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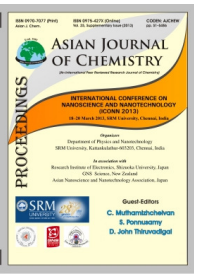

Interaction of Hydrogen, Oxygen and BH_3 with Graphene-A First Principles Study†

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Graphene is a zero gap semiconductor. A small or moderate band gap is essential for applications in nanoelectronics. The band gap opening through functionalization is widely reported. The highly planar surface is inert to adsorb chemical species. Moreover the adsorption mechanism depends on the chemical nature of the species. In this study, we have investigated the chemical activity of graphene with hydrogen, oxygen atoms and BH_3 molecules using *ab initio* density functional theory with an aim of achieving band gap opening. The functionalization with H atoms leads to the opening of a wide band gap in graphene whereas in the case of O a small gap opens up. The interaction of BH_3 with graphene is weak and there is no change in the band structure of graphene.

Key Words: Graphene, Dirac fermions, Borane, Adsorbtion, Band gap, Functionalization.

INTRODUCTION

Graphene has unusual and interesting properties[1]. It is considered to be a new material with new physics and it is causing major breakthrough in nanotechnology. It is a truly 2-D crystal with nano dimension. In the electronic band structure of graphene, valence and conduction bands cross the Fermi level at a single point (K points) in the Brillouin zone and hence it is a semimetal. Due to the linear dispersion of energy bands at the K point in the Fermi energy level, the electrons behave like massless Dirac fermions. A small or moderate band gap is essential for applications in nano-electronic devices. The manipulation of band gap in nano-structures is entirely different from that of the bulk materials[2]. Being a nanostructured 2-D crystal, graphene uniquely responds to the disturbances that are induced externally. Several methods on structural and band gap modulations in graphene are available in the literature[3].

Among them, the band gap opening through functionalization is widely reported. The chemical functionalization of graphene is a tough process. The highly planar surface is inert to chemical species. The adsorption mechanism depends on the chemical nature of the species[3]. In this study we have investigated the interaction of H, O atoms and molecule, BH_3, with graphene and looked into the possibility of band gap opening apart from the gas sensing character.

COMPUTATIONAL DETAILS

The calculations were carried out using DFT-implemented planewave code VASP[4,5] (Vienna *ab initio* simulation package). The generalized gradient approximation is used with PW 91 functional[5,6]. The projector-augmented wave potentials are used to represent the core region of all atoms. We have taken a slab of 24 carbon atoms in a super cell of size, a = 8.52 Å, b = 7.378 Å and $a = \beta = \gamma = 90^\circ$. In certain study, we repeated the calculations for 96 atom system[1]. We have functionalized graphene with the above (H, O) atoms and molecule (BH_3) with different coverages and have examined the structural and band structure modification in graphene. The band structure calculations are carried out with 200 k-points along the line joining the high symmetry points. A vacuum space of 11 Å is introduced between the periodic images of graphene sheets along the z-axis such that the interaction between the images is negligible. The γ-centered 10 × 10 × 1 k-point grid is used in structural relaxations within Monkhorst and Pack Scheme. The k-point grid is made denser with 50 × 50 × 1 k-points for accurate density of states (DOS) analysis with the smearing width of 0.1 eV. The geometrical structures are fully relaxed without any constraints using conjugate gradient algorithm. The convergence criterion for energy is set as 1×10^{-5} eV. The structures are relaxed until the force on each atom becomes[2] 1×10^{-3} eV/Å.

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RESULTS AND DISCUSSION

We have functionalized graphene with H, O and BH_3, in order to explore the gas sensing property and the chance of band gap opening. The relaxed structure of graphene is shown is Fig. 1(a). The presence of delocalized π electrons is obvious from the charge distribution plot. The band structure of planar graphene is shown in the Fig. 1(c). Then the graphene is hydrogenated and results are summarized in Fig. 2. In graphene the p_z (pi) electrons are free to move. During hydrogenation hydrogen atoms interact with carbon atoms through covalent bonds. As a result the carbon atoms are pulled out (Fig. 2a) and the C-C bonds are strained by 5.3 % and the bond length increases to 1.495 A. Localized charges in the carbon atoms are shown in Fig. 2(b) and (c). In the fully hydrogenated graphene a band gap of 2.92 eV opens up.

