



An ab initio study of atomic hydrogen sorption on the zigzag edge of pristine bilayer graphene

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Abstract: We studied the sorption mechanism of atomic hydrogen on the zigzag edge of pristine bilayer graphene (BLG) as groundwork effort in the realization of the material's utilization as the substrate in a hydrogen storage system. Using density functional theory, we performed total energy calculations, using pseudopotentials obtained from projector augmented wave (PAW) method. The Kohn-Sham equations were solved using plane waves with kinetic energies of 400 eV. The surface Brillouin zone integration was performed using the special-point sampling technique of Monkhorst and Pack (with $4 \times 4 \times 1$ sampling meshes). For the exchange correlation energy, we adopted the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. Each layer in the slab model we used in the calculations consisted of 28 sp^2 -bonded carbon atoms with in-plane carbon-carbon distance of 1.42 Å and out-of-plane equilibrium stacking distance of 3.5 Å. Results revealed at least two non-activated reaction paths (paths of least potential) on pristine bilayer graphene which confirmed the possibility of absorbing H in between the carbon layers. Also, the strong H trap near the surface C atoms conveyed the strong tendency of C atoms to form sp^2p_z hybridization in the initial stage of H adsorption. The results suggest the possible utility of the zigzag edge as a reaction channel to carry out the sorption process.

Key Words: density functional theory; hydrogen; graphene; hydrogen storage; hydrogen fuel

1. INTRODUCTION

Hydrogen is highly regarded as energy carrier for energy storage on a large scale, as long as the hydrogen can be generated renewably. It is generally deemed that the use of hydrogen as energy

carrier will alleviate environmental damage and economic destabilization caused by over-reliance on oil. However, to be suitable for road transport and other mobile applications, safe and compact hydrogen storage systems need to be developed. Several methods for hydrogen storage have been proposed but many researches focused on chemical storage

(Park, et al., 2012) because this method shows promise to overcome the volumetric density challenge in the storage process.

Carbon and other high surface area materials have been the subject of many hydrogen storage researches because of these materials' reported high hydrogen uptake (Cheng, Yang, & Liu, 2001; Froudakis, 2002).

In this work, the adsorption onto and absorption into of hydrogen on the zigzag edge of bilayer graphene (BLG) – a material consisting of two layers of carbon atoms arranged in a regular hexagonal pattern – is investigated in order to gain a fundamental physical understanding of the sorption processes which will help develop methods that will improve the materials' capacity for hydrogen storage.

Previously, density functional theory (DFT)-based studies revealed that H₂ dissociative adsorption on the zigzag edges of graphite (stacks of carbon atoms arranged in a regular hexagonal pattern as in BLG) are non-activated suggesting the use of the zigzag edge to dissociate H₂ for hydrogen storage (Diño, Nakanishi, Kasai, Sugimoto, & Kondo, 2004). Dynamics calculations also revealed very weak vibration assisted sticking effect and a differing scattering behavior of H₂ on the zigzag edges of graphite (Arboleda, Kasai, Nakanishi, Diño, & Sugimoto, 2004).

Density functional theory-based total-energy calculations are performed in this research work to obtain the potential energy surfaces (PESs) necessary to determine the reaction paths.

2. METHODOLOGY

All the calculations are performed using spin-polarized density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) (Kresse & Furthmüller, 1996a; Kresse & Furthmüller, 1996b). Generalized gradient approximation (GGA), within the Perdew-Burke-Ernzerhof (PBE) functional, is used to treat the exchange-correlation energy (Perdew, Burke, & Ernzerhof, 1996). Ionic cores are described by the projector augmented wave (PAW) method (Blochl, 1994). The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with energy cutoff of 400 eV. The surface Brillouin zone integration was performed using the special-point sampling technique of Monkhorst and Pack (with

4×4×1 sampling meshes).

The total energy is computed in a supercell geometry where the substrate is represented by periodically repeated slabs consisting of two layers of graphene, each composed of 28 sp²-bonded carbon atoms with in-plane carbon-carbon distance of 1.42 Å and out-of-plane equilibrium stacking distance of 3.5 Å (see Fig. 1). Because of the AB Bernal stacking of BLG, one layer is slightly elevated compared to the other. Vacuum layers of 13 Å and 14 Å will be introduced along the x-axis and z-axis, respectively, in order to avoid the interaction of slabs when repeated periodically.

