add atom E_{BE} of the functionalized graphene was calculated using the following formula:

$$E_{BE} = [E_T - E_G - nE_A] / n, \quad (1)$$

Table 1. C-C, C-H and C-F bond lengths, band gap, transverse displacement (*d*) of C atoms and binding energy (BE) per add atom for nanostructures of functionalized graphene with 18C atoms.

Nano Structure	C-C		C-H		Band gap (eV)	Transverse displacement of C atoms (Å)	BE/add atom (eV)
	Bond length (Å)		C-H				
	This simulation	Other simulation	This simulation	Other simulation			
18C	1.421	1.42 [6] 1.423 [7]	-	-	Nil	-	-
18C+9H	1.381-1.528	1.52 [6] 1.537 [7]	1.120-1.139	1.11 [6] 1.086 [7]	Nil	0.0069-0.7274	-3.2865
18C+14H	1.385-1.533	1.52 [12] 1.475[7, For 50% hydrogenation]	1.122-1.127	1.158 [7, For 50% hydrogenation]	2.9568	0.0105-0.5916	-3.6314
18C+18H	1.544		1.109		4.9793	0.2302-0.2305	-3.7562
	C-C		C-F				
18C+9F	1.3749-1.5031		1.3886-1.4242	1.386[18, For 100% fluorination]	Nil	0.0239-0.4195	-3.1246
18C+14F	1.3371-1.4819		1.3771-1.3923		2.8730	0.0084-0.3313	-3.2836
18C+18F	1.5078-1.5081		1.3818-1.3822		3.6374	0.1880-0.3132	-3.3507

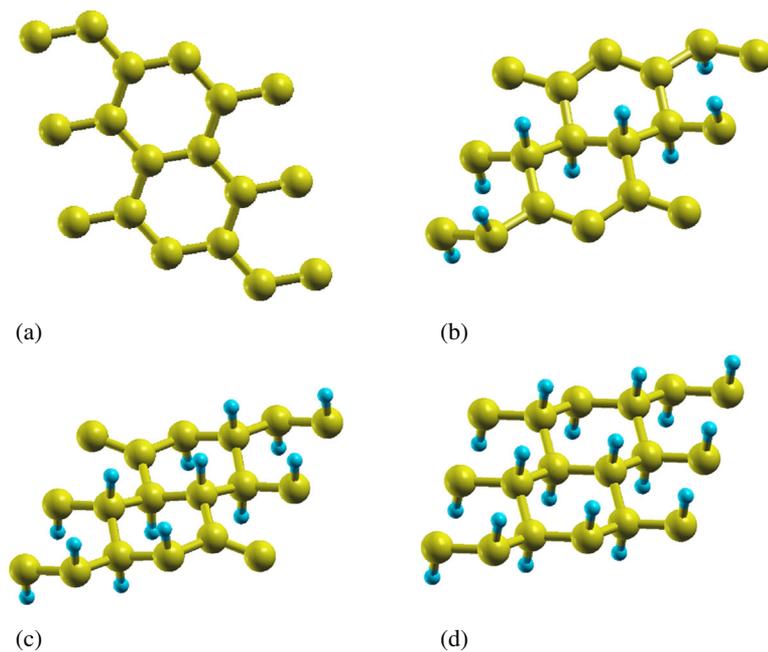


Figure 1. Optimized nanostructures of hydrogenated graphene in chair conformation. (a) Pristine structure (18C), (b) 18C+9H, (c) 18C+14H and (d) 18C+18H.

