Chemical functionalization of graphene

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Abstract
Experimental and theoretical results on chemical functionalization of graphene are reviewed.
Using hydrogenated graphene as a model system, general principles of the chemical
functionalization are formulated and discussed. It is shown that, as a rule, 100% coverage of
graphene by complex functional groups (in contrast with hydrogen and fluorine) is unreachable.
A possible destruction of graphene nanoribbons by fluorine is considered. The functionalization
of infinite graphene and graphene nanoribbons by oxygen and by hydrofluoric acid is simulated
step by step.

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

1. Introduction

Chemical functionalization is one of the main methods to manipulate the physical and chemical properties of nanoobjects [1–10] and to study mechanisms of interaction of the nanoobjects with their environment (e.g. to investigate the stability of desired properties with respect to oxidation, hydrogenation, etc). Initially, graphene was used by theoreticians as a simple model to describe properties of nanotubes [11–17]. After the discovery of graphene [18] and of its extraordinary electronic properties [19–22] the chemical functionalization of graphene became a focus of especial interest in contemporary chemical physics. The main motivations of these studies are (i) modification of electronic properties via opening the energy gap in the electron spectrum of single and bilayer graphene [23–31, 139, 149]; (ii) potential use of graphene for hydrogen storage [23, 24, 32–35, 100]; (iii) decoration of various defects in graphene [11, 37–41]; (iv) a way to make graphene magnetic for potential use in spintronics [42, 43, 24, 44, 41, 45]; (v) a search for ways to produce 'cheap graphene' by chemical reduction of graphite oxide and manipulation of its electronic [46–48] and mechanical [49–51] properties; (vi) the functionalization of graphene edges in graphene nanoribbons [52–70] and their protection [41]; and (vii) oxidation and cracking of graphene [71] as tools to create graphene nanostructures of a given shape [72–74].

There are two main types of functionalization, namely a covalent one, with the covalent bond formation, and non-covalent, due to the van der Waals forces only. Most of the works deal with covalent functionalization, and only a few of them [26, 27, 76–80] treat the non-covalent one which is, of course, not surprising. First, the covalent functionalization results in much stronger modification of geometric and electronic structures of graphene. Second, most of the density functional codes used now do not allow one to include the effects of the van der Waals interactions [81–83] playing a crucial role in the non-covalent functionalization. In those cases the local density approximation (LDA) [84] is mostly used, instead of the standard generalized gradient approximation (GGA) [85] which gives usually rather good results for layer compounds, such as graphite, hexagonal boron nitride and MoS_2, due to error cancellation [86].

Sometimes, the chemical functionalization in graphene is related to the ionic chemical bond. There are the cases of graphene layers in graphite intercalated compounds [87, 88] and graphene layers at metal surfaces [89–99, 36, 101]. This type of functionalization is important to study possible superconductivity in graphene, by analogy with the superconducting intercalates CaC_6 and YbC_6 [102, 103].

Here we restrict ourselves only by the case of covalent functionalization of graphene. We will start with the hydrogenation of graphene, as a prototype of chemical functionalization (section 3). In section 4, other examples will be considered, including realistic models of the functionalization by diatomic molecules, such as O_2 and HF. In section 5 we will discuss effects of finite width on the functionalization of the graphene nanoribbons (GNR). We will give a summary of the work and discuss some perspectives in section 5.

2. Computational method

Our calculations have been performed with the SIESTA code [104–107] using the generalized gradient approximation (GGA) [85] to DFT and Troullier–Martins [108] pseudopotentials. We used an energy mesh cutoff of 400 Ryd and a k-point mesh in the Monkhorst–Pack scheme [109]. During the optimization, the electronic ground states were found self-consistently by using norm-conserving pseudopotentials to cores and a double-ζ plus polarization basis of localized orbitals for carbon, oxygen and fluorine, and a double-ζ one for hydrogen. Optimization of the bond lengths and total energies was performed with an accuracy of 0.04 eV $\text{\AA}^{-1}$ and 1 meV, respectively.

In our study of geometric distortions induced by the chemisorption of a single hydrogen atom which will be described below (section 3), a supercell containing 128 carbon atoms with a k-point $4 \times 4 \times 1$ mesh is used. For the cases of maximal coverage of graphene by various chemical species (section 4) the standard elementary cell of graphene with two carbon atoms is used, similar to the case of full hydrogenation [24], with a k-point $20 \times 20 \times 2$ mesh. To simulate interaction of bulk graphene with hydrofluoric acid the supercell with 8 carbon atoms is used, similar to our previous works [24, 46, 25] with a k-point $11 \times 11 \times 1$ mesh. To investigate chemical functionalization of graphene nanoribbons (section 5) zigzag stripes with widths of 22 and 66 carbon atoms are used, similar to [41], with a $1 \times 13 \times 1$ k-mesh.

