H₂ 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 H₂ 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/ejsnt.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 H₂ divided by the sum of the weight of the carbon-based nanomaterial and the adsorbed H₂), 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 H₂ onto a graphite sheet [22]. Our results show that the reconstruction of the C atoms plays an important role in understanding the H₂-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 H₂. 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 (H₂). The PES for H₂ 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 H₂ in between graphite layers. It would also be difficult to find them as H₂ 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 H₂ inside/between

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FIG. 1: (a) Calculated potential energy contours for H_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_2 center-of-mass from the zigzag edge. (b)(Upper Right Panel) H_2 configuration with respect to the zigzag edge: the H-H bond is oriented *perpendicular* to the graphite sheets. H_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 ($Z = \infty$, $r \approx 0.74$ Å). 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.

graphite layers [25], we considered the next probable surfaces on graphite, viz., the edges. Our results indicate that on the armchair edge [26], regardless of site, there is always an activation barrier hindering H_2 dissociative adsorption. Furthermore, our results show that it would be difficult to insert the whole H_2 through the armchair edge. This agrees with our earlier findings for H_2 inside/between graphite layers [25]. Here, we consider the interaction of hydrogen with the other remaining edge of graphite, viz., the zigzag edge.

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 (H_2 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 ≈ 476 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.

Figure 1(a) shows the calculated potential energy contours for H_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_2 center-of-mass from the zigzag edge. The H_2 is initially oriented with the H-H bond *perpendicular* 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)(Upper Right Panel) shows a top view of how H_2 is oriented with respect to the graphite sheets, when H_2 is far from the graphite edge. 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 H_2 is in the gas phase, far ($Z = \infty$) from the graphite. The interlayer distance between graphite sheets is ca. 3.5 Å.

From Fig. 1(a), we can see that there is no activation barrier hindering H_2 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 H_2 dissociation [22, 24, 25]. Compared to the graphite sheet, the C atoms at the outermost edges (arm-

FIG. 2: (a) Calculated potential energy contours for H_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_2 center-of-mass from the zigzag edge. (b) (**Upper Right Panel**) H_2 configuration with respect to the zigzag edge, the H-H bond is oriented at an angle with respect to the graphite sheets. H_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 ($Z = \infty$, $r \approx 0.74$ 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) 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_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_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_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_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_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_2 in the configuration shown in the Upper Right Panels of Figs. 1(b) and 2(b), respectively, and constrain H_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_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_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 efficient hydrogen-storing carbon nanomaterials.

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- [1] H. M. Cheng, Q. H. Yang and C. Liu: *Carbon* **39**, 1447 (2001).
 - [2] G. E. Froudakis: *J. Phys.: Condens. Matter* **14**, R453 (2002).
 - [3] J. P. Chen and R. T. Yang: *Surf. Sci.* **216**, 481 (1989).
 - [4] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben: *Nature* **386**, 377 (1997).
 - [5] Q. Wang and J. K. Johnson: *J. Chem. Phys.* **110**, 577 (1999).
 - [6] F. Darkrim and D. Levesque: *J. Chem. Phys.* **109**, 4981 (1998).
 - [7] A. Chambers, C. Park, R. Terry, K. Baker and N. M. Rodriguez: *J. Phys. Chem. B* **102**, 4253 (1998).
 - [8] L. Jelaica and V. Sidis: *Chem. Phys. Lett.* **300**, 157 (1999).
 - [9] V. V. Simonyan, P. Diep and J. K. Johnson: *J. Chem. Phys.* **111**, 9778 (1999).
 - [10] C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng and M. S. Dresselhaus: *Science* **286**, 1127 (1999).
 - [11] S. M. Lee and Y. H. Lee: *Appl. Phys. Lett.* **76**, 2877 (2000).
 - [12] K. A. Williams and P. C. Eklund: *Chem. Phys. Lett.* **320**, 352 (2000).
 - [13] K. Tada, S. Furuya and K. Watanabe: *Phys. Rev. B* **63**, 155405 (2001).
 - [14] S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga and G. Majer: *J. Appl. Phys.* **90**, 1545 (2001).
 - [15] M. Rutigliano, M. Cacciatore and G. D. Billing: *Chem. Phys. Lett.* **340**, 13 (2001).
 - [16] F. H. Yang and R. T. Yang: *Carbon* **40**, 437 (2002).
 - [17] T. Fukunaga, K. Itoh, S. Orimo, M. Aoki and H. Fujii: *J. Alloy. Comp.* **327**, 224 (2001).
 - [18] X. Sha and B. Jackson: *Surf. Sci.* **496**, 318 (2002).
 - [19] R. G. Ding, G. Q. Lu, Z. F. Yan and M. A. Wilson, *J. Nanosci. Nanotechnol.* **1**, 7 (2001).
 - [20] <http://www.mpi-stuttgart.mpg.de/klitzing/research/nano/HydrogenStorage.html>
 - [21] L. Schlapbach and A. Züttel: *Nature* **414**, 353 (2001).
 - [22] Y. Miura, H. Kasai, W. A. Diño, H. Nakanishi and T. Sugimoto: *J. Appl. Phys.* **93**, 3395 (2003).
 - [23] Y. Miura, H. Kasai, W. A. Diño, H. Nakanishi and T. Sugimoto: *Jpn. J. Appl. Phys.* **42**, 4626 (2003).
 - [24] Y. Miura, H. Kasai, W. A. Diño, H. Nakanishi and T. Sugimoto: *J. Phys. Soc. Jpn.* **72**, 995 (2003).
 - [25] W. A. Diño, Y. Miura, H. Nakanishi, H. Kasai and T. Sugimoto: *J. Phys. Soc. Jpn.* **72**, 1867 (2003).
 - [26] W. A. Diño, Y. Miura, H. Nakanishi, H. Kasai, T. Sugimoto and T. Kondo: submitted.
 - [27] T. Zecho: private communication.
 - [28] T. Zecho, A. Güttler, X. Sha, B. Jackson and J. Küppers: *J. Chem. Phys.* **117**, 8486 (2002).
 - [29] <http://www.fysik.dtu.dk/CAMPOS>.
 - [30] D. Vanderbilt: *Phys. Rev. B* **41**, 7892 (1990).
 - [31] H. J. Monkhorst and J. D. Pack: *Phys. Rev. B* **13**, 5188 (1976).
 - [32] M. Rasolt and D. J. W. Geldart: *Phys. Rev. B* **34**, 1325 (1986).
 - [33] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais: *Phys. Rev. B* **46**, 6671 (1992).