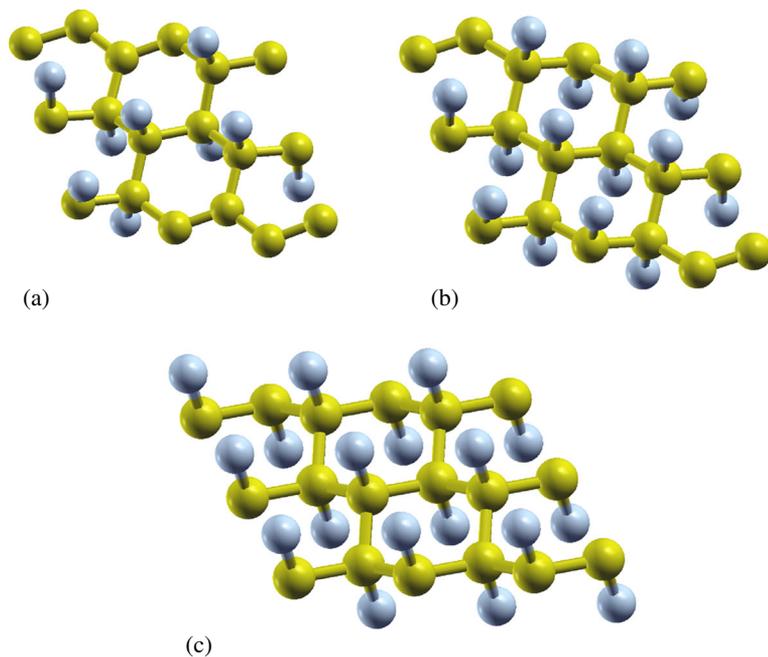


Figure 2. Optimized nanostructures of fluorinated graphene in chair conformation. (a) 18C+9F, (b) 18C+14F and (c) 18C+18F.

where E_T is the total energy of the functionalized graphene, E_G is the total energy of pristine graphene (18C) and E_A is the total energy of the single add (H or F) atom as obtained from converged SIESTA runs (n is the number of add atoms).

3. Results and discussion

3.1 Band structure and partial density of states

3.1.1 Hydrogenation of graphene. The electronic band structure has been calculated along Γ -M-K- Γ direction of the irreducible part of hexagonal Brillouin zone. Pristine graphene is a zero-gap semimetal because the conduction and valence bands meet at the Γ point (see figure 3a).

As the number of hydrogen atoms (n) are increased from 1 to 18, variation appears near the Fermi energy in the band structure (see figures 3b–3d). For odd number of hydrogen atoms, a band line crosses the Fermi energy, indicating that such nanostructures are good conductors (see figure 3b).

For $n = 2, 4$ and 12 , band gap is small, ranging from 0.20 eV to 0.34 eV. However, when $n = 10$, the band gap becomes 1.72 eV, indicating that this structure is a semiconductor. When $n = 14, 16$ and 18 , the band gap is found to be still larger, ranging from 2.95 eV to 4.98 eV where the valence band maximum (VBM) and conduction band minimum (CBM) are found at Γ point (except for $n = 14$, where VBM and CBM are at M point), which makes hydrogenated graphene a direct wide-band-gap semiconductor. It is clear that fully hydrogenated graphene is an insulator. By varying the number of hydrogen atoms, the band gap may be tuned to the desired value.

Sofa *et al* [6] studied a nanostructure of graphene by adding hydrogen atoms in chair and boat conformations for first-principle calculations using CASTEP. Their plots for the band structure (figure 3 in [6]) are in close agreement with our results.

The right column of each of figures 3a–3d shows the partial density of states (PDOS) due to $2s$ and $2p$ orbitals of carbon and $1s$ orbital of hydrogen for pure as well as hydrogenated graphene. As the numbers of hydrogen atoms are incremented one by one from 1 to 18 in the chair conformation, a variation in PDOS appears near the Fermi energy. When the number of hydrogen atoms is odd, the $2p_z$ orbital of carbon atom dominates the contribution to PDOS near the Fermi energy and a peak appears at the Fermi energy, indicating that the nanostructure is a conductor (see figure 3b). When the number of hydrogen atoms is even, PDOS in the vicinity of the Fermi energy is mainly derived from $1s$ state of H, while a strong hybridization between $1s$ orbitals of H and $2p_z$ orbitals of C is found in highest occupied molecular orbital (HOMO) region. It is found that HOMO and lowest unoccupied molecular orbital (LUMO) gaps near the Fermi energy increase (see figures 3c and 3d) for $n = 10, 14, 16$ and 18 , indicating that these nanostructures are semiconductors/insulators (n is the number of H atoms). However, for $n = 8$ and 12 , peak appears at the Fermi energy even though n is even. For $n = 2, 4$ and 6 , there is no gap at the Fermi energy.

Sofa *et al* [6] studied a nanostructure of graphene by adding hydrogen atoms in chair and boat conformations for first-principle calculations using CASTEP. Their plots for density of states (figure 3 in [25]) are in close agreement with our results.

