Molecular adsorption in graphene with divacancy defects

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We have investigated theoretically the adsorption of molecules onto graphene with divacancy defects. Using ab-initio density functional calculations, we have found that O₂, CO, N₂, B₂ and H₂O molecules all interact strongly with a divacancy in a graphene layer. Along with a complex geometry of the molecule-graphene bonding, metallic behavior of the graphene layer in presence of CO and N₂ molecules have been found with a large density of states in the vicinity of the Fermi level suggesting an increase in the conductivity. The adsorption of N₂ is particularly interesting since the N atoms dissociate in the vicinity of the defects, and take the place where the missing C atoms of the divacancy used to sit. In this way, the defected graphene structure is healed geometrically, and at the same time doped with electron states.

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I. INTRODUCTION

In the last few years, graphene has been considered as one of the most sensational materials for its many exotic properties. Graphene is known theoretically for several decades but the real breakthrough came when it was discovered experimentally in 2004. The electronic properties of this sp²-bonded two-dimensional allotrope of carbon have striking similarities with those of massless relativistic Dirac fermions. The linear band dispersion at the so called Dirac point is a special feature of the graphene band structure. Apart from this, graphene has been considered as an excellent candidate for future electronics due to the extraordinarily high mobility of its charge carriers. As today’s Si based electronics faces the fundamental limitation of spatial dimension lower than a few nanometers, graphene may stand as a potential alternative.

The electronic structure of graphene may be engineered by the interaction with supporting substrates, gate voltage or by chemical doping with molecules. Research on graphene is being pursued in different directions to achieve novel properties. One of the routes is to tune the properties of graphene by controlled defect formation through chemical reactions. In a recent paper, it has been shown that chemically treated graphene nanosheets have oxygen-containing defects, which were identified by X-ray absorption spectroscopy (XAS). The oxygen containing groups were introduced by the acid treatment of the nanosheets, and follow a reaction pathway similar to what happens for the case of carbon nanotubes with the addition of chemical reagents to carbon network defects in the graphene sheets. Electronic structure calculations revealed that the defect states arise from a network of vacancy defects, where carbon atoms have been removed. Moreover, it was shown theoretically that the carbon atoms around such a lattice defect show metallic behavior due to the presence of high density of states at Fermi level in contrast to a vanishing density of states (DOS) for a pure graphene sheet. Such a defect would also be very reactive due to the highly strained structure, and hence efficiently undergo acid-catalyzed water addition, the initial product of which rapidly rearranges to form a pyrane-like structure that possess the characteristics found in the XAS of acid-treated carbon nanosheets (CNS).

One effective route to induce charge carriers in graphene would be by molecular doping, e.g., by NH₃, NO₂ etc. It has been shown by Hall measurements that NO₂ introduces holes whereas electrons are introduced by doping with NH₃. This way has opened up an excellent playground for both experimentalists as well as theoreticians. Wehling et al. have demonstrated by density functional calculations that a NO₂ molecule acts as a strong acceptor and produces special features in the density of states (DOS) that is suitable for chemical sensor applications. It was also shown recently by density functional calculations that chemical functionalization of a bilayer graphene can open up a gap up to 3 eV. It is noteworthy to mention that the detection of gas molecules adsorbed in graphene has been possible recently in experiments by Schedin et al. These graphene based gas sensors have an extraordinary sensitivity to detect the change in local charge carrier concentration by minute amount due to the extremely low noise in graphene. Besides the characterization and modification of the properties of infinite graphene sheets, a considerable effort has been made recently to predict properties of graphene nanoribbons (GNRs). Modification of electronic properties using edge functionalization, substitutional doping...
and also the transport and magnetic properties of GNRs have been studied in great detail. The edges of GNRs resemble the vacancy defects in graphene and hence are relevant for the present discussion.

The experimental information on the acid-catalyzed addition of water to edges and strained defects without dangling bonds, such as the thermally mobile 5/7 membered rings are available from the research on carbon nanotubes (CNTs) and also some transmission electron microscope (TEM) work on graphites. The addition of water is reversible and heating at low pressure removes quite a lot of water molecules to form a very reactive surface, e.g., defects with dangling bonds that would relax to still quite reactive but more stable 5-8-5 or related lattice defects. The defects in carbon-bond-network has been studied in detail theoretically by Dias. The purpose of this paper is to study the chemical interaction between divacancy defect centers in graphene and chemisorbed molecules with the aid of theoretical analysis. Using density functional based electronic structure calculations, we have analyzed the reaction between water molecules and defect centers and consequently the passivation of these highly reactive centers by several molecular species.