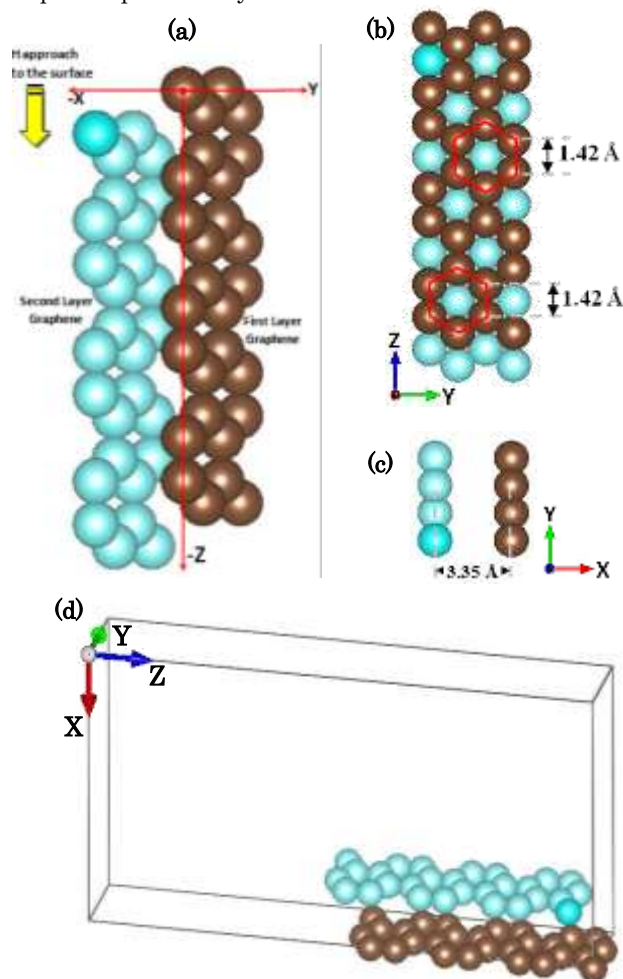


Fig 1. (a) Slab model of pristine BLG showing a total of 56 carbon atoms in the unit cell. The location of one of the top-most C atoms is randomly chosen as the origin of the coordinate system. Incident H atom

will be allowed to approach the surface of the slab ($z=0$ Å) onto the zigzag edge of the BLG. (b) The in-plane carbon-carbon distance in the substrate is 1.42 Å. (c) The out-of-plane equilibrium stacking distance of the graphene sheets is 3.5 Å. The first layer is set at $x=0.0$ Å while the second layer at $x=-3.35$ Å. (d) The supercell geometry showing the vacuum layers inserted in the model to avoid interaction in the slabs when periodically repeated.

Hydrogen sorption on the surface and subsurface is modeled by introducing single H atom in the unit cell. The incident H atom from the vacuum region approaches and enters the pristine substrate. In this manner, the dangling bonds of the top-most carbon atoms are protruding at the entrance of the incident H.

The distances between each H atom in the periodically repeated unit cell is large enough, and thus, the effect adsorbate-adsorbate repulsion can be avoided and the behavior of the incident H can be described accurately.

Total energy calculations for the H-BLG system are performed for different locations of the incident hydrogen atom, where X, Y, and Z range within [-4.24 Å, 0.89 Å], [0.00 Å, 1.23 Å], and [-4.62 Å, 3.20 Å], respectively. From these calculations, the binding energy E_b of H at each scan point is determined using the equation

$$E_b = E_{\text{system}} - (E_{\text{substrate}} + E_H) \quad (\text{Eq. 1})$$

where:

$$\begin{aligned} E_{\text{system}} &= \text{total energy of the H-BLG system} \\ E_{\text{substrate}} &= \text{total energy of isolated BLG substrate} \\ E_H &= \text{total energy of free hydrogen} \end{aligned}$$

A more negative value that will be obtained from this equation implies a more energetically preferred configuration. From the results, potential energy surface (PES) is constructed and the reaction path for H sorption from the surface to the subsurface is then identified.

3. RESULTS AND DISCUSSION

The results of the total energy calculations for $z = 2.840$ Å are shown in the PES contour plot in

Fig. 2. This contour plot corresponds to binding energies for H sorption along the xy-plane, which is perpendicular to the graphene sheets, on top of the substrate.

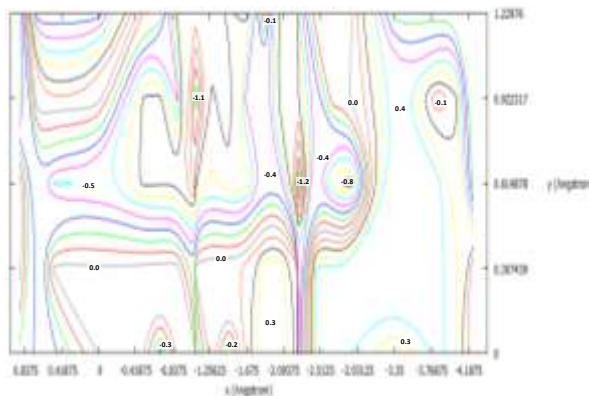


Fig. 2. Contour plot of the potential energy surface on top of the pristine bilayer graphene ($z = 2.840$ Å).