For each step of the functionalization, its energy is defined as $E_{\text{chem}_n} = E_n - E_{n-1} - E_{\text{ads}}$, where E_n and E_{n-1} are the total energies of the system for nth and $n-1$th steps, and E_{ads} is the total energy of the adsorbed molecule. In contrast with the standard definition of chemisorption which we used in the previous works, this definition allows us to evaluate energy favor or disfavor of each step separately. We choose E_{ads} as a total energy of the corresponding molecule in the gaseous phase. This is the most natural choice to estimate the stability of chemically modified graphene. This is the crucial issue, for example, for the case of graphite oxide where the desorption of hydroxy groups is the main obstacle in deriving a 'cheap graphene' [46]. Note that molecular oxygen exists in both triplet (spin-polarized) and singlet (non-spin-polarized) states, the former being more energetically favorable by 0.98 eV (we have found for this energy difference the value 1.12 eV). We will use here, as well as in the previous work [46], the energy of singlet O_2; to obtain the data with respect to magnetic oxygen one needs merely to shift up the presented energies by 1.12 eV. When considering oxidation of nanotubes both the energy of singlet [110–113] and triplet [114, 112, 113] oxygen is used.

3. Hydrogen on graphene

Hydrogenation of carbon nanoobjects is a subject of special interest starting from the discovery of fullerenes [115], due to the potential relevance of this issue for the hydrogen storage problem and its general scientific importance for chemistry. Soon after the synthesis of the first fullerenes theoretical [116, 117] and experimental [118] works appeared
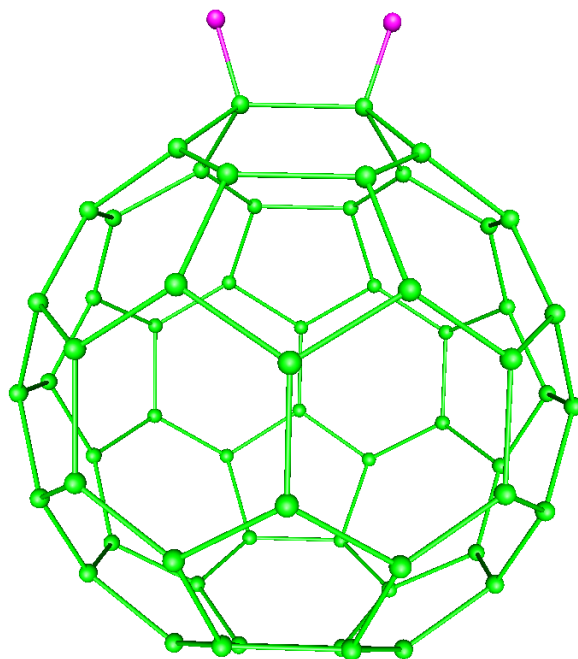

Figure 1. Optimized geometric structure of $C_{60}H_2$.

on the minimal hydrogenated fullerene, $C_{60}H_2$. It was shown in these works that the most stable configuration of hydrogen on the fullerene corresponds to the functionalization of the neighboring carbon atoms (1, 2, according to chemical terminology, see figure 1). Further investigations result in the discovery of numerous systems with larger contents of hydrogen, up to $C_{60}H_{36}$ [119]. Further hydrogenation of the fullerenes turns out to be impossible, due to their specific geometric structure. It is important that all known stable compounds $C_{60}H_x$ contain even numbers of hydrogen atoms. Together with other known facts [2, 3] it allowed us to formulate the main principle for the hydrogenation of the fullerenes: hydrogen atoms can be bonded either with the neighboring or with the opposite atoms in carbon hexagons (1, 2 or 1, 4, in chemical terminology). Another issue of special interest was magnetism of hydrogenated fullerenes caused by unpaired electrons on broken bonds. This can be realized only for odd numbers of hydrogen atoms per buckyball [120]. Unfortunately, these hydrogenated fullerenes are unstable and observed only as intermediate products of some chemical reactions; for even numbers of hydrogen atoms magnetism does not survive and disappears in time [121]. It is worth noting that the hydrogenated fullerenes themselves are quite stable chemically and do not lose hydrogen even under the action of high pressures [122].