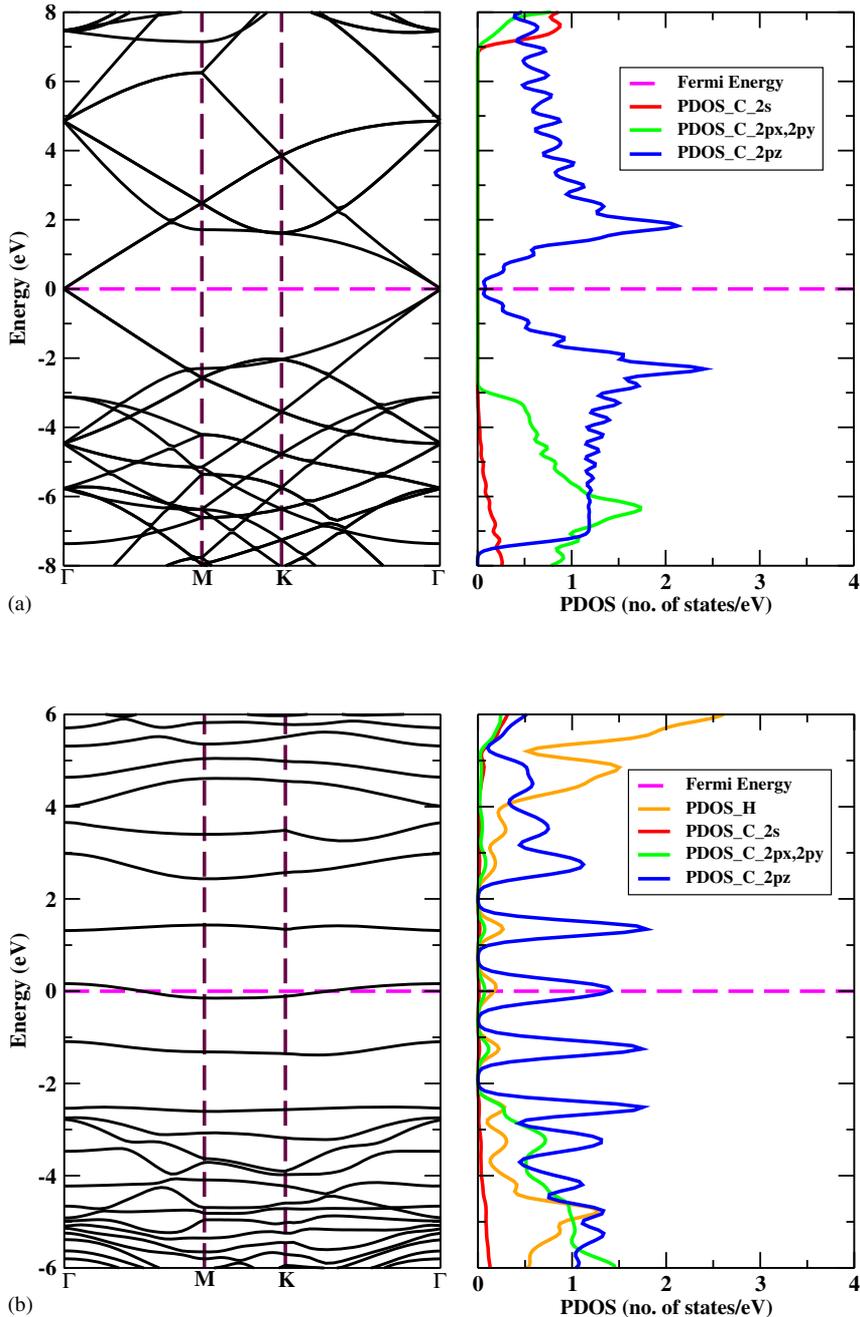


Figure 3. Electronic band structure (left column) and partial DOS (right column) for nanostructures of functionalized graphene with (a) 18C, (b) 18C+9H, (c) 18C+14H, (d) 18C+18H. The zero of the energy scale lies at the Fermi energy. High symmetry points of the band structure (left column of each figure) are at Γ ($k = 0$ and $0.71/\text{\AA}$), M ($k = 0.26/\text{\AA}$) and K ($k = 0.41/\text{\AA}$).

