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High-uptake graphene hydrogenation: a computational perspective

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Abstract

We review the physical mechanisms that lead toward the conversion of graphene into its fully hydrogenated counterpart, which is a material that possesses properties closer to those of diamond than graphene. These are discussed from a theoretical perspective, i.e., from calculations based on density functional theory. We first discuss stability trends in small clusters of adsorbed hydrogen, as well as surface structure and concurrent reactivity changes for graphene one-face and two-face hydrogenation. Effects of adsorbed hydrogen on graphene electronic states, which are essential to adsorbed hydrogen structure discrimination, are also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogenation of carbon materials has been the subject of decades of studies spanning a wide range of interests. Hydrogen in amorphous and diamond-like carbon has for example been studied for the tribological properties of the system, and studies on hydrogenation–dehydrogenation processes on graphitic surfaces have been fueled by the need to understand reactions in interstellar media. Also, the inherent lightness and reported high hydrogen uptake of carbon materials have led to much interest in using this class of materials in hydrogen-powered automobiles, and the recent attention given to graphene for carbon-based nanoscale devices has revived interest in the chemical modification of carbon materials with hydrogen. Furthermore, on a more academic perspective, hydrogenation of graphene is one direct bridge that links concepts in organic chemistry with the possibilities in condensed matter physics.

Our primary motivation in investigating hydrogen in carbon systems is realizing high hydrogen uptakes on surfaces for practical hydrogen storage in solid-state materials. In order to achieve this, it is always beneficial to know how the road to adsorption saturation on the surface looks like in terms of the physical mechanisms involved, and how one can control required reactions given this knowledge. Much theoretical and experimental work has been done globally in this area in the

past decade, and in this paper we revisit some key concepts that we have reported in the past few years. This paper discusses systems involving hydrogen in chemisorbed states on graphene, which have been studied with density functional theory. We outline our recent findings crucial to understanding graphene defects brought about by hydrogen, which serves as a benchmark for covalently adsorbed species on the carbon surface. Emphasis is given to the underlying mechanisms related to the growth of defect structures, which have been shown to drastically change the properties of graphene.

2. Hydrogen atom adsorption and clustering on graphene

Investigations on the physical/chemical modification of graphene by the addition of adsorbed species on one or both faces of graphene have been carried out for a wide range of reasons. Reactions with gas molecules, for example, have been studied for sensing applications, while studies involving adsorbed metals have been carried out in light of addressing the demands of post-silicon electronics. On the latter, recent studies [1–4] have predicted the tendency of metal atoms to attach onto graphene through the hexagonal C ring centers (i.e., the hollow sites), with binding energies ranging from about 0.1 to 2.0 eV. It was shown that strong changes in the carbon

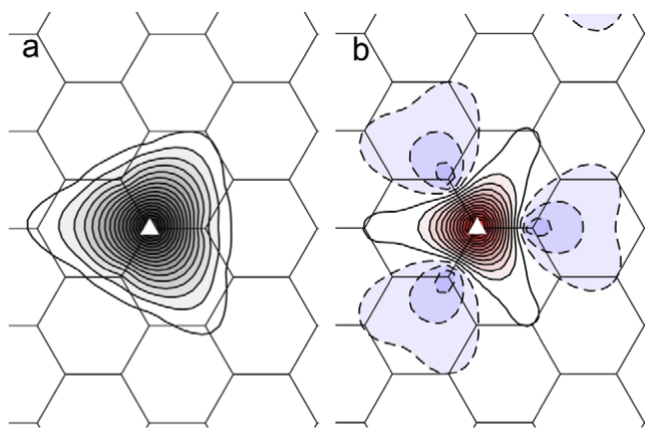


Figure 1. Contour maps describing adsorbed H-induced graphene reconstruction. (a) Displacement of C atoms from the original graphene plane, and (b) local planar distortion. For (b), dashed (solid) contours indicate downward (upward) local planar distortion. Contours are separated by 0.02 Å. Positions of H atoms are marked by the white triangles.

sheet’s properties can indeed be induced by such attachments to graphene, the extent dependent on the bonding mechanisms involved.