The discovery of single-wall carbon nanotubes [123, 124] (in the following we will discuss only this kind of nanotube) and successful attempts at their reversible hydrogenation [125, 126], which makes the nanotubes more prospective materials for hydrogen storage than fullerenes, have inspired numerous theoretical models of nanotube hydrogenation. The geometric structure of the nanotubes differs essentially from that of the fullerenes. Single-wall carbon nanotubes can be

represented as a graphene scroll of length up to a few microns and width 1–1.5 nm.

Importantly, armchair and zigzag nanotubes exist with different structures of the honeycomb net on their surface, and the nanotubes can be chiral which is essential for their chemical functionalization [4]. To avoid these complications, graphene is frequently used to simulate chemical functionalization of the nanotubes [11–15]. However, as was discussed in [24], a curvature radius of typical nanotubes (1.0–1.5 nm) is comparable with the radius of geometric distortions induced by hydrogen. Effects of the curvature of nanotubes on hydrogenation was studied in detail recently [127] and appeared to be quite essential, the hydrogenation being different in two directions, along and around the nanotubes. The influence of different types of chirality on the chemistry of nanotubes and differences with graphene was also discussed in [128, 129].

Let us discuss briefly the main results of these works. Potential barriers for the cases of adsorption of a single hydrogen atom on graphene and several types of nanotubes, as well as formation of hydrogen chains on graphene and around the nanotubes, have been studied in [13]. Modification of the electronic structure of perfect graphene and graphene with the Stone–Wales defect at the adsorption of a single hydrogen atom was discussed in [11]. The authors [12] investigated a relation of magnetism with chemisorption of hydrogen for perfect graphene and for two types of defects, that is, monovacancy and interlayer carbon atoms in graphite. Sluiter and Kawazoe [14] used the cluster expansion algorithm to find the most stable configuration for complete coverage of graphene by hydrogen, to model the hydrogenation of nanotubes. This configuration corresponds to so-called graphane which has been studied afterwards by the DFT calculations [23, 24]. Wessely *et al* [15] simulated the core level spectra of carbon for the case of chemisorption of a single hydrogen atom on graphene, to interpret existing experimental data on hydrogenated nanotubes.

Graphene was also used to model the hydrogenation of graphite [130–133]. After the discovery of graphene several works have been carried out on the hydrogenation of graphene itself, to modify its physical properties. In [44] the chemisorption of a single hydrogen atom was studied in more detail than before, as well as interactions of magnetic moments arising, due to unpaired electrons, at the hydrogenation of carbon atoms belonging to the same sublattice (it was shown that in this case the interaction turns out to be ferromagnetic). At the same time, according to [44] the combination of three hydrogen atoms (two of them belonging to sublattice A and the third one to sublattice B) remains magnetic which may be important in the light of discussions of potential magnetism of carbon systems.

Sofo and co-workers [23] considered theoretically a hypothetic material, graphane, that is, graphite with completely hydrogenated carbon layers (in each layer, all hydrogen atoms coupled with one sublattice are situated above, and with another sublattice below, the layer). This structure corresponds to weakly coupled diamond-like layers, with sp^3 hybridization, instead of sp^2 in graphite. This change of hybridization results
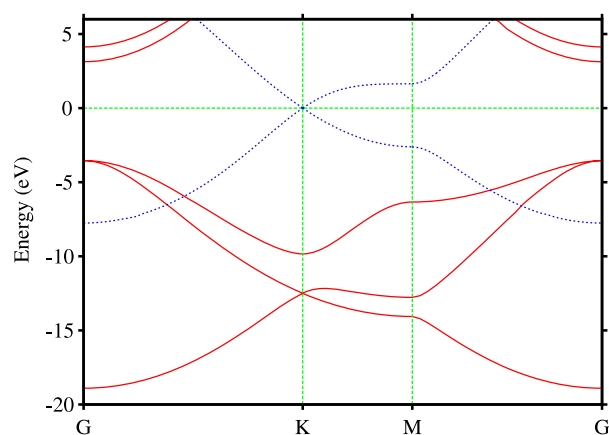

Figure 2. Band structure of a single graphene layer. Solid red lines are σ bands and dotted blue lines are π bands.

in opening a gap of order 3 eV in the electron energy spectrum, due to a transformation of π and π^* orbitals to σ and σ^* (see figure 2). The cohesive energy was found to be relatively small (of the order of 0.4 eV per hydrogen atom) which allows us to make the process of hydrogenation reversible [24]. Roman and co-workers [42, 43] considered different configurations of hydrogen on graphene for the case of one-side hydrogenation and have found that configurations when hydrogen atoms are bonded with different sublattices (similar to figure 3(c)) are the most stable. In our work [24] some general principles of hydrogenation of graphene have been formulated based on calculations for various configurations in a broad range of coverage.