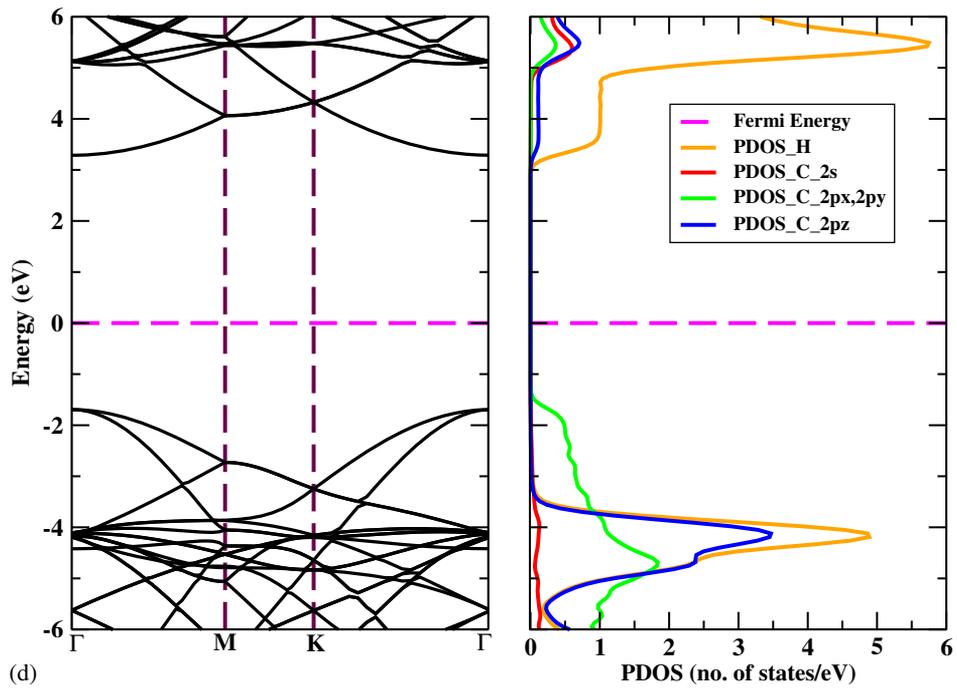
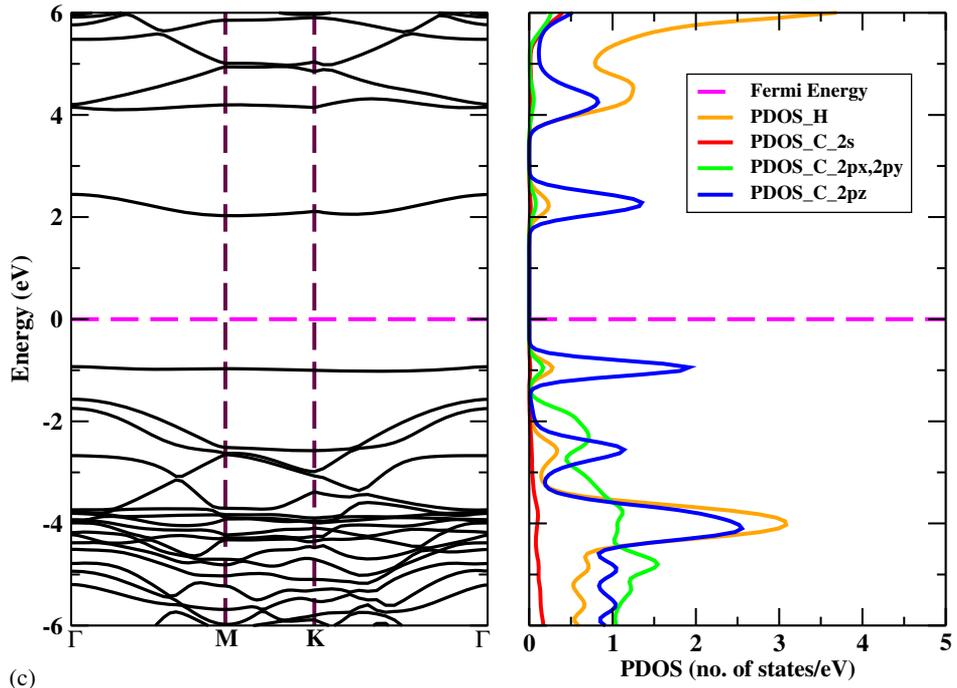


Figure 3. (Continued)

Chandrachud *et al* [11] have studied a nanostructure of graphene having 50 carbon atoms by varying the percentage of hydrogen atoms for *ab initio* study using VASP. Their plots for electron density of states (figure 3 in [11]) are in qualitative agreement with our results.

3.1.2 Fluorination of graphene. The electronic band structure has been calculated for fluorinated graphene along the Γ -M-K- Γ direction of the irreducible part of hexagonal Brillouin zone. Pristine graphene is a zero-gap semimetal because the conduction and valence bands meet at the Γ point (see figure 3a). As the numbers of fluorine atoms (n) are increased, the bonds formed between the fluorine p_z and carbon p_z orbitals force the carbon atoms into sp^3 hybridization, breaking the symmetry of graphene [18]. This opens a gap via the formation of new C-F bonding states in the valence band maximum and C-F antibonding states in the conduction band minimum (see figures 4a-4c). As the number of fluorine atoms (n) is increased from 1 to 18, variation appears near the Fermi energy in the band structure (see figures 4a-4c). For odd number of fluorine atoms, a band line crosses the Fermi energy indicating that such nanostructures are good conductors (see figure 4a).

