H$_2$ Dissociative Adsorption at the Zigzag Edges of Graphite

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Based on the density functional theory, we investigate and discuss how hydrogen behaves at the edges of graphite sheets/layers, in particular the zigzag edge. Our calculation results show that the zigzag edge is very reactive. It is possible to dissociatively adsorb H$_2$ on these surfaces without any activation barrier hindering the reaction. To be able to use carbon nanomaterials as a means to store hydrogen, one of the crucial factors necessary would be the ability to dissociate hydrogen first, and then (somehow) induce them to stick to the carbons on each sheets. The results we present here suggest the possible utility of the zigzag edge as a reaction channel to carry out the aforementioned process. [DOI: 10.1380/ejssnt.2004.77]

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In recent years, carbon-based nanomaterials, e.g., carbon nanotubes (CNTs) and graphite nanofibers (GNFs), have attracted much attention because of their suggested potentials as materials for gas storage. In particular, the reportedly high hydrogen uptake of these materials makes them attractive as hydrogen storage devices in fuel-cell-powered electric vehicles [1, 2]. However, although various theoretical and experimental studies have been made (cf., [3–18], and references therein), and initial reports seem to show promising and spectacular results (more than 60wt% in some cases), research in this field remains contentious [2, 19], as later studies reveal trends significantly less encouraging than first contemplated [20, 21].

A storage density of 60wt% (storage density unit determined from the weight of the adsorbed H$_2$ divided by the sum of the weight of the carbon-based nanomaterial and the adsorbed H$_2$), e.g., corresponds to almost 10 times the 6.5wt% efficiency required for vehicular hydrogen storage (cf., e.g., [4] and references therein). These spectacular results have yet to be reproduced by other experimental and/or theoretical groups [2, 19–21]. We can view the above situation as an indication of, not only the need for more systematic investigations, but also the necessity to develop a microscopic picture of the mechanism underlying hydrogen adsorption onto, absorption into, and desorption from carbon related materials. With this in mind, we have done several studies on the interaction of hydrogen with various surfaces of graphite [22–26].

Invoking the density functional theory (DFT), we calculated the potential energy surfaces (PES) relevant to the dissociative adsorption of H$_2$ onto a graphite sheet [22]. Our results show that the reconstruction of the C atoms plays an important role in understanding the H$_2$-graphite surface interaction. We observe a lowering of the dissociation barrier by ca. 1 eV, as a result of the relaxation outwards of the C atoms (changing its structure from sp$^2$ to sp$^3$-like), to meet the incoming H$_2$. This is however not enough, as the dissociation barrier still remains high at ca. 3 eV. Furthermore, when the C atoms involved are very close to each other (ca. 1.42 Å, nearest neighbor C-C distance), it becomes more difficult for the C atoms to move out of the graphite sheet plane, to meet the incoming H (H$_2$). The PES for H$_2$ dissociation on the surface plane of a graphite sheet is thus azimuthally corrugated. The relaxation of the C atoms also stabilizes the H-graphite surface interaction, with a corresponding binding energy of 0.67 eV. We were later informed [27] that the theoretical results quantitatively agree with recent experimental results [28].

Based on these observations, we could also understand how hydrogen behaves when it interacts with a single-walled carbon nanotube (SWCNT) [23]. As we would expect, a SWCNT with a small diameter adsorbs H quite easily. However, as the diameter increases, the potential energy features approach that for hydrogen interaction with the surface plane of a graphite sheet.

We also considered the possibility of finding hydrogen in between graphite layers [25]. As expected from earlier results [22–24], the reconstruction of the C atoms plays an important role in determining what stable configurations hydrogen will take once found inside/between graphite layers. A H atom takes a position ca. 1 Å from one C atom on one sheet and ca. 2 Å from the C atom on the other sheet. On the other hand, it would be difficult to dissociate H$_2$ in between graphite layers. It would also be difficult to find them as H$_2$ in between graphite layers. Again, we were later on informed regarding the amazing agreement between our results and that of recent neutron diffraction [17] and thermal desorption [14] studies on deuterated nanographite.

After concluding that it would be difficult for the H atom to reach inside/between the graphite layers through the hexagonal holes at the surface planes [22, 24], and that it would also be difficult to find H$_2$ inside/between
From Fig. 1(a), we can see that there is no activation barrier hindering H₂ dissociation on the zigzag edge of graphite. This result may be compared to the activated dissociative adsorption on a graphite sheet [22, 24, 25] and at the armchair edge [26]. The spectacular change in reactivity mainly lies in the difference in structure of the C atoms at these surfaces. On a graphite sheet, all of the C atoms are bonded to three neighboring C atoms, with \( sp^2\)-structure. The robustness of the \( sp^2\)-structure prevents the C atoms on the graphite sheet from forming new bonds. Recall that a C atom must first form an \( sp^3\)-like structure before it can accommodate a H atom, directly impinging on the graphite sheet, or one coming as product of H₂ dissociation [22, 24, 25]. Compared to the graphite sheet, the C atoms at the outermost edges (arm-

Figure 1(a) shows the calculated potential energy contours for H₂ dissociation on the zigzag edge of graphite, as a function of the H-H separation \( r \), and the normal distance \( Z \) between the H₂ center-of-mass from the zigzag edge. The H₂ is initially oriented with the H-H bond \( perpendicular \) to the graphite sheet, and dissociation is constrained in a parallel orientation with respect to the zigzag edge, and a planar geometry. Figure 1(b)(Upper Right Panel) shows a top view of how H₂ is oriented with respect to the graphite sheets, and dissociation is constrained in a parallel orientation with respect to the zigzag edge, and a planar geometry. Figure 1(b)(Lower Right Panel) shows the top and side views of where the H atoms are, after dissociating. Energies are given in electronvolts relative to the values for the case when H₂ is in the gas phase, far \( (Z = \infty) \) from the graphite. The interlayer distance between graphite sheets is ca. 3.5 Å. (b)(Lower Right Panel) Side and top views, showing the configuration of the dissociated H atoms at the zigzag edge of graphite.

