Graphene to graphane: a theoretical study

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Abstract
Graphene is a two-dimensional system consisting of a single layer of fully saturated (sp³ hybridization) carbon atoms. In an ideal graphene structure C–H bonds exhibit an alternating pattern (up and down with relation to the plane defined by the carbon atoms). In this work we have investigated, using ab initio and reactive molecular dynamics simulations, the role of H frustration (breaking the H atoms’ up and down alternating pattern) in graphane-like structures. Our results show that a significant percentage of uncorrelated H frustrated domains are formed in the early stages of the hydrogenation process leading to membrane shrinkage and extensive membrane corrugations. These results also suggest that large domains of perfect graphane-like structures are unlikely to be formed, as H frustrated domains are always present.

1. Introduction

Carbon-based materials have been intensely investigated in recent decades. However, in spite of the enormous amount of theoretical and experimental work, the discovery of new structures seems endless, colossal carbon tubes [1] and graphene [2] being recent examples. Graphene is one of the most important subject in materials science today [2–4]. It is a two-dimensional structure of sp² carbon atoms with very unusual and interesting electronic and mechanical properties.

It has been theoretically predicted that a related structure, called graphane [5], could exist in a stable form. Graphane consists of a single-layer structure with fully saturated (sp³ hybridization) carbon atoms with C–H bonds in an alternating pattern (up and down with relation to the plane defined by the carbon atoms). Its two most stable conformations are the so-called chair-like (H atoms alternating on both sides of the plane) and boat-like (H atoms alternating in pairs) [5] (figure 1). In this figure we present the graphene structure and also the two possible graphane configurations (boat and chair), which do not have the same symmetry and number of atoms in the unit cells. A third member of these two-dimensional planar carbon structures, called graphyne [6–8], has also been predicted to exist but up to now only molecular fragments have been synthesized [7].

Indirect experimental evidences of graphane-like structures have been reported [9, 10]. More recently, in a series of very elegant experiments, Elias et al [11] demonstrated the existence of graphane formation from graphene membranes through its hydrogenation. They also demonstrated that this process is reversible. These fundamental discoveries open new and important perspectives to the use of graphene-based devices since the electronic gap values in graphanes could be controlled by the degree of hydrogenation [11, 12].

The Elias et al experiments consisted in exposing graphene membranes to H⁺ from cold plasma. The H incorporation into the membranes results in altering the C sp² hybridizations to sp³ ones. The experiments were also done with the membranes over SiO₂ substrates (only one membrane side exposed to H⁺) and produced a material with different properties. Detailed studies of hydrogen atoms on graphene have been recently reported [13–20]. One interesting aspect of graphane-like structures is the possibility of magnetism created by hydrogenation incorporation [17, 21], which could be the basis of many new potential applications in organic spintronics.

In this work we have investigated using ab initio and classical molecular dynamics methods the structural and dynamics aspects of the hydrogenation mechanisms leading to graphane formation from graphene structures. Our results suggest that large domains of perfect graphane-like structures are unlikely to be formed due to the always-
Figure 1. Structural carbon membrane models considered in the DMol3 geometry optimization calculations. (a) Graphene, having two atoms per unit cell, (b) graphane boat-like, with four carbon atoms and four hydrogen atoms per unit cell and (c) graphane chair-like, with four (two C and two H) atoms per unit cell. The dashed lines indicate the corresponding unit cell. See text for discussions.

Present H frustrated domains, which significantly contribute to membrane shrinkage and extensive corrugations.

This paper is organized as follows: in section 2 we describe the methodology used. The results and discussions are presented in section 3, followed by the summary and our conclusions in section 4.

2. Methodology

We have used different methods to carry out our investigations. Initially, we performed ab initio quantum calculations in order to optimize the geometry of graphene-like structures. For comparison purposes, graphene structures were also calculated. Secondly, we used the classical reactive bond order approach in order to investigate the effects of hydrogenation on geometrical structures for a number of graphene membrane models. Finally, molecular dynamics (MD) simulations were used to address the dynamics of hydrogen incorporation into graphene membranes.