For $n = 2, 4, 8$ and 16 , band gap is small, ranging from 0.12 eV to 0.93 eV, indicating that such structures are semiconductors. In these cases, the valence band maximum (VBM) and conduction band minimum (CBM) are at M point. When $n = 10, 14$ and 18 , the band gap is large, ranging from 1.80 eV to 3.64 eV. Therefore, these nanostructures of fluorinated graphene behave as wide-band-gap semiconductors. When graphene is fully fluorinated, there is a band gap of 3.64 eV.

Junkermeier *et al* [18] have studied nanostructures of graphene by adding fluorine atoms in different conformations for *ab initio* calculations using Quantum Espresso. Their patterns of plots for band structure (figure 4 in [18]) are in close agreement with our results.

The right columns of figures 4a-4c show the PDOS due to orbitals of carbon and fluorine atoms for fluorinated graphene. As the number of fluorine atoms is incremented one by one from 1 to 18 in the chair conformation, a variation in PDOS appears near the Fermi energy. When the number of F atoms is odd, the dominant contribution to PDOS near the Fermi energy is from $2p_z$ orbital of carbon atom and $2p_x, 2p_y$ orbitals of fluorine atom and a peak appears at the Fermi energy due to $C_{-2}p_z$ orbital, indicating that the nanostructure is a conductor. When the number of F atoms is even, PDOS in the vicinity of Fermi energy is mainly due to $2p$ orbital of F, while a strong hybridization between $2p_x, 2p_y$ orbitals of F and $2p_z$ orbitals of C has been found in the HOMO region. It is found that the HOMO-LUMO gap near the Fermi energy is large (see figures 4b and 4c) for $n = 14, 16$ and 18 , indicating that these nanostructures are semiconductors/insulators (n is the number of F atoms). However, for $n = 6$, sharp peak appears at the Fermi energy even though n is even. For $n = 2, 4, 8, 10$ and 12 , there is a broad peak at the Fermi energy.

3.1.3 Comparison of band gap due to hydrogenation and fluorination. Figure 5 shows the graph of variation of band gap with the add atoms. Blue line is for hydrogenation and red line is for fluorination. When the number of add atom is odd, the band gap is zero. Also in the case of hydrogenation, the band gap is zero for $n = 6$ and 8 . In the

