



Atomic Hydrogen Absorption into Hydrogen Terminated Armchair Edges of Bilayer Graphene

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Abstract: Density functional theory (DFT)-based calculations are performed to determine the effects of preadsorbed atomic hydrogen (H) and substrate reconstruction on the absorption of H into bilayer graphene via the armchair edge. The total energy is calculated using the Vienna Ab-initio Simulation Package (VASP) software for various X-,Y- and Z-positions of H with respect to a predetermined reference point. The potential energy along Z (surface normal) is plotted as functions of the X- and Y-lateral positions of H. From these plots, the potential energy surface (PES) is obtained and the reaction path for the absorption of H into bilayer graphene via the armchair edge is determined. Results show that without surface reconstruction, absorption of H into the region between the graphene sheets is hindered by the preadsorbed H atoms since a barrier exists on the surface. By allowing surface reconstruction, this barrier is lowered thus enhancing H absorption into the bilayer.

Key Words: density functional theory; graphene; hydrogen storage; potential energy surface

1. INTRODUCTION

Carbon materials such as carbon nanotubes, activated carbons and graphene-based materials are considered promising candidates in hydrogen storage technologies because of their notable properties such as low mass density, high specific surface areas, tunable pore structure and stability for large scale production. Initial experimental studies on hydrogen storage in carbon materials show high hydrogen storage capacities (more than 60 wt% in some cases). However, the more recent experimental studies show less encouraging results with a large variation in the

amount of hydrogen stored. Thus, there is a need for more systematic investigations to gain a full understanding of hydrogen sorption mechanism on these materials.

Previous studies (Dino et al., 2004) have performed DFT-based investigations on the dissociative adsorption of molecular hydrogen H₂ on the zigzag and armchair edges of graphite sheets. These studies show a non-activated process for H₂ dissociative adsorption on the zigzag of graphite sheets and an activated process on the armchair edges. This result suggests that dissociative adsorption of H₂ on the zigzag edge of graphite is more favorable than on the armchair edge. Dynamics

calculations reveal very weak vibration assisted sticking effect for H_2 (Arboleda et al., 2004).

The absorption behaviors of atomic hydrogen H incident on the region between two graphite sheets through the armchair edge were investigated by Arboleda et al. (Arboleda and Kasai, 2011). DFT-based total energy calculations were performed and the potential energy curve and PESs were obtained to determine the reaction path corresponding to H absorption. The results of their calculations show the existence of a reaction path where H can enter the region between the graphite sheets. H termination of the edge C atoms' dangling bonds is most likely to occur during absorption since a strong trap for H atom is found to exist just above the surface C atoms. The negative potential energy along the reaction path fluctuates and seems to approach zero beyond the surface which strongly suggests that H absorption becomes more difficult without reconstruction as H goes deeper into the subsurface. They also found out that during absorption, H stays near one of the graphite sheets. Also observed was the motion of H parallel to a C row, while the occurrence of interlayer hopping was found to be most unlikely. Moreover, the barrier to H desorption between rows is always less than that to absorption.

In this study, DFT-based total energy calculations are performed to determine the effects of preadsorbed H atoms and substrate reconstruction on the absorption of H into bilayer graphene via the armchair edge.

2. METHODOLOGY

DFT-based total energy calculations are performed using the Vienna Ab-initio Simulation Package (VASP). Pseudopotentials and plane-wave basis sets are employed and the generalized gradient approximation (GGA) for the exchange correlation energy is utilized, with the interaction between ions and electrons described using ultrasoft Vanderbilt pseudopotentials (US-PP) or the projector augmented wave method (PAW). The total energy is computed in a supercell geometry where the substrate (see Fig. 1) is represented by periodically repeated slabs consisting of 8 preadsorbed H atoms and 52 carbon atoms, separated by 9 vacuum layers (10\AA). Each graphene sheet contains 13 rows of 2 carbon atoms.