We have carried out ab initio total energy calculations in the framework of the density functional theory (DFT), as implemented in the DMol3 code [22]. Exchange and correlation terms were treated within the generalized gradient (GGA) functional by Perdew et al [23]. Core electrons were treated in a non-relativistic all-electron implementation of the potential. A double numerical quality basis set with polarization function (DNP) were considered, with a real-space cutoff of 3.7 Å. The tolerances of energy, gradient and displacement convergence were 0.000 27 eV, 0.054 eV Å⁻¹ and 0.005 Å, respectively.

We investigated fully and partially hydrogenated infinite (periodic boundary condition—PBC) graphene structures, which require the use of slab supercells. Sofo et al [5] in their graphane work considered compact (interacting layers) structures. Here, in order to mimic the experimental conditions [11], we have considered isolated (non-interacting) layers. For all cases considered here, the c axis was fixed at 20 Å (large enough to prevent interactions among different layers), and the remaining free parameters were fully optimized (figure 1). Internal atomic positions were free to vary in all the geometry minimization calculations. The total energy results as a function of the unit cell volumes were fitted following the well-known Murnaghan procedure [24]. We have also considered small finite structures (figure 2) with hydrogen passivated borders. For these molecular structures, we have carried out spin unrestricted calculations. In order to investigate larger structures, where ab initio quantum calculations become computationally prohibitive, we used the ReaxFF binding energy bond order (BEBO) method [25–27].

ReaxFF is similar to standard non-reactive force fields, like MM3 [28], where the system energy is divided into partial energy contributions associated with, amongst others,
valence angle bending and bond stretching, as well as non-bonded van der Waals and Coulomb interactions [25, 26]. However, one main difference is that ReaxFF can handle bond formation and dissociation (making/breaking bonds) as a function of bond order values. ReaxFF was parameterized against DFT calculations, the average deviation between the predicted ReaxFF heat of formation values and the experimental ones being 2.8 and 2.9 kcal mol$^{-1}$ for non-conjugated and conjugated systems, respectively [26]. ReaxFF is a reactive force field developed by van Duin, Goddard III and co-workers for use in MD simulations. This method allows the simulation of many types of chemical reactions. Similar to the procedures we adopted in DFT calculations we have considered both finite and infinite (PBC) structures. We have carried out geometry optimizations using gradient conjugated techniques (convergence condition, gradient values less than $10^{-3}$).

The dynamics of hydrogen incorporation on graphene layers was studied under different conditions of temperature (300, 500 and 650 K) and hydrogen atmospheres (number of H atoms up to twice the number of carbon ones). We considered H distributed over one and both sides of the graphene layers (infinite membranes with $11 \times 11$ unit cells). For each temperature different H velocity distributions were used. In order to speed up the hydrogen incorporation in the first 500 fs of the simulations, after each MD run of 10 fs, the hydrogen velocities were recalculated and the H atoms directed towards the graphene membrane. In order to verify whether our conclusions could be dependent on these accelerated dynamics protocols we run extensive tests. We observed that the overall conclusions were not affected by these protocols. Typical total MD runs were of 50 ps, timesteps of 0.5 fs and using a Berendsen thermostat [29]. These timescales are long enough to take into account hydrogen reorganization and defect elimination.

### Table 1. DMol$^3$ results for the crystalline structures shown in figure 1.

|                      | Graphene | G-chair | G-boat |
|----------------------|----------|---------|--------|
| Energy (Ha)          | −304.68  | −309.41 | −309.38 |
| Lattice parameters   |          |         |        |
| $a$ (Å)              | 2.465    | 2.540   | 4.346  |
| $b$ (Å)              | 2.465    | 2.540   | 2.509  |
| $\gamma$ (deg)       | 120      | 120     | 90     |
| C–C bond length (Å)  | 1.423    | 1.537   | 1.581  | 1.537 |

