Density-Functional Study of Electronic Band Structure of Graphene with H₂, H, and N Impurities

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Abstract

Graphene is widely investigated for many applications because of its unique properties. One of the most surprising phenomena is the change of its electronic band structure due to impurities adsorption. The density-functional study has been performed to obtain the electronic band structure of graphene with molecular hydrogen H_2, atomic hydrogen H, and atomic nitrogen N impurities. Pure graphene has no band gap because the bonding and anti-bonding states are degenerate at the K point at which the Fermi level passes. Molecular hydrogen H_2 adsorption gives the same result, while atomic hydrogen H and nitrogen N adsorptions on graphene could result in indirect-band gaps of 2.67 and 4.68 eV, respectively. These results bring impure graphene as a promising candidate for electronic device applications in the future.

Keywords: Density functional theory, Electronic band structure, Graphene, Binding energy, Charge difference density

1. Introduction

Graphene, as the building block of many carbon-based materials, has been predicted to possess many applications because of its unique properties. Graphene can be considered as a single layer of graphite in a structured hexagonal system. Several graphene layers could be united by the van der Waals force yielding a graphite structure. There are many methods on producing graphene. However, after the micromechanical cleavage method to produce graphene has been found[1], graphene is now being widely investigated.

Several interesting applications of graphene have been revealed recently. It has been reported that graphene could store molecule such as hydrogen[2-4] and any other molecules. Graphene could therefore be a strong candidate as a prospective hydrogen-storage in mobile application. Another surprising phenomenon is the change of electronic band structure depending on absorbed molecules[3,4]. The adsorption of atomic hydrogen H on graphene to open the band gap of graphene was reported[5].

This paper reports on controling the band gap of graphene by selecting adsorbed atoms or molecules. The electronic band structure calculation of graphene-H system will be compared with that computed by Choi and Park[5]. To obtain the stable position of H, we only used a binding energy method, in which the distance of H is varied while carbon atoms in graphene are at fixed positions, instead of using a relaxation method as Choi and Park did. The change in the electronic band structure of graphene was also investigated by adsorbing molecular hydrogen H₂ and atomic nitrogen N.

2. Calculation Method

The first-principles ultrasoft (Vanderbilt) pseudopotential[6] calculations based on the density-functional theory (DFT) were performed by using the Quantum ESPRESSO (opEn Source Package for Research in Electronic Structure, Simulation, and Optimization), which is an open-source program that can be used to calculate electronic structure and material modeling in nanoscale[7]. The electron exchange-correlation energy was approximated by the Perdew-Wang generalized gradient approximation (PW-GGA) using the GGA PW91[8]. The Kohn-Sham wave functions were expressed in the plane wave basis set with the cut-off energies of 40 Ry and 240 Ry for the charge density cut-off. The Fermi-surface effects were treated by the smearing technique of Methfessel-Paxton[9], using a smearing parameter of 0.06 Ry. The methodology and calculation parameters were previously tested for convergence.

To calculate the electronic band structure of pure graphene, a unit cell given in Fig. 1.(a) was used. This unit cell produces an infinite graphene sheet as shown in Fig. 1.(b). The k-points used in band structure calculation are those along the path of high-symmetry k-points (M-Γ-K-M) in the first irreducible Brillouin zone of graphene as given in Fig. 2.(b). Due to computational cost issue, not more than 60 k-points were employed.

To calculate the band structure of impure graphene, the unit cell in Fig. 3.(a) was chosen with the same k-points as the previous one. This cell consists of 8 carbon atoms and an atom or a molecule (atomic hydrogen H, molecular hydrogen H₂, or atomic nitrogen N) as impurities. Since a periodic cell

is used, the atomic or molecular impurities are periodically located according to the expansion of lattice vectors as given in Fig. 3.(b).
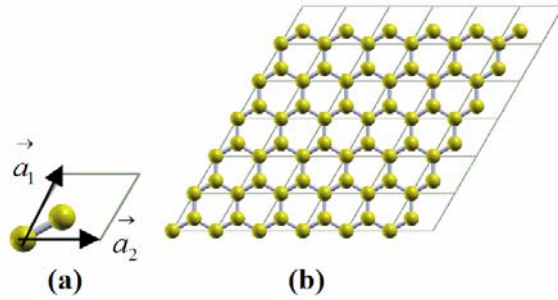