Carbon atoms in graphene are in the sp^2 hybridization state when each carbon atom has three σ and one π orbitals (figure 2). In contrast to numerous polyaromatic hydrocarbons with localized single and double bonds π-orbitals in graphene are delocalized and all conjugated chemical bonds are equivalent. Chemisorption of hydrogen atoms means a break of one of the π bonds and transformation from sp^2 to sp^3 hybridization. At the same time, unpaired electrons, one of those forming the π-bond, remain at the neighboring carbon atoms. This electron is smeared in one of the sublattices (figures 4(b) and (a)) and forms a magnetic moment. The distribution of spin density in a radius of 1 nm correlates with distortions of the crystal lattice (figure 4(b)). However, this situation is not robust in a sense that the chemisorption of the next hydrogen atom bonds this unpaired electron and kills the magnetic moment [24].

Thus, the first principle of chemical functionalization is the absence of unpaired electrons or, in other words, of dangling bands. As a consequence of this principle, chemisorption of functional groups on different sublattices are much more energetically favorable than on the same sublattice.

The next principle is a minimization of geometric frustrations. One can see in figure 4(b) that the chemisorption of a single hydrogen atom results in essential atomic displacements inside a circle of radius 5 Å (two periods of the graphene crystal lattice) and in smaller but still noticeable distortions with a characteristic radius 10 Å (figure 5). The
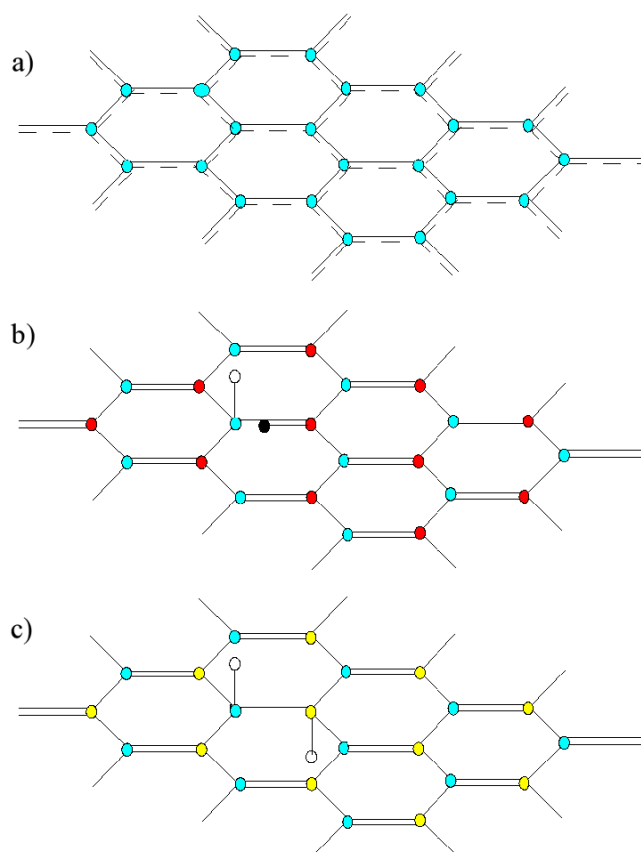
Figure 3. A schematic representation of chemical bonds in (a) pure graphene (dashed lines correspond to delocalized double bands), (b) graphene with single chemisorbed hydrogen atom (white circle, the black circle corresponds to unpaired electron at the broken bond, it distributes in the sublattice shown in red (dark)), (c) graphene with chemisorbed pair of hydrogen atoms (nonequivalent sublattices are shown in different colors).

Figure 4. Charge distribution for unpaired electron as a function of the distance from the central carbon atom where hydrogen is chemisorbed (a) and deviations of carbon atoms from flat configuration for the cases of single hydrogen atoms (red (dark) line) and two atoms chemisorbed on neighboring sites from different sides of the graphene sheet (green (light) line) (b).

chemisorption of a single hydrogen atom leads to a strong shift up of the carbon atom bonded with the hydrogen and a shift down for two neighboring atoms. It is worth noticing that if one fixes positions of all carbon atoms except nearest and next-nearest neighbors of the central atom [136] it changes essentially the picture of atomic displacements. Such a procedure may be reasonable to simulate chemical functionalization for constrained systems such as graphene on graphite [150], Ru [95, 96, 98], Ir [97] and Pt [98] where part of the graphene lattice is strongly coupled with the substrate.