As shown in the figure, two local minima appear in the PES for this plane: (-1.10 Å, 0.92 Å, 2.84 Å) and (-2.26 Å, 0.61 Å, 2.84 Å) with binding energies of -1.1 eV and -1.2 eV, respectively. Each of these points appears to be a convenient entry for hydrogen sorption onto the zigzag edge of the pristine BLG substrate because these points are more energetically preferred configuration compared to other hydrogen location on this plane.

Successive total energy scans along the xy-plane revealed energetically favored configurations in the lower planes (i.e., nearer the BLG surface), which can be taken by incident H as it is adsorbed onto the BLG substrate. It is interesting to note that the points of strongest binding energy appear to be close in proximity as the local minima in the previous z scan point. This suggests that interlayer hopping is very unlikely since incident H tends to take the nearer location with higher binding energy. In addition to this, a high potential barrier is observed in between the graphene sheets hindering the incident H to hop from one layer to another.

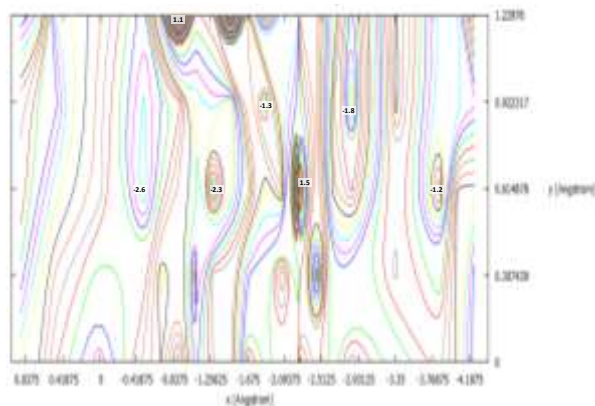


Fig. 3. Contour plot of the potential energy surface in the XY-plane at $z = 1.775 \text{ \AA}$. A potential barrier of up to +1.5 eV exists in between the graphene sheets in this plane.

Moreover, it is as interesting to note that the binding energy associated to these favored configurations progressively become stronger as the incident H approach the surface of the substrate. The peak binding energy is observed to be -5.3 eV at $(0.00 \text{ \AA}, 0.00 \text{ \AA}, 1.07 \text{ \AA})$ and $(-3.35 \text{ \AA}, 0.00 \text{ \AA}, -0.36 \text{ \AA})$. These correspond to locations where H is directly on top of the top-most C atom in the zigzag edge of the graphene sheets. Fig. 4 shows a 3D representation of the potential energy surface associated to -5.3 eV binding energy.

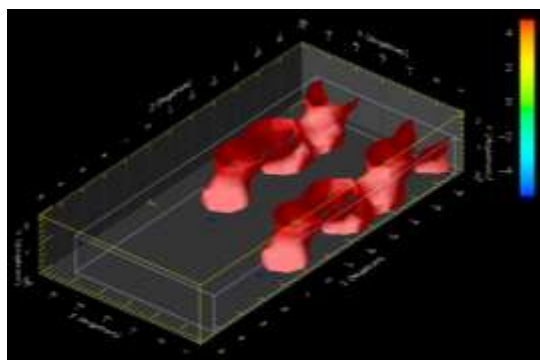


Fig. 4. 3D representation of the surfaces (in blue) with the strongest binding energy. Location of the carbon atoms are shown by the red surface.

With the very strong adsorption energy, it can be said that these regions are highly probable traps for early incident H atoms. It can be viewed that when the incident H is at these locations, the nearest C atom exhibits strong tendency of undergoing sp^2p_z hybridization by giving one of its two dangling bonds to H. This can be verified from the charge density distribution shown in Fig. 5a. It can be noticed that there exists a strong charge density distribution in between H and C suggesting the formation of H-C bond. Additionally, the H-C distance is measured at 1.065 \AA (see Fig. 5b). This value agrees very well with calculated value (Sharp, 2011) of H-C equilibrium bond length of 1.09 \AA .