In the case of hydrogen, an atom approaching graphene preferentially ends up at top sites, i.e., H prefers single coordination, and given appropriate time to relax, it reaches a very stable chemisorbed state, albeit having to go through a barrier of about 0.2 eV [5]. Reported H atom adsorption energies vary slightly across computational studies (roughly in the range of -0.6 to -0.8 eV, the negative sign denoting adsorption exothermicity), the values primarily depending on how isolated the H atom is treated on graphene. The chemisorption is associated with the receiving carbon atom being pulled out by about 0.33 Å from the initial planar geometry of graphene. Reconstruction due to the adsorption of a single H atom is however not limited to the receiving C atom, as clearly described in figure 1(a), which plots the displacement of C atoms from the original graphene plane along z , taken to be the direction normal to the graphene plane. Local planar distortion, which is the distance a C atom moves out of the plane determined by its three nearest neighboring C atoms, is shown in figure 1(b). It becomes apparent that C–C bonds within a certain range of the adsorption site are strained out of their initial planar geometries in order to minimize the energy of the system. Even longer ranging is the H atom’s effects on the graphene electronic states—but let us firstly consider the behavior of small groups of hydrogen adsorbed on graphene, starting with hydrogen pairs.

Stable hydrogen molecule adsorption on graphene [6] requires molecular dissociation. Breaking up the incoming molecules requires a large amount of energy (in particular, the H_2 binding energy is about 4.5 eV), but graphene reconstruction reduces the barrier to reaching stable adsorbed states. The configuration with atoms attaching to opposite corners of a graphene hexagon (i.e., in the para configuration) was found to be the most stable configuration for an adsorbed pair, and from the constructed potential energy surface was additionally found to be the most accessible.

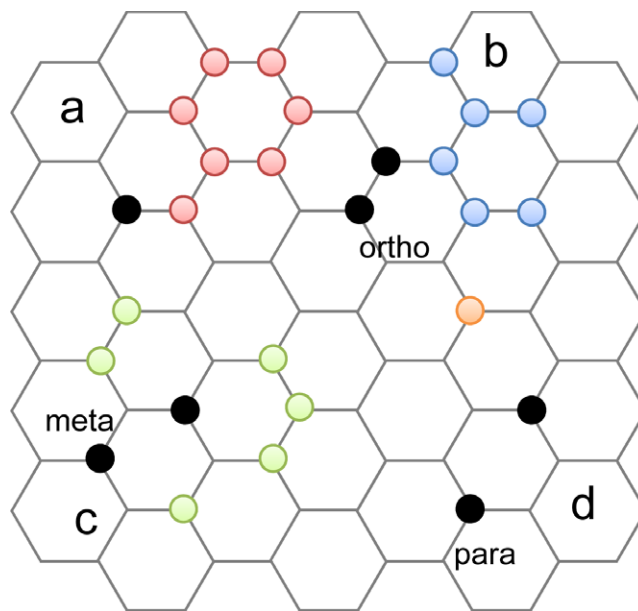


Figure 2. Closest-packing hydrogen clusters: (a) seven pairs, and ((b)–(d)) thirteen trios adsorbed on one face of graphene. The component atom/pairs are drawn in black.