3. Results and discussions

We started carrying out DMol$^3$ calculations for the infinite (PBC) structures shown in figure 1. The results are displayed in table 1. In table 1 we present the important geometrical data for the different structures. The values of the bond lengths, lattice parameters and energy per atom are presented. The chair-like graphane (figure 1(c)) is more stable than the boat-like (figure 1(b)) by 0.03 Ha (≈0.82 eV). The G-boat presents two non-equivalent carbon–carbon distances due to the existence of two different C–H alignments. Although the C–C distances in graphane are much longer (8%) than the ones present in graphene, its cell parameter is just slightly larger (3%) than the latter due to out-of-plane topology. We have also considered the case of the minimum unit cell with H atoms parallelly aligned (just one side of the membrane). Our results show that this system is unstable, with the tendency of H$_2$ recombination and/or C–C breaking bonds. The results are in good agreement with previous work [5, 13, 14, 30] and with the available experimental data [2, 11].

One important aspect to be investigated is how different hydrogenation patterns affect the geometry of the graphene membranes. One practical way to do this is to measure some representative distances, as the ones indicated in figure 2 and the second-neighbor C–C distances (which would correspond to the lattice parameter in ideal crystalline structures). In figure 2 we present a scheme of the graphene fragments we have investigated. We considered fragments of different sizes. The letters indicated in the figure are used to measure critical distances that allow us to evaluate the level of shrinkage and corrugation of the hydrogenated graphene fragments.

If we consider that H atoms are randomly incorporated during plasma exposure [2], there is a significant probability for the existence of H frustration (figure 3), which is a configuration where the sequence of alternating up and down H atoms is broken (frustrated) (see movie01 available at stacks.iop.org/Nano/20/465704). In figure 3 we present the scheme of the formation of hydrogenated domains that leads to this frustration. This is similar to spin frustration in magnetic materials [31]. Two different H frustration configurations are possible (figure 4), one with parallel H atoms (Frust-1) and the other with missing H atoms (Frust-0).

In figure 3(a) we show a domain of up and down H atoms. It is expected that, after the first (up or down) H incorporation, the next favorable site is its first inverse neighbor (down or up), and so on. If the system is large enough uncorrelated domains might be formed (figure 3(b)). As the number of incorporated H atoms is increased it can occur that an alternating sequence of up and down H atoms is no longer possible (figure 3(c)).

We have investigated finite fragments with and without H frustrations. We analyzed the associated geometrical changes (figure 2) in order to determine whether the structures expand or contract in relation to an equivalent ideal graphene structure. We have carried out DMol$^3$ (table 2) and ReaxFF (for larger fragments) calculations (table 3 and figure 2). In these tables we present the values of the critical distances that allow us to have an estimate whether the hydrogen incorporation is producing an expansion or contraction of the graphene structures. As we can see from these tables, DMol$^3$ and ReaxFF show similar and consistent results. The H frustration increases out-of-plane distortions which induce in-plane geometrical shrinkage. This effect is amplified when first-neighbor H atoms are parallelly aligned (figure 4).

The representative distances indicated in (figure 2) (tables 2 and 3) provide a general view of the geometric
Table 2. Distances (in Å) between reference points for the molecular systems depicted in figure 2 calculated with DMol³. G-chair (39.6% H) and G-boat (37.5% H) are related to the structures in table 1. Frust-1 (22.9% H) and Frust-0 (20.8% H) refer to parallel (figure 4(a)) and missing (figure 3(b)) hydrogen atoms in frustrated domains, respectively. Values in parentheses refer to the standard deviation, calculated over all atoms and configurations. More detailed geometrical data are provided in the supplementary materials (available at stacks.iop.org/Nano/20/465704).