The slab thickness is 14.76\AA , while the shortest distance between two C atoms is 1.42\AA .

To determine the effects of surface reconstruction on H absorption into bilayer graphene, we consider two cases: (1) a rigid substrate (i.e. the substrate's H and C atoms are fixed) and (2) a relaxed substrate (i.e. the substrate's H and C atoms are allowed to move as H approaches the surface). For each case, the potential energy of the system is determined for various H positions x , y and z with respect to a predetermined reference point (point 0 in Fig. 1). The value for x ranges from -0.5\AA to -2.85\AA , for y from 0.0\AA to 3.905\AA , and for z from 4.304\AA to -4.304\AA . The potential energy surfaces (PESs) are generated for the absorption of H along the plane parallel to the graphene sheets (parallel to the z -axis).

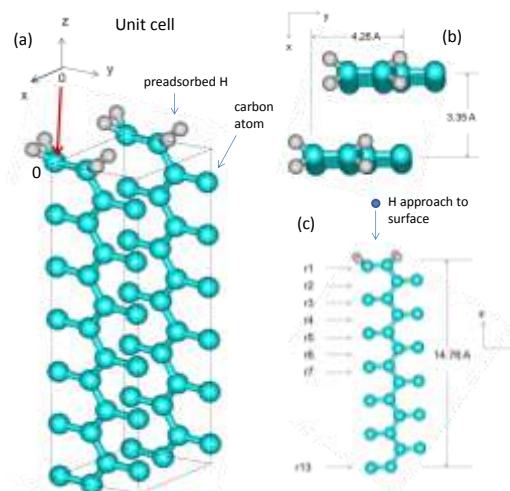


Fig. 1. Schematic diagrams of (a) the unit cell; (b) the bird's eye view of the substrate; and (c) the graphene sheet consisting of thirteen 2-carbon atom rows.

3. RESULTS AND DISCUSSION

3.1 Rigid Substrate

Figure 2 shows the 2-D and 3-D PES contour plots for the rigid substrate where the system's potential energy is plotted as a function of the H coordinates y and z , for $x = -1.68\text{\AA}$. These PESs correspond to H absorption along the yz -plane, which

is parallel to the graphene sheets. It can be observed from the plots that a barrier of 1.5 eV exists on the surface ($z = 0$). This barrier is due to the repulsion of the approaching H atom by the surface H atoms. Thus, without substrate reconstruction, the preadsorbed H atoms prevent the incident H from being absorbed into the region between the graphene sheets.

3.1 Relaxed Substrate

Figure 3 shows the 2-D and 3-D PES contour plots for the relaxed substrate where the system's potential energy is plotted as a function of the H coordinates y and z , for $x = -1.68\text{\AA}$. The thick solid blue line on the PES (Fig. 3a) represents the reaction path which is the path of least potential as H atom is absorbed into the substrate. It can be observed from the plots that H can be absorbed into the bilayer since H does not encounter a barrier as it approaches the substrate. The lowest energy is -1.5eV at $y = 3.905\text{\AA}$ and $z = -1.23\text{\AA}$.