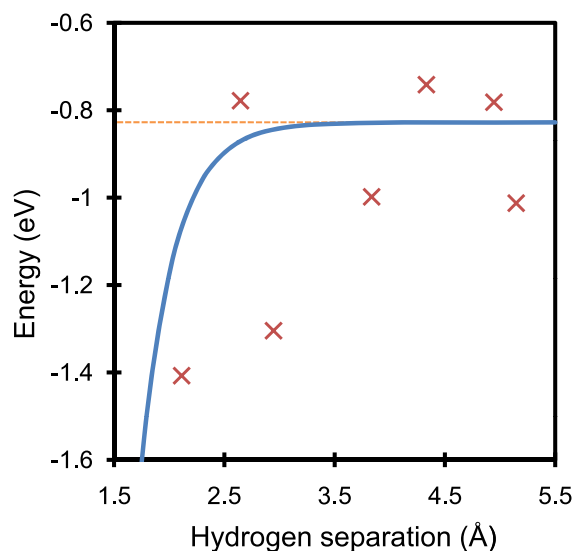


Figure 3. Adsorption energy per H atom of single face-adsorbed two H clusters ($E_{\text{ads}} = 1/2[E_{\text{gr}+2\text{H}(\text{ads})} - (E_{\text{gr}} + 2E_{\text{H}(\text{g})})]$), plotted against hydrogen atom separation. The reference dashed line ($E_a = 0.83$ eV) corresponds to the binding energy of an isolated hydrogen atom on graphene. The solid blue line shows the interaction of two H atoms in a vacuum, i.e. the formation/dissociation of H_2 far from the graphene surface, adjusted to the above-mentioned energy reference.

Understanding the stability of small groups of hydrogen adsorbed on graphene is fundamental in tracing succeeding steps to achieving levels of saturation. It is with this motivation that the stability of adsorbed two hydrogen [7] and three hydrogen [8] clusters on graphene were investigated. Geometries for these clusters, which span H–H separations approximately within the bounds of two graphitic hexagons, are shown in figure 2, and the corresponding adsorption energies for the adsorbed pairs and trios are shown in figures 3

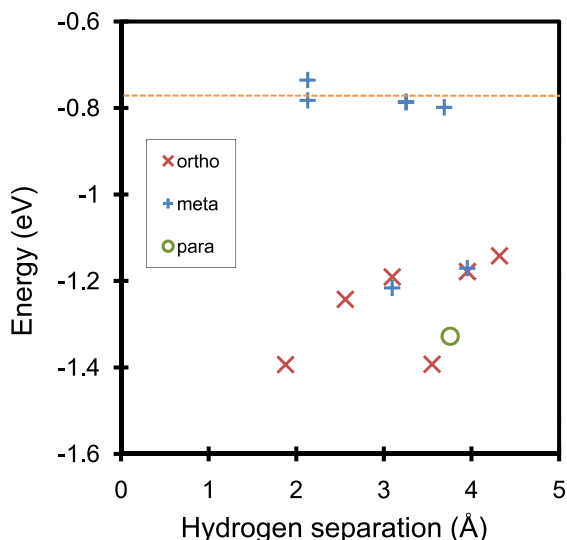


Figure 4. Adsorption energy of a three H cluster (per H atom, single face, $E_{\text{ads}} = 1/3[E_{\text{gr}+3\text{H}(\text{ads})} - (E_{\text{gr}} + 3E_{\text{H}(\text{g})})]$) plotted against hydrogen separation. The reference dashed line ($E_{\text{a}} = 0.78$ eV) corresponds to the binding energy of an isolated hydrogen adatom on graphene. Hydrogen separation in this case is defined as the distance of the third H atom from its component (ortho/meta/para) pair (figure 2)

and 4, respectively. Results shown here were obtained from unconstrained structure optimization calculations. Differences in the employed supercell size led to slight differences in isolated H atom adsorption energy.

The closest pairing, most commonly labeled in related literature as the ortho pair given that its hydrogen atoms are directly attached to adjacent carbon atoms, is found to be the most stable pairing, in contrast to findings at a higher coverage [5], and hence suggesting one specific coverage effect on pairing stability. The para pair however does not come too far behind in energy. The two most stable pairs are followed by that with the farthest atomic separation among pairings considered, and then by a not immediately foreseeable sequence of the rest of the pairings. Despite this apparent irregularity with regard to H–H separation, results noticeably favor hydrogen pair attachment to locations involving carbon atoms from different sublattices, i.e. the case in which the two adatoms are separately attached to an α and a β carbon atom. As seen in figure 3, the four most stable adsorbed pair configurations are more stable than the state comprised of two isolated H adatoms, while the remaining pairings are not. Bound pairs are all chemically stable with respect to free hydrogen atoms, but the results support the greater likelihood of odd-neighbored pairs being present on hydrogenated graphite surfaces. This is in exact agreement with recent findings involving different deuterium atom dosages [9, 10].