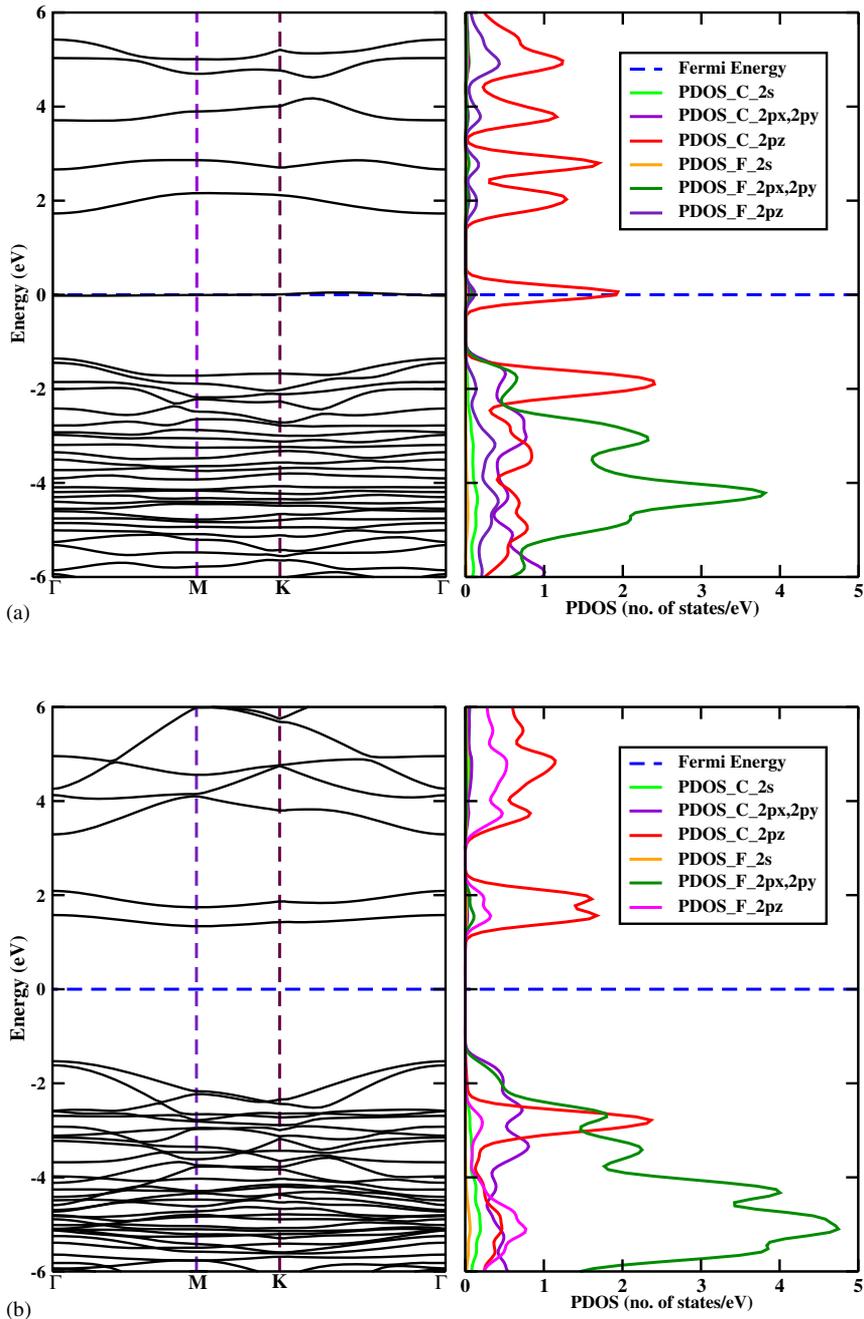


Figure 4. Electronic band structure (left column) and partial DOS (right column) for nanostructures of fluorinated graphene with (a) 18C+9F, (b) 18C+14F, (c) 18C+18F. The zero of the energy scale lies at the Fermi energy. High symmetry points of the band structure (left column of each figure) are at Γ ($k = 0$ and $0.71/\text{\AA}$), M ($k = 0.26 \text{\AA}$) and K ($k = 0.41/\text{\AA}$).

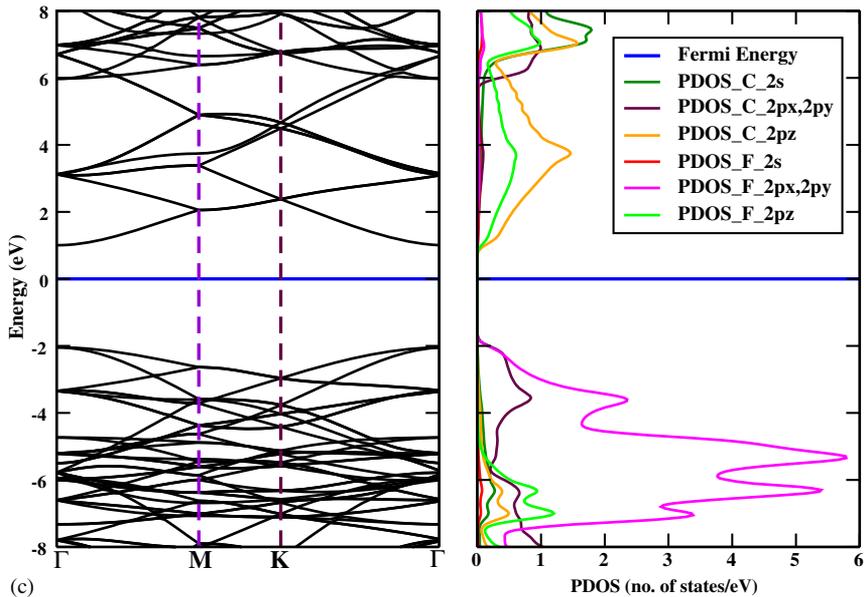


Figure 4. (Continued)

case of fluorination, the band gap is zero for $n = 6$. For $n = 4$ and 8, the magnitude of band gap is more for fluorination than for hydrogenation. But for $n = 10, 12, 14, 16$ and 18, band gap is higher in the case of hydrogenation when compared to fluorination. The maximum band gap is for $n = 18$ (100% functionalization), which is 4.98 eV for hydrogenation and 3.00 eV for fluorination (also see table 1). The band gap for $n = 14$