Chemisorption of the next hydrogen atom is more favorable when it results in minimal additional distortions. This means that the most energetically stable configuration arises if two hydrogen atoms are chemisorbed by neighboring carbon atoms at different sides with respect to the graphene sheet. One can see in figure 4(b) that in this case no essential additional atomic shifts are necessary. If only one side is available for the chemisorption the most favorable configuration of two hydrogen atoms is the bonding with carbon atoms in opposite corners of the hexagon in the honeycomb lattice (sites 1, 4, or para-position, according to chemical terminology) [25]. For the case of two more distant hydrogen atoms they should migrate to this optimal position
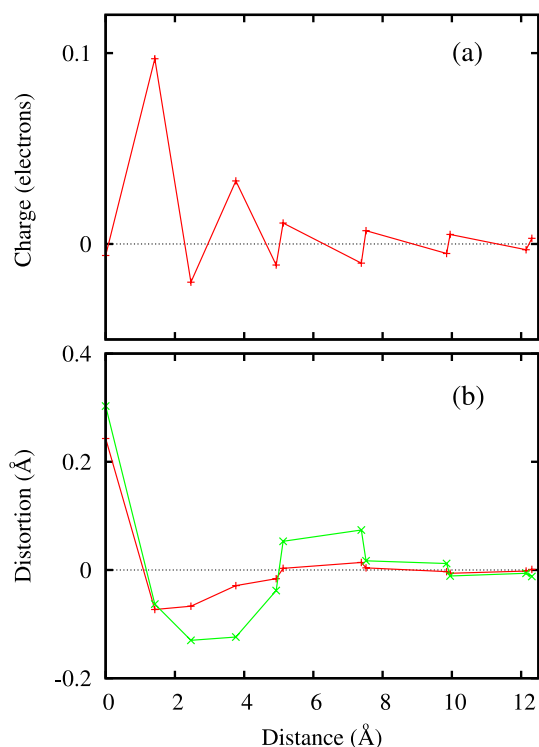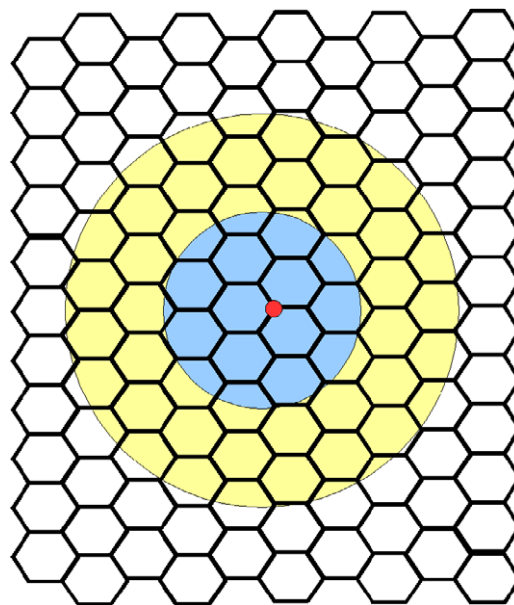

Figure 5. Regions of strong (blue circle) and weak (yellow (light) circle) distortions of graphene lattice at the chemisorption of a single hydrogen atom (small red (dark) circle).

overcoming some potential barriers [135], which was observed experimentally for both graphite [130] and graphene [134].

These two principles of chemical functionalization predict that in the most stable configuration for a hydrogen pair on

Table 1. Dependence of the carbon–carbon bond length (d), in Å, and the electron energy gap (ΔE), in eV, on chemical species for the case of 100% two-side coverage of graphene.

Chemical species	d	ΔE
NO	1.622	None
NH_2	1.711	2.76
CN	1.661	2.11
CCH	1.722	0.83
CH_3	1.789	0.84
OH	1.620	1.25
H	1.526	3.82
F	1.559	4.17
H and F	1.538	5.29
H and Cl	1.544	4.62

graphene the hydrogen atoms will sit on neighboring carbon atoms at opposite sides with respect to the graphene sheet. Due to geometric distortions a region of radius 5 Å around the pair is more chemically active than pure graphene, similar to the case of graphene with defects [12, 37, 40, 39, 41] and, thus, the next hydrogen atoms will be chemisorbed near the pair. In the case of graphene with defects this process involves some potential barriers whereas for ideal infinite graphene it will proceed without any obstacles, up to complete hydrogenation and formation of graphane.