These results also suggest that the first adsorbed hydrogen can induce nearby neighbor reactivity: it is clearly shown here that the presence of adsorbed hydrogen on graphene has a significant effect on the adsorption of a second one, even to a relatively distant H–H separation of 5 Å. Energetics of multiple adsorbates on surfaces can in most cases be described by

direct coadsorbate interaction and electronic screening effects, but the case of pairs on graphene shows one of the clearest examples of substrate effects being much more important in determining the nature of clustering. In particular, we have associated the reported stability trends with the high stress due to bonds involving both sp^2 and sp^3 carbon atoms. Certain configurations for example leave the C atoms located in between receiving C atoms strained, leading to higher system energy.

Adsorbed groups of three hydrogen atoms are generally stable: only one case is found less stable than isolated adsorbed H atoms (figure 4). Comparing these with the pair adsorption [8], we see that most of the trios are unlikely to dissociate into a pair and an atom on the surface, especially when one considers the high barriers to H atom diffusion. These results further affirm the likelihood of clustering of hydrogen adatoms on graphene. Also, while we expect that the probability for meta pairs existing on graphene is low, it is shown here that a third H adatom attaching nearby in most cases stabilizes that pair.

Comparing the stabilities of trios with that of pairs, another trend is obvious. The most stable pairs, the ortho and para pairs, are components of the most stable trios in the set considered in this study. The least stable trios are entirely comprised of three least stable pairs discussed earlier on, and thus one may actually make good qualitative estimates on the stability of adsorbed groups of three based on the knowledge of pair and single atom adsorption. As a final note on this section, the threefold-symmetric configurations of three hydrogen atoms are shown to be the least stable, and so STM structures with threefold/sixfold symmetry are not likely originating from closely clustered trios. This fact is advantageous for more precise H adatom identification, which is discussed in more detail in the succeeding section.

3. Effects of adsorbed hydrogen on the electronic states of graphene

In this section we comment on the surface electronic states in the presence of adsorbed hydrogen, which are important in the identification of adsorbed hydrogen structures [11], as well as in providing fundamental knowledge on how graphene electronics can be tailored by hydrogenation. Panels (a)–(c) of figure 5 show two-dimensional cross sections of representative electronic states near the Fermi level for the systems involving an H atom, an ortho pair, and a meta pair adsorbed on graphene, respectively. Figure 5(a) indicates that the presence of adsorbed hydrogen atom should be very well observable from the strong disruption of the graphene surface electronic states: the presence of the H atom breaks the resonance of the original π -network at the Fermi level of clean graphene. An obvious manifestation of this effect is that every other p_z orbital on the C lattice is skipped by the wavefunction, i.e. the electronic state has maxima only in the graphene sublattice which does not include the receiving C atom, aside from the maximum at the location of the H atom itself. The corresponding simulated STM image for H atom adsorption is shown in figure 5(d), which

