Sticking and Desorption of Atomic Hydrogen on the Armchair Edges of Bilayer Graphene

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ABSTRACT

The coupled channel method via the Local Reflection (LORE) matrix is employed to investigate the quantum mechanical behavior of the sticking or adsorption and desorption of hydrogen (H) atom on bilayer graphene via the armchair edge. The sticking and desorption probabilities of H are calculated and are plotted against the initial translational energy of H. The sticking probability plot shows a barrierless reaction indicating that hydrogen is easily adsorbed on the armchair edge of graphene. The desorption probability plot, however, shows that desorption of H from the graphene sheets is an activated process with a barrier height of 4.19 eV suggesting that a strong bond exists between the adsorbed H atom and the edge carbon atom. Thus, temperatures higher than the operating temperatures (300 - 1500 K) of conventional fuel cells are necessary to release the adsorbed H atom from the armchair edge of graphene.

Keywords : Graphene, Hydrogen, Armchair, Adsorption, Desorption

Received : 24 November 2014, Accepted : 17 September 2015

1. Introduction

At present, the full implementation of a hydrogen-based energy system is being hindered to some extent by the challenge of storing hydrogen gas, especially onboard fuel-cell powered automobiles. The existing technologies for onboard hydrogen storage include: (i) physical storage via compression or liquefaction, (ii) chemical storage in irreversible hydrogen carriers (e.g., methanol, ammonia), (iii) reversible metal hydrides and (iv) gas-on-solid adsorption [1]. However, the first three approaches do not satisfy all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. For physical storage, the main disadvantages include the need of high pressure and/or low temperature (21 K for liquefaction) and the high cost. For chemical storage, a conversion process is needed which makes the system more complicated. Storage by metallic hydrides

has the advantage of low pressure, but the storage system is heavy and additional heating is needed to release hydrogen. The last option, hydrogen adsorption on solids, has the potential to become a safe and efficient way to store energy for stationary as well as mobile applications [2]. Thus, several studies [3-9] on the interaction of hydrogen with solids have been performed to find the ideal material that will allow the storage of desirable amounts of hydrogen and other applications.

Carbon-based 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 [10,11] on hydrogen storage in carbon nano-materials show promising results, indicating high hydrogen storage capacities (more than 60 wt% in some cases). However, more recent experimental studies [12,13] using different methods and on various carbon nanostructures 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 detailed, atomic-level understanding of the mechanism underlying hydrogen adsorption, absorption, and desorption on/from carbon related materials such as graphene.

Previous studies [14,15] have performed DFT-based investigations on the dissociative adsorption of molecular hydrogen H_2 on the zigzag and armchair edges of graphite sheets. These studies show a non-activated process for H_2 dissociative adsorption on the zigzag of graphite sheets and an activated process on the armchair edges. This result suggests that dissociative adsorption of H_2 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 [16].