(a)   **(b)**

Figure 1. The balls represent carbon atoms. (a) a unit cell of graphene with two vectors $\vec{a}_1$ and $\vec{a}_2$. (b) an infinite graphene lattice generated by expanding the unit cell to those two directions.
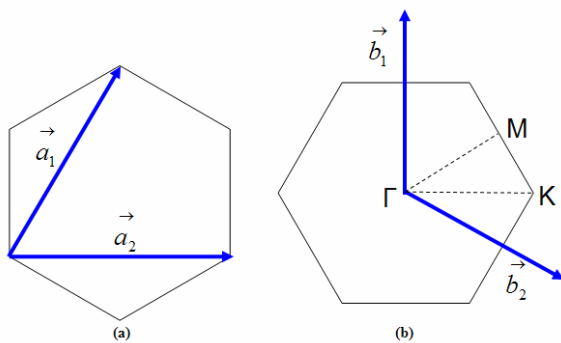

Figure 2. (a) lattice vectors of real space. (b) lattice vectors of reciprocal space with high symmetry k-points (M-Γ-K-M) in the first Brillouin zone.

The atomic or molecular impurities were placed on top of carbon atom because this site has the most negative binding energy as reported in the previous study.[10] Before investigating the band calculation of both pure and impure graphenes, each system has to be optimized first. The bond length of graphene-X system (X refers to atomic hydrogen H, molecular hydrogen H_2, and atomic nitrogen N) was found by varying the separation distance of both. The bond length is obtained when the binding energy reaches its minimum value. The binding energy between X and graphene can be achieved by employing

$$E_{bind} = E_{C-X} - E_C - E_X , \qquad (1)$$

where E_{C-X} is the total energy of the graphene-X system, E_X is the energy of isolated atomic or molecular X, and E_C is the total energy of graphene. The exact bond length is achieved when the binding energy reaches the most negative value.
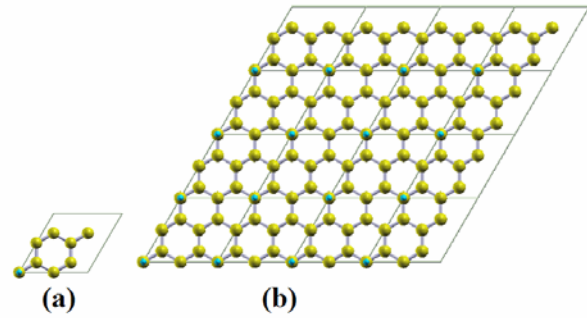

(a)   **(b)**

Figure 3. The big balls (yellow) represent carbon atoms and the small ones (green) are the atomic or molecular impurities. (a) a unit cell consisting of 8 carbon atoms and 1 atomic or molecular impurities. (b) atomic or molecular impurities are periodically located according to the expansion of lattice vectors.

The charge difference density (CDD) of the graphene-X system can be calculated by employing

$$\Delta n = n_{C-X} - n_C - n_X , \qquad (2)$$

where n_{C-X} is the charge density of the graphene-X system, n_X is the charge density of atomic or molecular X in the same lattice parameters as graphene-X system has, and n_C is the charge density of graphene also in the same lattice parameters.

3. Calculated Results and Discussion

Figure 4 gives the binding energy versus the separation distance of graphene-X system. The binding energies of graphene-H_2, graphene-H, and graphene-N systems are 0.02, 0.83, 1.93 eV, respectively and their bond lengths are 3.50, 1.19, 1.52 Å, respectively.

The calculated result of electronic band structure of pure graphene is given in Fig. 5.(a). The partial density of states (DOS) is also shown in Fig.5.(b) to see the states around the Fermi level. It is quite obvious that the states around Fermi level belong to $C\text{-}Pz$ orbitals since the graphene is located in x-y direction. The $C\text{-}Pz$ orbitals indicate the bonding and anti-bonding states. These states are degenerate at the K momentum direction yielding a gapless structure.
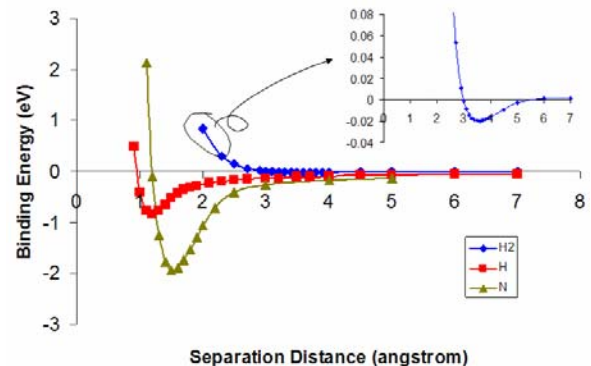