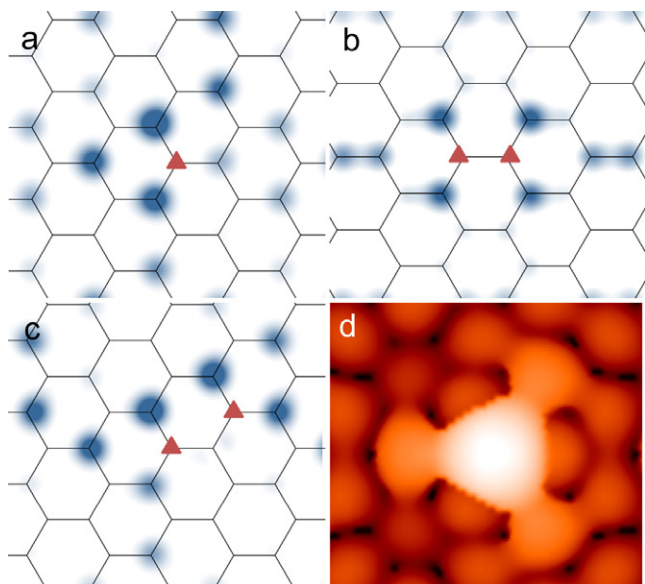


Figure 5. Cross sections of a representative electronic states near the Fermi level for the systems involving (a) atomic H on graphene, (b) the ortho pair on graphene, and (c) the meta pair on graphene. The maxima at the H atoms are not shown. Positions of H atoms are marked by the filled triangles.

can be compared with the high resolution image attributed to adsorbed D in [9]. The simulation reproduces the image from experiment satisfactorily in terms of its size and general shape and symmetry. Analogous results on bilayer graphene also affirm this [11]. While the H atom adsorption on graphene exhibits a distinct threefold symmetry, the pairs, by their very nature, have to break such symmetry completely. Another point that should be emphasized here is the fact that the two closest pairs show a marked difference in disrupting graphene electronics. The ortho pair has its hydrogen atoms separately attached to C atoms of both substrate sublattices, and hence the electronic states in the vicinity of the Fermi level reveal the complete hexagonal network. The meta pair on the other hand reproduces the ‘cloaked sublattice’ effect found in the atomic adsorption. These two pairs have been shown to differ significantly in terms of adsorption strength, and are shown here to differ as well on how they modify the graphene electronic states (and thus how they would look like under the STM).

The electronic effects of H adsorption also provide fundamental insights on clustering stability. More precisely, the location of the wavefunction maxima in panels (a)–(c) of figure 5 are not coincidentally the most preferred locations for the additional H atoms if one were to create a strongly adsorbed pair from an initially adsorbed H atom, or a strongly adsorbed trio from initially adsorbed ortho and meta H pairs. This is in agreement with a recent study which also tackled H pairing on graphene, attributing pairing stability from their magnetic properties [12].

4. Graphene two-face hydrogenation and saturation

While one-face hydrogenation of graphene is itself a fertile ground for academic discussion, the problem with one-face

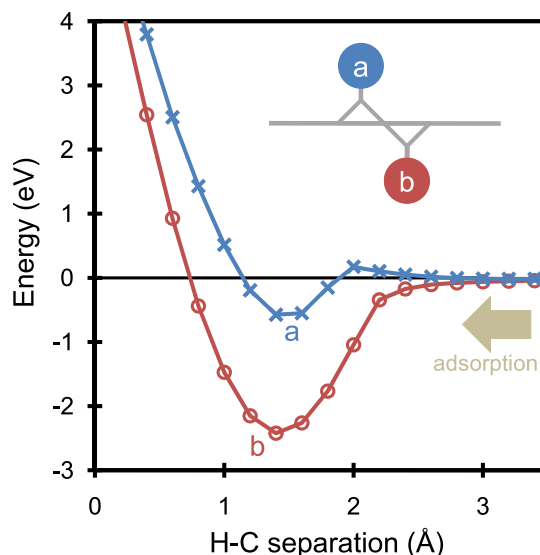


Figure 6. Calculated potential energy curves showing increased substrate reactivity brought about by adsorption of a first hydrogen: (a) single hydrogen atom adsorption on pristine graphene, (b) adsorption of the second hydrogen atom, towards a nearest neighbor carbon on the opposite face.

hydrogenation when considering practical applications is that a full monolayer hydrogen coverage is impossible to achieve, since there is no way for the carbon atoms to be in sp^3 configurations all at the same time. This is disadvantageous, for example, if one needs to maximize the hydrogen content on graphene. The situation however changes drastically when both faces of graphene can have access to hydrogen [13]. This is best illustrated with a pair of hydrogen atoms adsorbed closely, but on opposite faces of graphene, i.e. in a way forming the two-face analogue of the ortho pair discussed earlier.