The absorption behavior of atomic hydrogen H incident on the region between two graphene sheets through the armchair edge was investigated by Arboleda et al. [17]. DFT-based total energy calculations were performed and the potential energy curve and potential energy surfaces (PES) 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 graphene 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 the armchair edge of the graphene sheets. Also observed was the motion of H parallel to a C row, while the occurrence
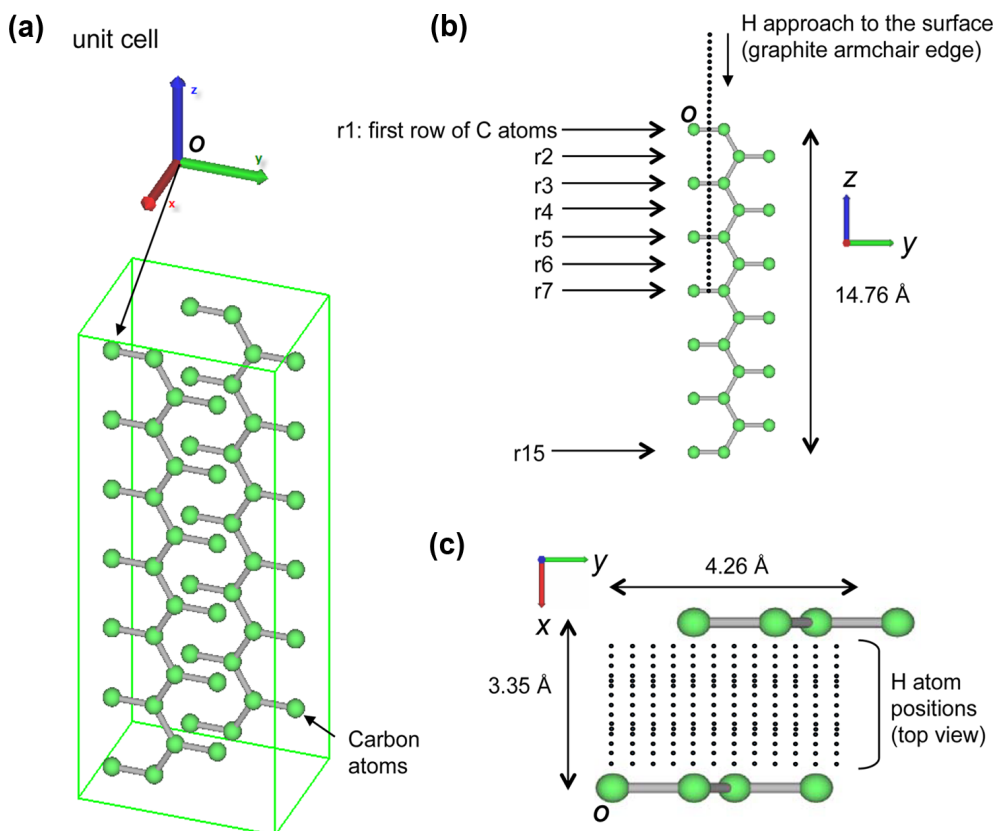

Fig. 1. Schematic diagrams of (a) the unit cell, (b) the side-view of the substrate and H approaching the graphene armchair edge, and (c) the various lateral positions of the hydrogen approach (dot) as seen from a bird's eye view [10].

of interlayer hopping was found to be most unlikely. Moreover, the barrier to H desorption between rows is always less than that to absorption.

This paper investigates the quantum mechanical behavior of the sticking and desorption of hydrogen atom on bilayer graphene via the armchair edge. The sticking and desorption probabilities of H are calculated using the coupled channel method via the Local Reflection (LORE) matrix and are plotted against the initial translational energy of H.

2. Methodology

The system used in the study performed by Arboleda et al. [17] to investigate the absorption of atomic hydrogen incident on the region between two graphene sheets through the armchair edge is shown in Fig. 1. The bilayer graphene substrate is represented by periodically repeated slabs consisting of thirteen rows of carbon atoms (two in each row). The potential energy of the system was determined for various H positions X, Y and Z with respect to a predetermined reference point 0 (see Fig. 1). The potential energy curves were then determined, and the contour plots of the PESs were generated from these curves for the absorption of H along the plane parallel and perpendicular to the graphene sheets (parallel to the z-axis).

In order to investigate the quantum mechanical behavior of the adsorption and desorption of H atom on bilayer graphene via the armchair edge, the potential energy curve obtained from the aforementioned study is used to calculate the sticking and desorption probabilities of H. The coupled channel method via the Local Reflection (LORE) matrix [18] is used in the calculations. The probabilities are then plotted as functions of the initial translational energy of H. The range of the initial translational energy E_t is 0.0-1.2 eV (0.0-4.5 eV) for the sticking (desorption) of H, with an interval of 0.001 eV (0.0015 eV). For the piecewise constant potential approximation, the area under the potential curve is divided into 100 sub-regions.