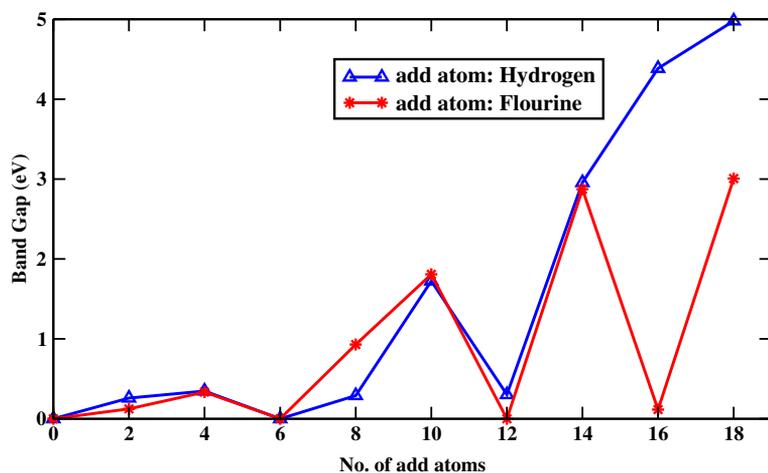


Figure 5. Variation of band gap with the number of add atoms (blue line is for hydrogenation and red line is for fluorination).

is 2.95 eV for hydrogenation and 2.20 eV for fluorination. For $n = 16$, the band gap is 4.38 eV for hydrogenation and 2.60 eV for fluorination. Thus, the nanostructures with 18C+14H, 18C+14F, 18C+16H, 18C+16F, 18C+18H and 18C+18F atoms are wide-band-gap semiconductors, whereas the nanostructures with 18C+2H, 18C+4H, 18C+4F, 18C+8F, 18C+10F and 18C+10H atoms are small-band-gap semiconductors. The rest of the nanostructures are conductors.

3.2 Binding energy, bond lengths and buckling due to functionalization

3.2.1 Hydrogenation of graphene. Binding energy per H atom (calculated using eq. (1), §2) is plotted against the number of hydrogen atoms in figure 6 (red line for odd number of H atoms and blue line for even number of H atoms) and tabulated in table 1. The BE increases as the number of hydrogen atoms increase, indicating that hydrogenated graphene is more stable than pristine graphene. It is observed that the binding energy per H atom is slightly more for even number of H atoms than for odd number of H atoms except for $n = 8$ and 12 (see figure 6). For fully hydrogenated graphene (18C+18H) it is found to be -3.7563 eV per H atom.

C–C and C–H bond lengths, as obtained from converged SIESTA runs, are tabulated for nanostructures in table 1. The value of C–C bond length for pristine graphene is 1.421 Å, which is in close agreement with the experimental value of 1.42 Å, frequently quoted in [2]. The C–C bond length for 50% hydrogenation lies between 1.381 Å and 1.523 Å. For fully hydrogenated graphene, the C–C bond length is 1.544 Å. The C–H bond length for 50% hydrogenation is found to lie between 1.121 Å and 1.139 Å. For fully hydrogenated

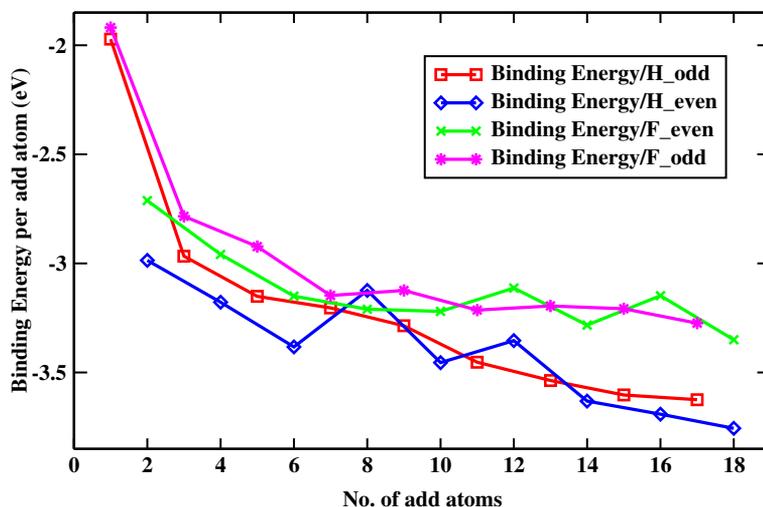


Figure 6. Graph of binding energy per add atom vs. no. of add atoms for functionalized graphene with 18C atoms.

graphene, the C–H bond length is 1.109 Å. Furthermore, as H atoms are added, the C atoms move perpendicular to the plane and there is buckling in the nanostructure due to hydrogenation [9], which varies between 0.0053 Å and 0.7487 Å. The upper limit of transverse displacement of C atom is maximum for 50% hydrogenation (0.7487 Å) and for fully hydrogenated graphene it is 0.2305 Å.