We perform DFT-based total energy calculations, using plane waves and pseudopotentials [29]. The graphite supercell in the slab model we used in the calculations consists of two graphite sheets/layers, which are separated by ca. 3.5 Å and shifted relative to each other as shown on the Right Panels of Figs. 1 and 2. Each graphite layer consists of 21 carbon atoms with a nearest neighbor distance of 1.42 Å. We have chosen a sufficiently large (graphite) supercell, in order to avoid interactions between the H atoms (H₂ molecules) in the neighboring supercells. The electron-ion interaction is described by optimized ultrasoft pseudopotentials [30], and the Kohn-Sham equations are solved using plane waves with kinetic energies up to \( \approx 476 \text{ eV} \). The surface Brillouin zone integration is performed using the special-point sampling technique of Monkhorst and Pack (with \( 4 \times 4 \times 1 \) sampling meshes) [31]. For the exchange correlation energy, we adopt the generalized gradient approximation (GGA) [32, 33]. No significant change in the numerical results was observed when we increased the kinetic energy cutoff and the number of sampling points.
FIG. 2: (a) Calculated potential energy contours for H\textsubscript{2} dissociation on the zigzag edge of graphite, as a function of the H-H separation \(r\), and the normal distance \(Z\) between the H\textsubscript{2} center-of-mass from the zigzag edge. (b) (Upper Right Panel) H\textsubscript{2} configuration with respect to the zigzag edge, the H-H bond is oriented at an angle with respect to the graphite sheets. H\textsubscript{2} is constrained to dissociate over the indicated site in a parallel orientation and a planar geometry. Energies are given in electronvolts relative to the values at \((Z = \infty, r \approx 0.74\ \text{Å})\). The interlayer distance between graphite sheets is ca. 3.5 Å. (Lower Right Panel) Side and top views, showing the configuration of the dissociated H atoms at the zigzag edge of graphite.

Chair and zigzag (armchair and zigzag) are bonded to only two neighboring C atoms. This makes the edges more reactive (more susceptible to forming new bonds) to H adsorption and/or H\textsubscript{2} dissociation, as compared to the graphite sheet. The difference in reactivity between the armchair and the zigzag edge lies in the way the C atoms at the edges are bonded. As mentioned earlier, each of the outermost C atoms at the armchair edge has two neighboring C atoms, one of which is also located at the armchair edge. In effect, every reaction occurring at an armchair edge, e.g., H adsorption or H\textsubscript{2} dissociation, involves an armchair edge C-C pair. When one of the C atoms in the armchair edge C-C pair forms a new bond with the incoming H atom, the other remaining C atom (of the C-C pair) must somehow compensate for the resulting change in covalency [26]. Although a C atom located at the outermost part of a zigzag edge is also bonded to two neighboring C atoms, neither of these neighboring C atoms are located at the edge. The C atoms at the zigzag edge are, thus, already in a favorable configuration, and ready to welcome the incoming hydrogen. (Here, we restrict the discussion to geometric effects and defer the discussion on the corresponding electronic effects to [26].) In the configuration shown in Fig. 1, once the H\textsubscript{2} dissociates, we find that H atoms finally assume a position 0.58 Å from the C atom, with an adsorption energy of ca. 3.22 eV.

Figure 2(a) shows the results for the case when the H-H bond is oriented at an angle with respect to the graphite sheets. From Fig. 2, we can see that the adsorption energy increases by ca. 1.5 eV. Along the path of least potential, we also find the H\textsubscript{2} center-of-mass going partly into the graphite layers. The reason for the increased adsorption energy is quite apparent, when we compare the final configurations of the dissociated H atoms shown in the Lower Right Panels of Figs. 1(b) and 2(b). It should be noted that the calculated PES shown in Figs. 1 and 2(b) are just two cuts through the full, multi-dimensional potential energy hyper-surface for describing H\textsubscript{2} interaction with the zigzag edge of graphite. The configurations shown in the Lower Right Panels of Figs. 1(b) and 2(b) give us the final positions of the dissociated H atoms, if we insert the H\textsubscript{2} in the configuration shown in the Upper Right Panels of Figs. 1(b) and 2(b), respectively, and constrain H\textsubscript{2} dissociation in a parallel orientation with respect to the zigzag edge, and a planar geometry, as mentioned above. We could thus interpret the results presented here as an indication of the existence of, at least two, non-activated (barrier-less) paths to H\textsubscript{2} dissociation on the zigzag edge.

In summary, based on the density functional theory, we investigate and discuss how hydrogen behaves at the edges of graphite sheets/layers, in particular the zigzag edge. Our calculation results show that the zigzag edge is very reactive. It is possible to dissociatively adsorb H\textsubscript{2} on these surfaces without any activation barrier hindering the reaction. Based on the results we have so far gathered, we conclude that to be able to use carbon nanomaterials as a means to store hydrogen, the crucial steps would be to dissociate hydrogen first, and then (somehow) induce them to stick to the carbons on each sheets. The results we present suggest the possible utility of the zigzag edge as a reaction channel to realize efficient hydrogen-storing carbon nanomaterials.
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[29] http://www.fysik.dtu.dk/CAIMOS.