Figure 4. Binding energy vs separation distance of the graphene-X system (X refers to H_2 (blue), H (red), and N (green)). H_2, H, and N impurities have 0.02, 0.83, 1.93 eV in binding energy and 3.50, 1.19, 1.52 Å in distance, respectively.
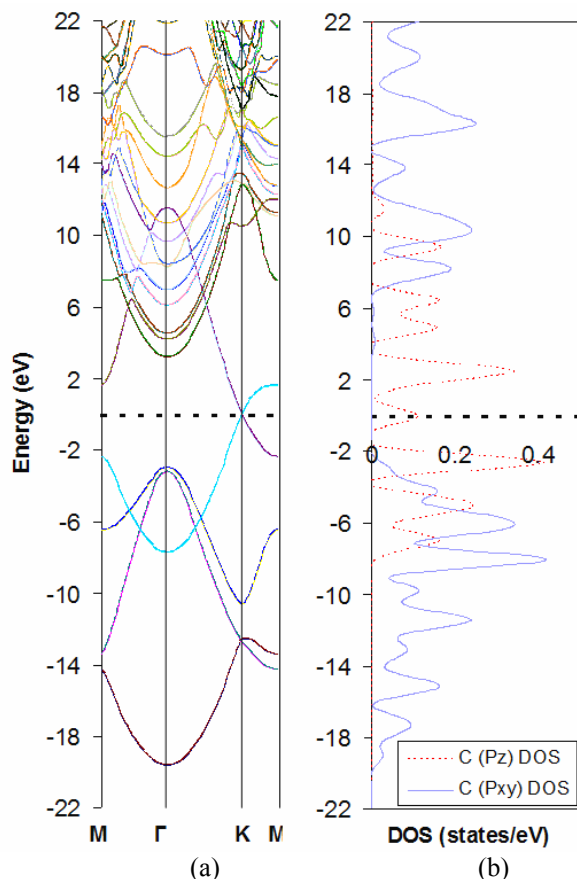
Figure 5. (a) the electronic band structure of graphene shows gapless in Fermi level (dashed line) (b). DOS projected to carbon atoms in *C-Pz* (red dotted line) and *C-Pxy* (blue solid line) orbitals.

The upper half of the energy dispersion (above the Fermi level) describes the π^*-energy anti-bonding band and the lower half (below the Fermi level) describes the π-energy bonding band. At $T = 0$ K, all the electrons occupy the lower π band (completely filled) and the upper π^* band is empty. The upper π^* band and the lower π band are degenerate at the K points at which the Fermi level passes. Since the DOS at the Fermi level is zero, the 2D graphite sheet or graphene layer is a zero-band gap semiconductor. Real graphite is actually a metal since the interaction between the graphene layers causes the bands to overlap such that the bands are partially filled at $T = 0$ K.

The electronic band structures of impure graphene were calculated as shown in Fig. 6. For the graphene-H_2 system (Fig. 6.(a)), although the band structure has changed significantly, there is no band gap revealed. The conduction and the valence bands just overlap in the K momentum direction. The molecular hydrogen H_2 partial DOS shows that the energy states around the Fermi level does not belong to H_2, but belong to carbon in graphene. This could happen because H_2 does not interact strongly with graphene since the binding energy formed is relatively weak (see Fig. 4).

The electronic band structure of graphene-H system is depicted in Fig. 6.(b). There is a wide indirect-band gap formed in the momentum directions of Γ (where the lowest conduction band exists) and K (where the highest valence band exists). The strong binding energy, about 0.83 eV (see Fig. 4), makes the orbitals overlap strongly. The hydrogen states revealed around Fermi level (shown by the H partial DOS in Fig. 6.(b)) causing an indirect band gap to be opened about 2.67 eV in width.

As comparison let us see the recent work of Choi and Park (see Fig. 4.(a) in Ref. 5). They calculated exactly the same system; that was placing atomic hydrogen in 2×2 graphene supercell; but using more accurate method in structural optimization. They used a relaxation mode to optimize the structure until the atomic positions are fully relaxed with the Hellman-Feynman force on each atom reduced down to 0.01 eV/Å. This makes the carbon atoms in graphene perhaps did not stay in original positions since atomic hydrogen could affect the structure of graphene. Meanwhile we only determined the atomic hydrogen position by calculating the binding energy where carbon atoms in graphene were conditioned in fixed positions. However, the results are still in agreement. They calculated a direct-band gap (in the Γ direction) of 3.96 eV, which is only slight different with our result of 3.93 eV if we also consider a direct-band gap in the Γ direction.