Boukhvalov *et al* [7] have considered a nanostructure of graphene having 32 carbon and 50 carbon atoms with adding hydrogen atoms for *ab initio* study of hydrogenated graphene using SIESTA. They have obtained C–C bond length of 1.475 Å for 50% hydrogenation, 1.537 Å for fully hydrogenated graphene and C–H bond length of 1.158 Å for fully hydrogenated graphene.

Sofo *et al* [6] have taken a nanostructure of graphene by adding hydrogen atoms in chair and boat conformations for first-principle calculations of hydrogenated graphene using CASTEP. They have obtained C–C bond length of 1.52 Å and C–H bond length of 1.11 Å for fully hydrogenated graphene.

Berashevich *et al* [12] have also considered a nanostructure of graphene having 42 carbon atoms by adding 42 hydrogen atoms in alternated spaces for studying fully hydrogenated graphene. They have obtained C–C bond length of 1.52 Å for fully hydrogenated graphene. These results for C–C and C–H bond lengths are in close agreement with our results (see table 1).

In their computational study of hydrogenated graphene, Boukhvalov *et al* [7] have observed that the magnitude of transverse displacements of C atoms lies between 0.096 Å and 0.364 Å (see table 1 in [7]), which is in close agreement with our results for buckling (see table 1 in this paper).

3.2.2 Fluorination of graphene. Binding energy per F atom (calculated using eq. (1), §2) is plotted against the number of fluorine atoms in figure 6 (green line for odd number of F atoms and magenta line for even number of F atoms) and tabulated in table 1. The BE increases as the number of fluorine atoms increase, indicating that fluorinated graphene is more stable than pristine graphene. For fully fluorinated graphene (18C+18F) it is found to be -3.3507 eV per F atom.

C–C and C–F bond lengths (as obtained from converged SIESTA runs) have also been tabulated for nanostructures in table 1. The C–C bond length for 50% fluorination lies between 1.3749 Å and 1.5031 Å. For fully fluorinated graphene, the C–C bond length varies between 1.5078 Å and 1.5081 Å. The C–F bond length for 50% fluorination is found to vary between 1.3886 Å and 1.4242 Å. For fully fluorinated graphene the C–F bond length varies between 1.3818 Å and 1.3822 Å. Furthermore, as F atoms are added, the C atoms move perpendicular to the plane and there is buckling in the nanostructure due to fluorination, which varies between 0.0002 Å and 0.5379 Å. The upper limit for transverse displacement of C atom is maximum for C18+12F atoms (0.5349 Å) and for fully fluorinated graphene it is 0.3132 Å.

Junkermeier *et al* [18] have studied nanostructures of graphene by adding fluorine atoms in different conformations for *ab initio* calculations using Quantum Espresso. They have obtained C–F bond length of 1.386 Å and band gap of 3.00 eV for fully fluorinated graphene (see table 1, columns 9 and 11, row 49 in [18]) are in close agreement with our results (see table 1 in this paper).

4. Conclusions

In summary, it has been observed that on functionalization of graphene with hydrogen and fluorine, a variation appears in the partial density of states and band structure near the Fermi energy and the nature of nanostructures undergo a change in electronic properties from conductor to semiconductor/insulator.

- (1) Fully hydrogenated graphene is found to have a band gap of 4.98 eV and binding energy of -3.7562 eV per H atom.
- (2) For fully fluorinated graphene, the band gap is 3.6374 eV and the binding energy is -3.3507 eV per F atom. This implies that functionalized graphene is a wide-band-gap semiconductor, which is more stable than graphene.
- (3) Fully hydrogenated graphene is slightly more stable than fully fluorinated graphene.
- (4) A large amount of buckling is also observed in the carbon lattice (0.0053 \AA – 0.7487 \AA due to hydrogenation and 0.0002 \AA – 0.5379 \AA due to fluorination).
- (5) Buckling is more for hydrogenation as compared to fluorination.
- (6) The nanostructures with 18C+14H, 18C+14F, 18C+16H, 18C+16F, 18C+18H and 18C+18F atoms are wide-band-gap semiconductors.
- (7) The nanostructures 18C+2H, 18C+4H, 18C+4F, 18C+8F, 18C+10F and 18C+10H atoms are small band gap semiconductors.
- (8) The rest of the nanostructures are conductors.

Thus, it is possible to tune the electronic properties of graphene through functionalization, making it a suitable material for applications in microelectronics devices.

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