| System     | \(d_{A-B}\) | \(d_{B-C}\) | \(d_{C-D}\) | \(d_{D-A}\) | \(\bar{d}\) | \(\bar{a}\) |
|------------|--------------|--------------|--------------|--------------|-------------|-------------|
| Graphene   | 9.804        | 9.799        | 9.804        | 9.799        | 9.974       | 1.417(19)   |
| G-chair    | 9.852        | 9.841        | 9.882        | 9.847        | 10.050      | 1.470(61)   |
| G-boat     | 9.788        | 9.857        | 9.876        | 9.823        | 10.003      | 1.448(54)   |
| Frust-0    | 9.740        | 9.802        | 9.866        | 9.786        | 9.990       | 1.451(59)   |
| Frust-1    | 9.884        | 9.799        | 9.804        | 9.799        | 9.974       | 1.417(19)   |

Figure 3. Scheme of the formation of H frustrated domains. Closed circles refer to up hydrogen atoms and open circles refer to down ones, in relation to the plane defined by the carbon atoms. Carbon atoms are omitted for clarity. (a) Initial stage of the hydrogen incorporation. (b) Hydrogenation occurring at different regions. (c) H frustrated site, shown by an open cross. See text for discussions.

Figure 4. Examples of different possible frustration types. (a) Frust-1, H frustration with parallel first-neighbor H atoms; (b) Frust-0, H frustration with ‘missing’ first-neighbor H atoms. For clarity the H atoms outside this region were made transparent.

Figure 5. Distribution of the second-neighbor carbon–carbon distances of the finite fragments listed in table 2. Vertical lines indicate the lattice parameter values of ideal infinite graphene (dotted) and chair-like graphene (dashed), respectively.

changes produced by the different hydrogenation patterns. More local information can be obtained averaging the C–C second-neighbor distances (which would correspond to the lattice parameter for ideal structures). As can be seen from the tables and from figure 5 the H frustration systematically reduce these distances to smaller values in comparison to ideal graphane structures. For particular configurations these distances can be even smaller than the corresponding graphene values (see also supplementary materials available at stacks.iop.org/Nano/20/465704).

Finally, we investigated the dynamics of H incorporation using MD simulations. We have carried out MD calculations to investigate the formation of graphane-like structures through hydrogen reactions with the C carbons of the graphene layers. We have used infinite (using periodic boundary conditions) graphene structures. In figure 6...
we show representative snapshots from the early and final stages of a simulation at 500 K (see movie02 available at stacks.iop.org/Nano/20/465704). The results show that a significant percentage of uncorrelated H frustrated domains are formed in the early stages of the hydrogenation processes, leading to membrane shrinkage and extensive membrane corrugation. These results also suggest that large domains of perfect graphane-like structures are unlikely to be formed, as H frustrated domains are always present. The number of these domains seems to be sensitive to small variations of temperatures and H gas densities. We run annealing cycle simulations to analyze the stability of these domains once formed. Our results show that H frustrated domains are very stable, as high temperatures are needed to reverse (dehydrogenation processes) graphane-like structures to their original graphene configurations.

4. Summary and conclusions

We have performed geometry optimizations and molecular dynamics simulations using ab initio DMOl3 and classical reactive bond order ReaxFF, respectively, for the hydrogenation process of graphene leading to graphane-like structures. Graphane is a two-dimensional system consisting of a single planar layer of fully saturated (sp3 hybridization) carbon atoms with H atoms attached to them in an alternating pattern (up and down in relation to the plane defined by the carbon atoms).

Our results show that H frustration is very likely to occur. H frustration is a configuration where the sequence of up and down H atoms is no longer possible. The H frustration increases out-of-plane distortions (in relation to ideal graphane structures) which induces in-plane dimensional shrinkage. The net result is a decrease of the carbon–carbon
distances in relation to the ideal graphane values. This effect is amplified when first-neighbor H atoms are parallelly aligned. The results show that a significant percentage of uncorrelated H frustrated domains are easily formed in the early stages of the hydrogenation process leading to decreased lattice values and extensive membrane corrugation. These results also suggest that large domains of perfect graphane-like structures are unlikely to be formed, as H frustrated domains are always present. The molecular dynamics simulations of hydrogenation showed that, once formed, hydrogenated domains are very stable.

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