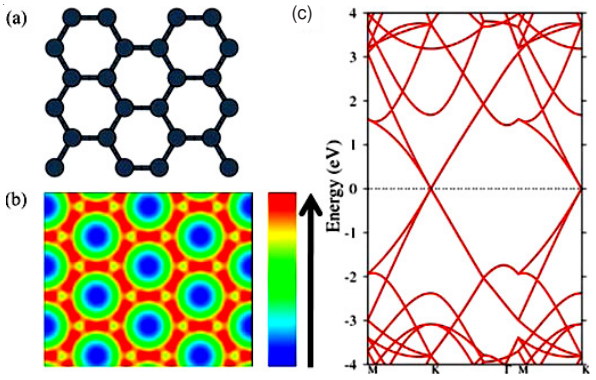

Fig. 1. (a) Relaxed structure of graphene. (b) Charge distribution plot of relaxed graphene. (c) Band structure of graphene

It is a direct band gap (Fig. 2d). The band gap opening is a synergetic effect of both electronic and structural changes. In the chemical picture the perfect hybridization between orbitals of carbon and hydrogen atoms has resulted in the formation of C-H bonds. In the physical point of view, the graphene lattice is strained. Over all we can conclude that both electronic and structural modifications are responsible for the band gap opening in the hydrogenated graphene. The band gap opening may be taken as the signature for the sensing of H. When electric field strength 0.5 V/A is applied, there is no change in the band structure (Fig.2e). When the field is increased to 1 V/A, the band gap decreases to 0.5 eV.

We have studied both structural and electronic modifications due to adsorption of oxygen atoms for different coverages (Fig.3a-h). Initially, single O is attached on the bridge

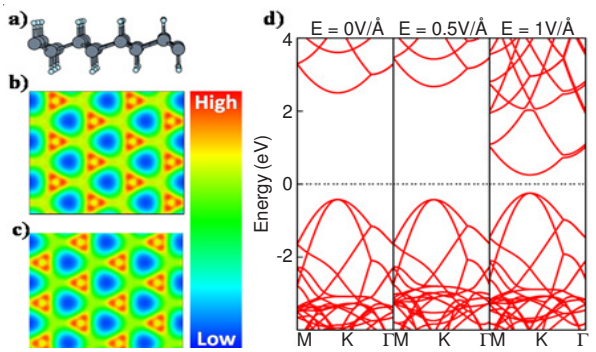

Fig. 2(a-d): Hydrogenated graphene

site of basal plane (Fig. 3a-b). This configuration is the most energetically favourable one and is denoted as epoxide. In the relaxed structure, the C-C bond associated with O is buckled up and confirms the presence of strong covalent bond between C and O atoms. The C-C bond is stretched by 6 %. Secondly, the O atoms are attached in the central row of C-C sites (Fig. 3c-d). This configuration is referred as 1/3 coverage (1/3 C) because one third of the hexagonal rows are functionalized. After relaxation, we observed that the oxygen atoms get into the middle of C-C bonds, thereby weakening the bonds. This process may be used for cutting graphene sheets through controlled chemisorptions of oxygen atoms. The graphene sheets can be cut by removing the oxygen atoms through suitable process. Here, the C-C bond lengths increased by 50 %. In another study we have attached O atoms on both sides of central row (Fig. 3e-f). After relaxation there are no notable changes. In this alternate doping case, the structural integrity is retained. This observation is similar to the reported work of Nourbakhsh *et al.*[7]. The C-C bond lengthened by 3.3 %. The alternate O coverage case corresponds to the clamped structure of the epoxy phase. The full coverage (AC) case belongs to unzipped structure of epoxy phase. Here O is attached to all the C-C bridge sites (Fig. 3g-h). This resulted in the formation of structurally modified curved graphene. The basal plane is strained such that the C-C bonds are stretched

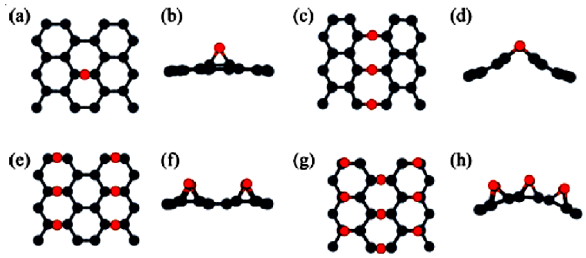

Fig. 3(a-h). Relaxed structures of graphene + O atoms

by 4.3 %. As the interaction distance increases, the binding energy per O decreases. But the 1/3 coverage case is exceptional. The binding energy is (2.79 eV) higher than the other values corresponding to the two coverages, AC (2.31 eV) and FC (2.64 eV). The band structures of the four systems are given in Fig. 4. Corresponding to FC case the band strucutre