Results for relevant adsorption pathways are shown in figure 6, which unambiguously show that atomic hydrogen adsorption on a graphene sheet with pre-adsorbed hydrogen on the opposite side (b) can proceed much more easily compared to that onto a plain graphene sheet (a), since the difficulty of overcoming the energy barrier to chemisorption on graphene is removed. The final state for this pair is also a very stable one, significantly lower in energy as compared with any of the same-face pairs we discussed earlier.

One implication of these results is that the chemisorption of a first hydrogen atom actually has the potential of setting off a series of subsequent adsorption reactions, which, upon saturation of the substrate, forms the final assembly shown in figure 7. An independent study with similar conclusions is given in [14]. Such a network of fully covered sheets, with its hydrogen-to-carbon ratio of unity, can hold hydrogen to a commercially practical storage capacity of 7.7 wt% [13]. This assembly has also been shown to be the more stable conformation of hydrogen-saturated graphene (graphane) [15].

We have observed an expansion of the graphene lattice parameter by a factor of about 3%, producing C–C bonds with lengths of 1.54 Å when fully hydrogenated. This is somewhat in agreement with recent experimental work characterizing graphane [16], as local regions with in-plane expansion have

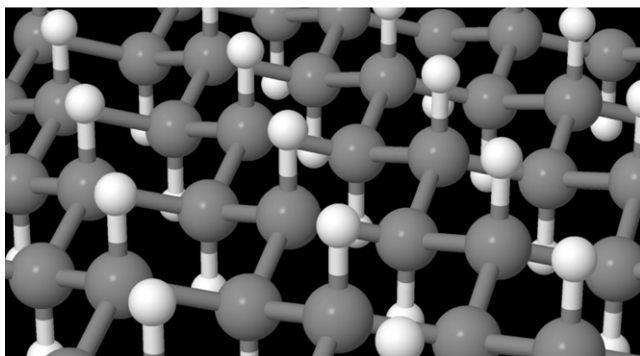


Figure 7. Stable form of fully hydrogenated graphene. Hydrogen atoms are shown in white.

been reported, albeit to a much greater extent. Finally, the hydrogen-saturated graphene is found to be more stable than graphene and hydrogen atoms (molecules) by 2.48 eV (0.24 eV), in terms of chemisorption energy per hydrogen atom.

5. Summary and concluding remarks

In this work, we firstly discussed the stability and likelihood of the presence of small hydrogen clusters on a face of graphene with a coverage $\Theta \approx 0.06$. The most stable adsorbed structures among groups of two and three H atoms were found to be the configurations in which the hydrogen atoms are immediately next to each other, i.e. in the closest possible clustering geometries. In both cases, the adsorption per H atom is stronger as compared with the adsorption of an isolated H atom on graphene, and so favorable cluster formation of H on the graphene surface is ascertained. Other stably adsorbed groups were explicitly pointed out. In all cases, the importance of reconstruction in reaching stable configurations was found. These results show that the H-graphene system is an excellent example of substrate effects being much more important, compared with direct adsorbate interaction, in determining the nature of grouping/ordering of adsorbed species on a surface. The trend of adjacent adsorption configurations having the strongest bound structures on graphene may still hold for the next larger clusters of bound hydrogen, but this trend is not expected to hold as bound hydrogen is increased infinitely unless both faces of a graphene sheet are hydrogenated.

A hydrogen atom on graphene was shown to be easily identified through its effects on graphene electronic states near the Fermi level. A comparison with effects brought about by pairs having H–H separations less than 2.7 Å show visible differences that make it possible to discriminate the atom from the pairs at a very local level. The adsorption of hydrogen was confirmed to break the strong C–C bonding network of graphene in a rather extended range—an event that affects the material’s reactivity to subsequent hydrogen, and hence promotes cluster formation. Calculations for the closest pairing

using both faces of graphene suggest not only more strongly adsorbed states, but barrierless entries for the subsequent adsorbing hydrogen. The ensuing fully hydrogenated material is stable, and has a structure greatly distinct from pristine graphene.

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