The graphene-N system (Fig. 6.(c)) also has a band gap, which is similar to the graphene-H system. Compared to the graphene-H system, the band gap of graphene-N system is wider, which is about 4.68 eV. This indirect-band gap is relatively larger because atomic nitrogen N has more orbitals. As a comparison, atomic hydrogen H has only *1s* valence orbital and atomic nitrogen N has *2s, 2px, 2py*, and *2pz* orbitals.
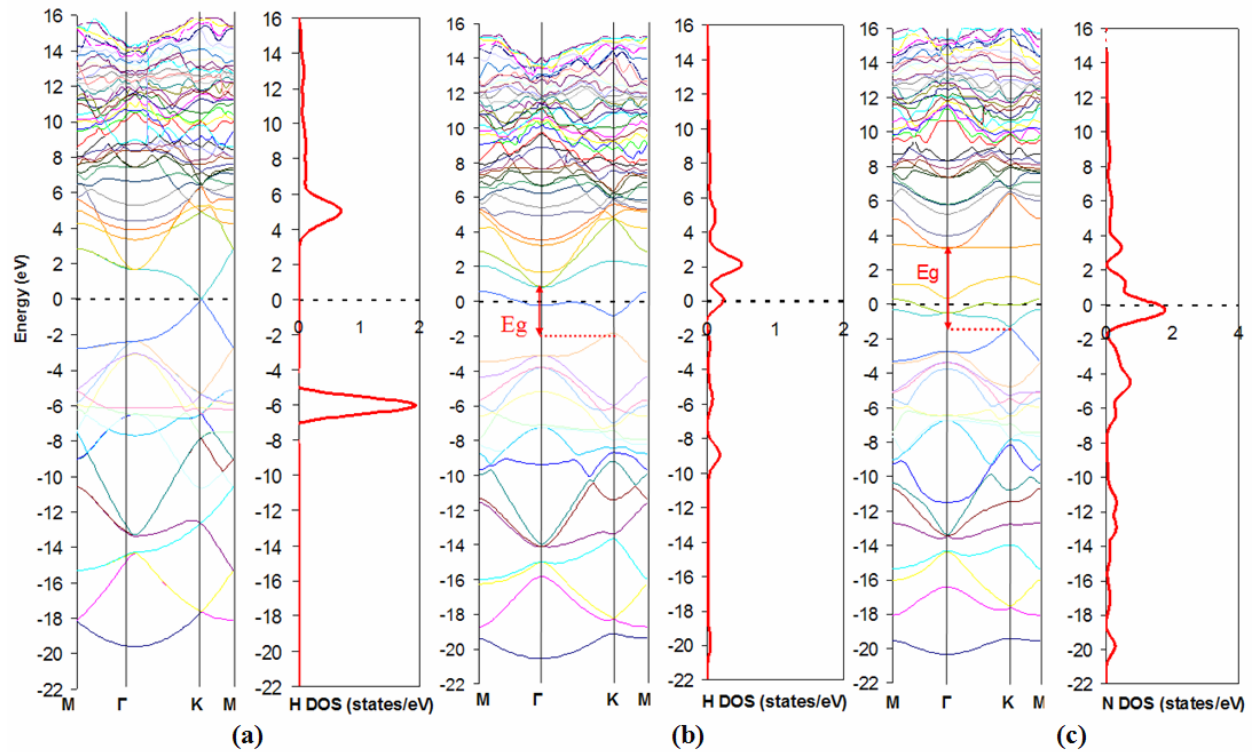
Figure 6. The electronic band structure and partial DOS of impure graphene. (a) molecular hydrogen H_2 impurity and partial DOS of $1s$ hydrogen orbital show gapless. (b) atomic hydrogen H impurity and partial DOS of $1s$ atomic hydrogen orbital show an indirect-band gap of 2.67 eV. (c) atomic nitrogen N impurity and partial DOS of $2s+2p$ atomic nitrogen orbitals show an indirect-band gap of 4.68 eV. Black dashed line represents Fermi level.
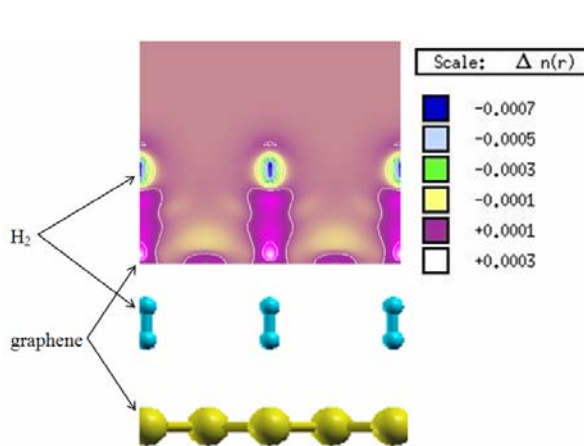

Figure 7. Contour of charge difference density (CDD) of graphene-H_2 system from top to bottom. Positive value (bright) represents electron-excess regions; negative value (dark) represents electron-deficit regions.