II. COMPUTATIONAL DETAILS

Here, we have performed ab-initio electronic structure calculations based on the density functional theory. The Vienna Ab-initio Simulation Package (VASP) employing a plane wave basis was used within the all electron projector augmented wave (PAW) method. The generalized gradient approximation (GGA) was used as the exchange-correlation functional. GGA reproduces very well the C-C bond length (1.42 Å) in graphene. The kinetic energy cut-off was chosen to be 400 eV. We have optimized the geometries by reducing the Hellman-Feynman forces down to 0.01 eV/Å.

We have considered five different molecules and studied their interactions with a divacancy center (e.g. as shown by the C network in Fig.2a) in a graphene sheet. The molecular species we have considered are O$_2$, N$_2$, B$_2$, CO and H$_2$O molecules. The graphene sheet was modeled with a 8x8 supercell in the lateral direction with a 15 Å vacuum in the vertical direction. This is a relatively large lateral supercell to reduce the interaction of the adsorbed molecules with their periodic images and can be approximated well by isolated ones.

From the total energy calculations, we have extracted the chemisorption energies for all the molecules considered. The chemisorption energy of the molecule is calculated as

$$E_{ch} = E_{DV+M} - E_{DV} - E_M,$$

where $E_{DV+M}$, $E_{DV}$ and $E_M$ denote the total energies of a graphene sheet with a divacancy and the molecule, a graphene sheet with a divacancy, and a free molecule, respectively. The calculated values of $E_{ch}$ are -8.44 eV, -4.53 eV, -13.83 eV and -3.86 eV respectively for O$_2$, N$_2$, B$_2$ and CO molecules. All these numbers are quite large and they indicate a very strong binding between the molecules and graphene divacancies. A large binding energy between O$_2$ molecule and defected graphene indicates it is rather easy to oxidize defected graphene. In case of B$_2$, a very large value may arise from the fact that this molecule doesn’t form naturally as a diatomic molecule.

III. RESULTS AND DISCUSSIONS

A. Geometry

Analysis by chemical models suggests that a defect lacking two carbon atoms forming a 5-8-5 lattice defect is more probable than a single vacancy. These defect centers are highly reactive as the carbon atoms at the defect edges have dangling bonds. When this non-perfect induced graphene is treated with water, chemical rearrangement occurs as shown in Fig. 1. In our study we have used a H$_2$O molecule as shown in Fig. 1(a) in the beginning of the simulation. In the presence of H$_2$O, one C atom at one side of the defect is saturated by H and the other C atom is saturated by OH. The two C atoms at the remaining pentagon of the lattice defect are left untouched. This is one of the probable configurations existing in the reaction. The final configuration after geometry optimization is shown in Fig. 1(b). The initial quite strained phenolic product is rearranged to a more relaxed pyramidal-type structure, with the O atom in a position that produces a hexagonal pattern and the two hydrogen atoms saturating the remaining two carbon atoms of the original defect. The H atoms are aligned at two opposite faces of the graphene sheet making an angle of around 28° to the graphene plane. The final structure is very stable, as all the dangling bonds are saturated.

Similar to the case of H$_2$O, a graphene with unsaturated dangling bonds will immediately absorb any molecular center close to it. We have considered O$_2$, CO, B$_2$
and N₂ molecules interacting with the lattice defect in the C network of graphene. Fig. 2(a) shows the initial configuration of the simulation. The molecule is kept at a horizontal position above the vacancy region and the geometry of the system was optimized by minimizing the forces. The final optimized configurations are shown in Fig. 2(b), 2(c), 2(d) and 2(e) for O₂, CO, N₂ and B₂ molecules respectively.