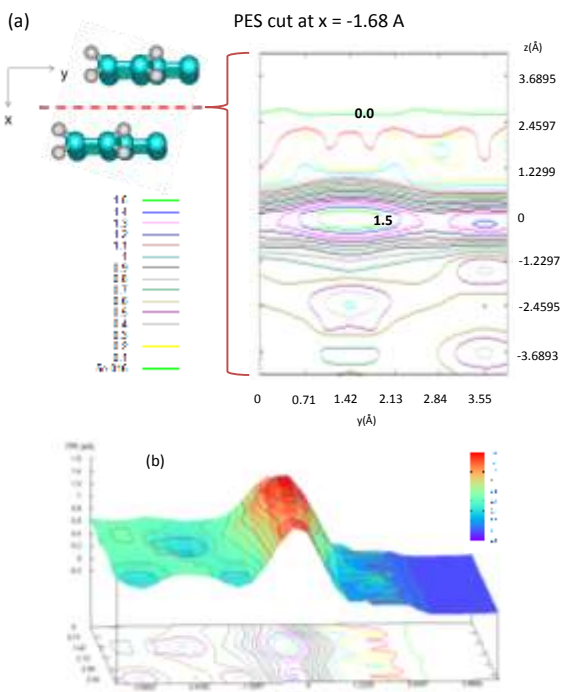


Fig. 2. (a) 2-D and (b) 3-D PES contour plots in the yz -plane at $x = -1.68\text{\AA}$ for the rigid substrate.

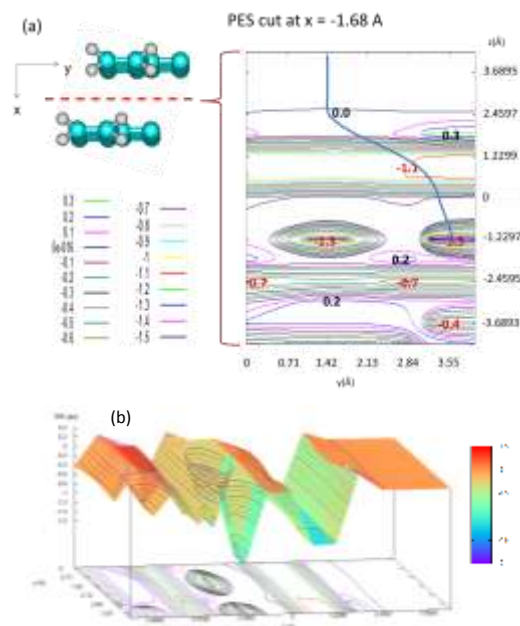


Fig. 3. (a) 2-D and (b) 3-D PES contour plots in the yz -plane at $x = -1.68\text{\AA}$ for the relaxed substrate.

Figure 4 shows the potential energy curve as a function of the reaction path coordinate s in the yz -plane at $x = -1.68\text{\AA}$ for the relaxed substrate. Also shown in the figure are the structures of the substrate as H is absorbed into the bilayer. It can be noted that the graphene sheets open up as H approaches the substrate. This minimizes the repulsive forces of the surface H atoms on the incident H atom. Thus, H encounters no barrier and goes further into the subsurface. Substrate reconstruction, therefore, enhances H absorption into bilayer graphene.

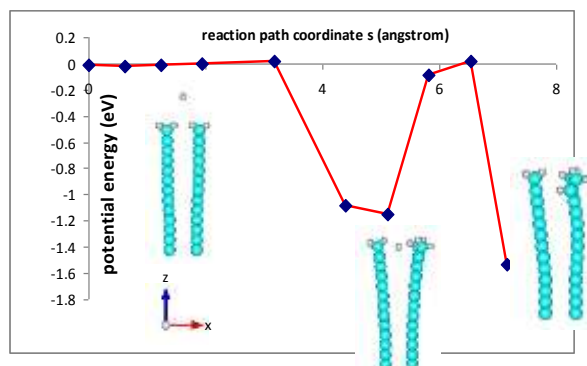


Fig. 4. Potential energy curve as a function of the reaction path coordinate s in the yz -plane at $x = -1.68 \text{ \AA}$ and the structure of the substrate as H is absorbed into the bilayer.

4. CONCLUSIONS

Based on the PES and PEC plots obtained, absorption of H into bilayer graphene via the armchair edge is affected by the preadsorbed H atoms and substrate reconstruction. Without surface reconstruction, the incident H atom is repelled by the preadsorbed H atoms thus preventing it from being absorbed into the bilayer. By allowing surface reconstruction, the repulsive forces of the preadsorbed H atoms on the incident H atom are minimized thus allowing H absorption into the bilayer.

5. ACKNOWLEDGMENTS

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