3. Results and Discussion

The plot of the sticking probability of H as a function of its initial translational energy is shown in Fig. 2. The plot shows that hydrogen is easily adsorbed on the surface of the graphene sheets since the sticking

probability rises rapidly to unity as the kinetic/translational energy is increased. This behavior of the sticking probability is characteristic of a barrierless reaction which agrees with the corresponding potential energy curve (see inset). The less than unity values of the sticking probability at low initial kinetic energies (0.0 eV - 0.006 eV) is due to quantum mechanical effects which are brought about by the very small mass of H.

Fig. 3 shows the desorption probability plot for H as a function of its initial translational energy. It can be observed from the plot that an S-shaped region
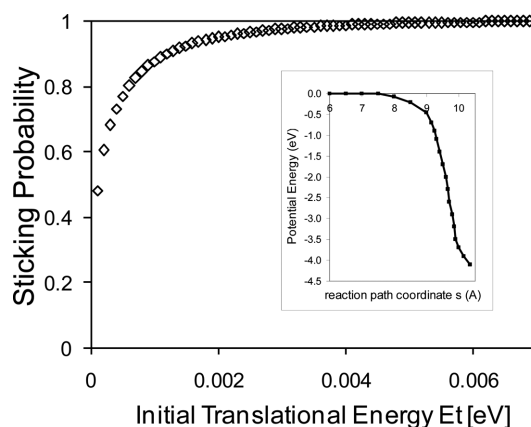

Fig. 2. The adsorption probability for atomic hydrogen H incident on bilayer graphene via the armchair edge, as function of the incident translational energy E_t of H. The inset shows the corresponding potential energy curve.
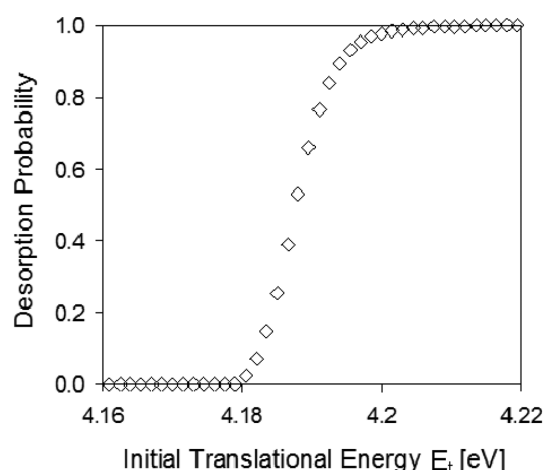

Fig. 3. The desorption probability for atomic hydrogen H incident on bilayer graphene via the armchair edge, as function of the incident translational energy E_t of H.

exists within the energy range 4.18 to 4.20 eV. Within this range, the desorption probability rises from 0 to 1. The energy at the center of the S-shaped region (~4.19 eV) corresponds to the barrier height for this reaction. The non-zero values of the desorption probability for E_t just below 4.19 eV suggest that even with an initial kinetic energy below the barrier height, desorption of H may still occur. On the other hand, the less than unity desorption probabilities for E_t just above 4.19 eV indicate that desorption may still not take place if the initial kinetic energy of H is higher than the barrier. This behavior of the desorption probability is attributed again to quantum mechanical effects which are brought about by the very small mass of H. It can also be noted from the plot that the S-shaped curve is not symmetric. This is due to the asymmetry of the potential energy curve (see inset of Fig. 2).

In order to determine the effects of the surface temperature on the desorption of H, the product of the desorption probability $D_p(E_t)$ and the energy distribution $f(Et)$ for different surface temperatures were calculated. The surface temperatures considered are $T_s = 300$ K, 500 K and 1500 K. These temperatures approximately represent the surface temperatures of conventional fuel cells such as the proton exchange membrane fuel cells and the solid oxide fuel cells.

Fig. 4 shows the plots of the energy distribution as a function of the translational energy for the surface temperatures $T_s = 300$ K, 500 K and 1500 K. It can be observed from the plots, that the particles' kinetic energy ranges from 0.0 - 0.2 eV for $T_s = 300$ K, 0.0 - 0.3 eV for $T_s = 500$ K and 0.0 - 0.8 eV for $T_s = 1500$ K. It can also be seen from the plots that most of the particles are in the ground state.