The contour of charge difference density (CDD) of the graphene-H_2 system shown in Fig. 7 tells us that carbon atoms try to give their electrons to H but there is no charge exchange because graphene still has electron excess. As a result, the π orbital of graphene is not broken and the electrons can still move freely along the graphene plane.
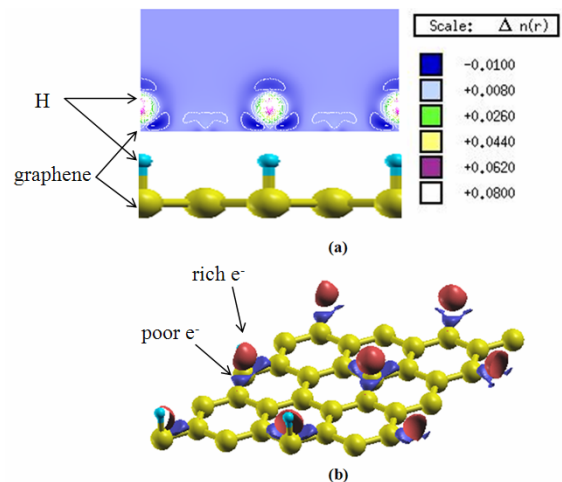

Figure 8. Charge difference density (CDD) of graphene-H system. (a) contour of CDD from top to bottom. Positive value (bright) represents electron-excess regions; negative value (dark) represents electron-deficit regions. (b) 3D isosurface CDD drawn in isovalue of ± 0.009 e/a_0^3. Charges flow from dark to bright regions.

The contour of CDD of the graphene-H system is demonstrated in Fig. 8. Carbon atoms in graphene give their electrons to H, resulting in the breaking of the π orbital of graphene. Therefore, electrons in graphene could not move freely along the plane and they need more energy to jump from the valence into the conduction band.

Since atomic nitrogen N has more orbitals compared to atomic hydrogen H, more orbitals overlap in the graphene-N system. Consequently, the electronic band structure is more severely distorted and more electrons are transferred from graphene into N as illustrated in Fig. 9. Thus, if we choose atomic impurity with large atomic number (means many atomic orbitals), perhaps it could give larger band gap. This will be our study in the future.
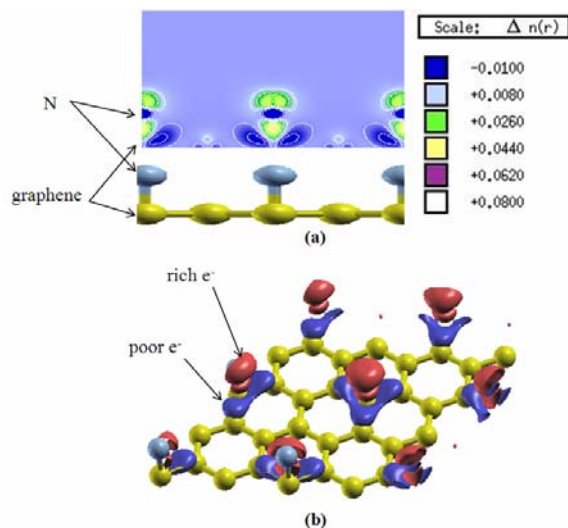

Figure 9. Charge difference density (CDD) of graphene-N system. (a) contour of CDD from top to bottom. Positive value (bright) represents electron excess regions; negative value (dark) represents electron deficit regions. (b) 3D isosurface CDD drawn in isovalue of ± 0.009 e/a_0^3. Charges flow from dark to bright regions.

Conclusion

Pure graphene has no band gap due to degenerate states of *C-Pz* orbitals at which Fermi level passes. Molecular hydrogen H_2 adsorption gives the same result. The H_2 adsorption does not open the band gap because H_2 is not strong enough to break the π orbital of graphene. On the other hand, atomic hydrogen H and nitrogen N adsorptions could break the bond and result in indirect-band gaps of 2.67 and 4.68 eV, respectively. The N adsorption causes larger band gap compared to that of the H adsorption because atomic nitrogen N binds stronger on graphene that makes the band structure distorted severely. Based on these results, impure graphene has a great potential in many electronic device applications.

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