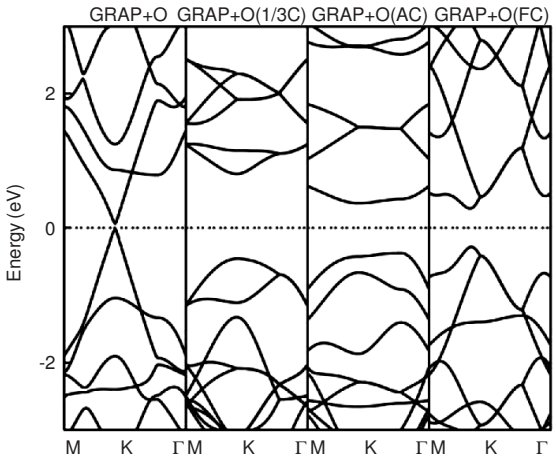

Fig. 4.

is completely altered. Since the density of O is higher than the other two cases, the band gap is lower than the other two cases. The band gap opening can be fine tuned to suit the device application.

Also the band gap opening can taken as the signature for the O sensing property of graphene. The results of interaction of BH_3 with graphene are summarized in Figs. 5 and 6. The binding energies for the full and half coverages cases are 0.80 eV and 0.85 eV respectively. This is weak chemisorption and there no changes in the band structure of graphene.

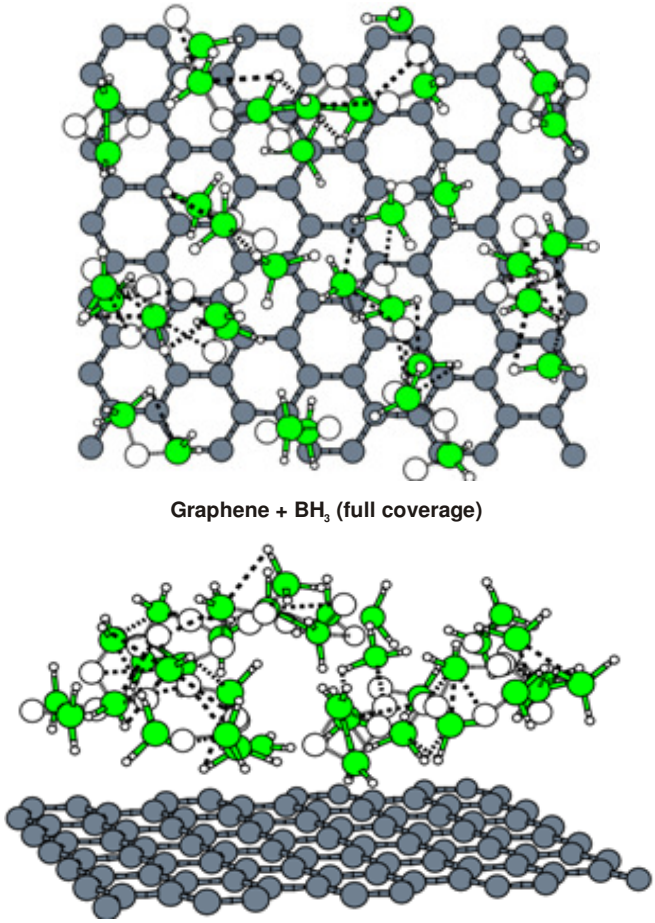

Fig. 5.

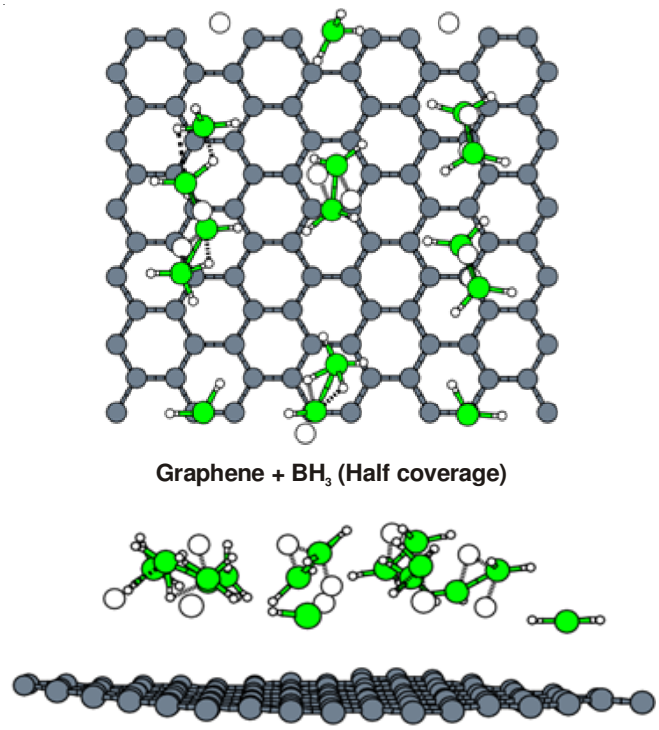

Fig. 6.

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