![Figure 2](image)

The three molecular species behave differently while being adsorbed in the graphene sheet. The O₂ molecule gets dissociated into two O atoms bound to two pairs of C atoms around the divacancy. The O atoms are moved in opposite directions out of the graphene plane, a situation similar to that of H atoms described in Fig. 1. For the case of CO, the C and O atoms still remain bonded to each other, while being bonded to two pairs of carbon atoms. Moreover, the CO molecule doesn’t remain in the plane of graphene. The C atom of the CO molecule stays in the plane making a usual hexagonal planar structure while the O atom moves a little bit out of the plane. The N₂ molecule is completely adsorbed in the plane of graphene. The two N atoms are substituted in the normal positions of a graphene network. So, a graphene sheet with substitutional N atoms is achieved in this process. This may serve as a route to dope N atoms in the graphene network and hence introduce extra charge carriers to achieve novel transport properties. In case of B₂, the B atoms are buckled out of the graphene plane by about 0.55 Å.

B. Electronic structure

![Figure 3](image)

We now present the electronic structure of graphene with CO, N₂ and B₂ chemisorbed to the lattice defect. The case for the CO molecule is shown in Fig. 3. C₇, O₇, C₅ (O) and C₅ (C) indicate DOSs for C atom in CO, O atom in CO, C atom in the graphene sheet connected to O and C atom in the graphene sheet connected to C atom of CO molecule respectively. For all the cases, DOSs projected on different p orbitals are shown.

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(E_F). This feature is very similar to the mid-gap states observed in graphene with defects. The C (C_G (C)) atom in the graphene layer connected to the C atom of CO has a usual graphene-like behavior, i.e., a vanishing DOS at E_F. For this atom the electronic structure is actually quite similar to that of defect free graphene, with the p_x and p_y orbitals being almost degenerate forming an occupied σ state, whereas the p_z orbital forms a π and π^* complex just below and just above the Fermi level, respectively. This picture is somewhat different for the other DOS curves in Fig.1, and it is clear that for C_H and C_G(O) the p_z and p_y orbitals are no longer degenerate, since symmetry is lowered due to the geometric reconstructions.

In conclusion, we have studied here the adsorption of different molecular species to a graphene with a divacancy, corresponding to a highly likely 5-8-5 lattice defect. The calculated chemisorption energies for the molecules are quite large, with a magnitude which is of order 3-13 eV. Our ab-initio density functional calculations indicate that N_2 is adsorbed in the plane of the graphene network as substitutional impurities, whereas H_2O, CO and O_2 have complex geometrical constructions at the divacancy site. The B_2 molecule more or less retains its bond length as in the isolated molecular state and is strongly bonded to the divacancy center in a position a little bit off the graphene plane. The significant observation is that the inclusion of N_2 in the graphene plane produces a perfect honeycomb lattice with electrons doped into the conduction band. A recipe for doing this experimentally is suggested.

IV. CONCLUSIONS

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1 A. K. Geim and K. S. Novoselov, Nat. Mater. 6, 183 (2007).
2 K. S. Novoselov et al, Science 306, 666 (2004).
3 S. Pisana, M. Lazzeri, C. Casiraghi, K. S. Novoselov, A. K. Geim, A. C. Ferrari and F. Mauri, Nat. Mater. 6, 198 (2007).
4 V. A. Coleman, R. Knut, O. Karis, H. Grenberg, U. Jansson, R. Quinlan, B. C. Holloway, B. Sanyal and O. Eriksson, J. Phys. D: Appl. Phys. 41, 062001 (2008).
5 T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim and A. I. Lichtenstein, Nano Lett. 8, 173 (2008).
6 D. W. Boukhvalov and M. I. Katsnelson, Phys. Rev. B 78, 085413 (2008).
7 F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, Nat. Mater. 6, 662 (2007).
8 F. Cervantes-Sodi, G. Csanyi, S. piscanec and A. C. Ferrari, Phys. Stat. Sol. (b) 245, 2068 (2008); L. Rosales, M. Pacheco, Z. Barticevic, A. Latge and P. A. Orellana, Nanotechnology 19, 065402 (2008); F. Cervantes-Sodi, G. Csanyi, S. piscanec and A. C. Ferrari, Phys. Rev. B 77, 165427 (2008); K. N. Kudin, ACSNano 2, 516 (2008).
9 J. R. Dias, Carbon 22, 107 (1984).
10 P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
11 G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993); G. Kresse, J. Furthmüller, Phys. Rev. B 54, 11169 (1996).