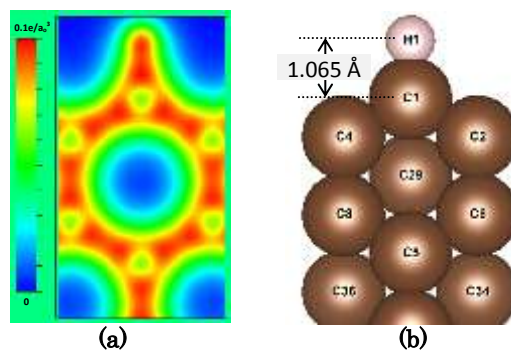


Fig. 5. (a) Contour plots of the charge density distribution along the XZ-plane. (b) Measurement of the distance of the H location with strongest binding energy from the top-most C atom in the BLG.

Further potential energy scans suggested the existence of, at least two, non-activated (i.e., barrier-less) paths of atomic hydrogen sorption on the zigzag edge of pristine bilayer graphene. These paths are in between the BLG substrate and tend to be located near the graphene sheets, one reaction path associated to each graphene layer. Fig. 6, which plots the total energy as a function of reaction path coordinate for each of these paths, shows that these reaction paths are indeed non-activated.

(a)

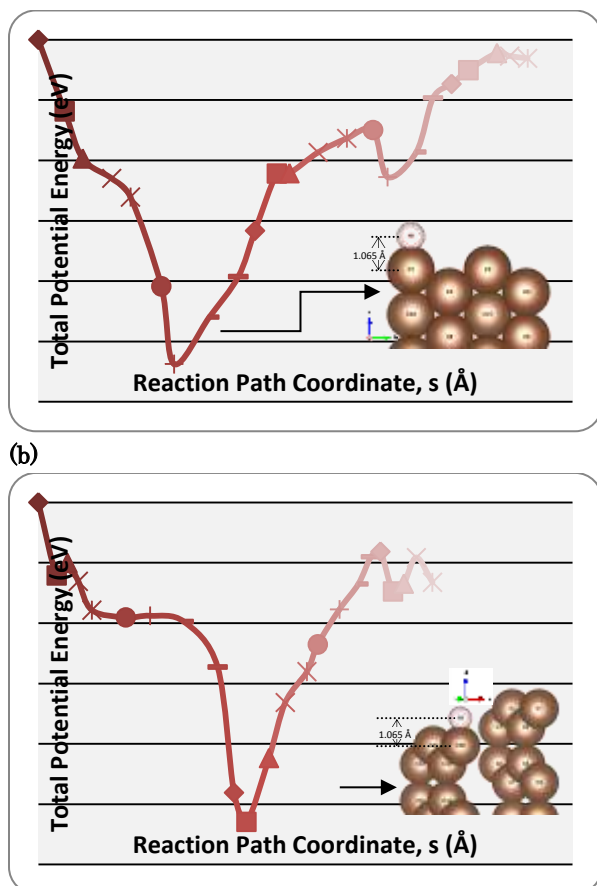


Fig. 6. Calculated potential energy along the (a) first and (b) second reaction path. Energies are given in electronvolts relative to the values at $z = \infty$.

4. CONCLUSIONS

We investigated the sorption mechanism of H atom on the zigzag edge of pristine bilayer graphene using spin-polarized density functional theory. Energy pathways from the surface to the subsurfaces are investigated using potential energy surface. We have confirmed that the zigzag edge of BLG is very highly reactive and that it can be the reaction channel to carry out the atomic H sorption process. We have found the existence of non-activated paths of atomic hydrogen sorption on the zigzag edge of pristine bilayer graphene. Lastly, we have also found that there exists a region of strong binding energy near the top-most C atoms suggesting the formation of sp^2p_z hybridization in the initial

stage of H adsorption. However, when early H atoms are trapped in these regions and will terminate the zigzag edge of the BLG substrate, there is no guarantee that succeeding H atoms can still enter into the substrate with no obstacles. Hence, further systematic investigations need to be undertaken to include sorption of atomic H in hydrogen-terminated zigzag edges.

5. ACKNOWLEDGMENTS

The authors would like to thank the University Research Coordination Office (URCO) of the De La Salle University (DLSU) for providing the funding for this research work. They would like to express their gratitude as well to DLSU and the Kasai Research Group of Osaka University for helping in the acquisition of the VASP program. Likewise, the authors extend their appreciation to the High Performance Computing Lab (HPCL) of the Center for Natural Sciences and Environmental Research (CENSER) for allowing the authors to conduct the calculations using the lab's computing facilities. RBB would also like to express his gratitude to CHED Faculty Development Program for his scholarship.

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Presented at the DLSU Research Congress 2014
De La Salle University, Manila, Philippines
March 6-8, 2014

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