Fig. 5 shows the plots for the product D_p x f at $T_s = 300$ K, 500 K and 1500 K for the H-graphene system as a function of the hydrogen's initial translational energy E_t. It can be seen from the plots that the product is approximately zero for surface temperatures $T_s = 300$ K and 500 K, and almost zero for $T_s = 1500$ K. This result is expected since as seen from Fig. 3, the minimum kinetic energy needed to overcome the barrier is 4.19 eV and from the energy distribution, it can be seen that very few or no particles have this kinetic energy. Thus, at these surface temperatures, thermal desorption of the adsorbed H atoms from the armchair edge of the graphene sheets is very unlikely to occur. This is due to the existence of a very strong bond between the adsorbed H and
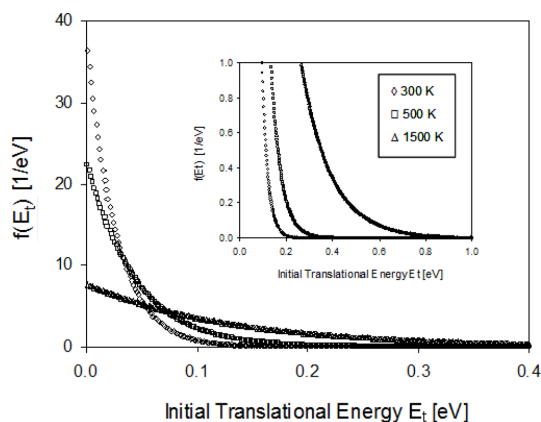

Fig. 4. Plots for the energy distribution f at $T_s = 300$ K, 500 K and 1500 K for the H-graphene system as a function of the hydrogen's initial translational energy E_t (in eV).
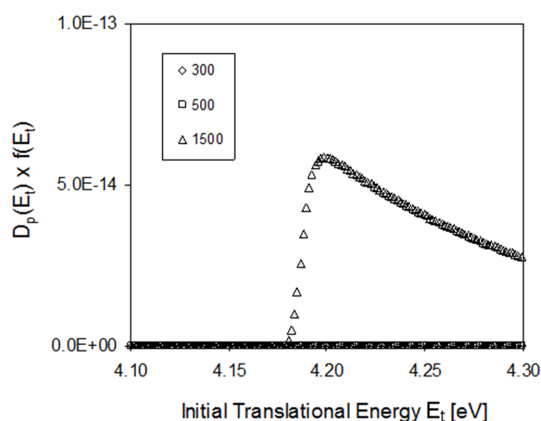

Fig. 5. Plots for the product D_p x f at $T_s = 300$ K, 500 K and 1500 K for the H-graphene system as a function of the hydrogen's initial translational energy E_t (in eV).

edge carbon atom.

The absence of reversibility (i.e. hydrogen is easily adsorbed but difficult to desorb) has also been observed in experimental studies [19-22] on the hydrogenation of ball-milled graphite. Results of these studies showed that hydrogen atoms are chemisorbed at the graphene edges. However, since the covalent bond between C and H is too strong to desorb hydrogen, temperatures higher than 700 °C are necessary to release all of the chemisorbed hydrogen from ball milled graphite [23]. A study done by Ichikawa et al. [24] demonstrated that reversibility can be achieved by the addition of lithium hydride (2:1 molar ratio of graphite and LiH).

4. Conclusions

By calculating the adsorption and desorption probabilities of H, this study was able to investigate the quantum mechanical behavior of the adsorption and desorption of H atom on bilayer graphene via the armchair edge. The adsorption probability plot shows a barrierless reaction which strongly suggests that hydrogen is easily adsorbed on the surface of the graphene sheets. The desorption probability plot shows that the desorption of H from the graphene sheets is an activated process with a barrier height of 4.19 eV. Due to this high barrier, desorption of the absorbed H atom from the surface of the graphene sheets at operating temperatures (300 - 1500 K) of conventional fuel cells is unlikely to occur.

Acknowledgement

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