In further works [35, 136] the results [24] on the stability of nonmagnetic pairs of hydrogen on graphene and on the formation energies have been confirmed; also the case of polyaromatic hydrocarbons $C_{54}H_{18}$ [35] and $C_{42}H_{16}$ [136] and $C_{96}H_{24}$ [137] being considered. A recent paper [138] dealing with adsorption and desorption of biphenyl on graphene demonstrates the importance of step-by-step simulation of the chemical reaction.

It is instructive to compare peculiarities of the chemical functionalization of graphene and carbon nanotubes. Similar to graphene, in nanotubes the most favorable place for chemisorption of the second hydrogen atom belongs to the opposite sublattice with respect to the first one [127]. There is no direct experimental evidence of this structure for the case of hydrogen: however, for other functional groups it is known that normally they are attached to pairs of neighboring carbon atoms [4, 9, 10]. Minimization of geometric frustrations plays an important role also in the case of nanotubes. In contrast with flat graphene, a particular shape of the nanotubes makes the chemisorption from the external side more favorable, with the adsorbed pairs situated along the nanotube. For large enough groups they are usually attached to opposite sides of the nanotube cross section [4], again, to minimize the carbon net distortions. In contrast with graphene where complete *one-side* hydrogenation is unfavorable for the case of nanotubes it turns out to be possible from the external side, as is shown both theoretically [13] and experimentally [125, 126].

4. Functionalization of graphene by other chemical species

As discussed above, graphane is not very stable which is actually quite good from the point of view of hydrogen storage
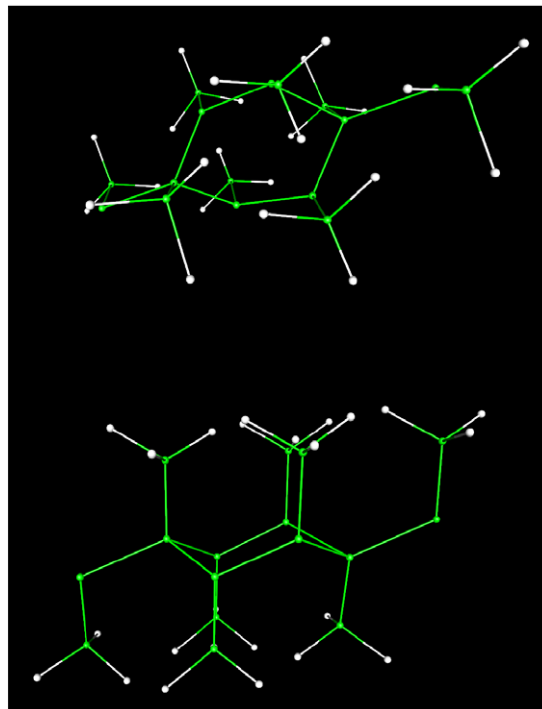

Figure 6. Top and side view of graphene functionalized by CH_3 groups (optimized atomic positions). Carbon and hydrogen atoms are shown in green (darker) and white, respectively.

since it allows us to hydrogenate and dehydrogenate graphene at realistic temperatures [29]. At the same time, for potential use of graphane in electronics this can be considered as a shortcoming. Therefore it is interesting to consider other functional groups to search for a compound with an electronic structure similar to graphane but with larger cohesive energy.

The computational results are presented in table 1 and figure 6. Based on them one can divide all the functional groups into two classes: (a) with the energy gap of order 3 eV and large enough cohesive energy and (b) with much weaker bonding and much smaller energy gap, or without a gap at all. This difference can be related with the length of chemical bonds between carbon atoms (carbon–carbon distance). For substances from the first class it is almost equal to that in diamond, 1.54 Å, whereas for substances from the second class it is larger. This means that for the latter case, due to mutual repulsion of the functional groups, graphene is destabilized which diminishes the cohesive energy. This situation is observed experimentally in graphite oxide which cannot be completely functionalized due to interaction between hydroxy groups [46], in agreement with the XPS data [140].

As examples of chemical species which can provide, similar to hydrogen, a complete coverage of graphene, we will consider F_2, HF and HCl. Fluorine seems to be very promising for the functionalization of graphene since it should produce a very homogeneous structure, with a complete coverage by atoms of the same kind. Therefore, this might be a way to create a two-dimensional crystal with a rather large energy gap but high electron mobility, due to a small degree of disorder. However, fluorine is very toxic and very aggressive, which
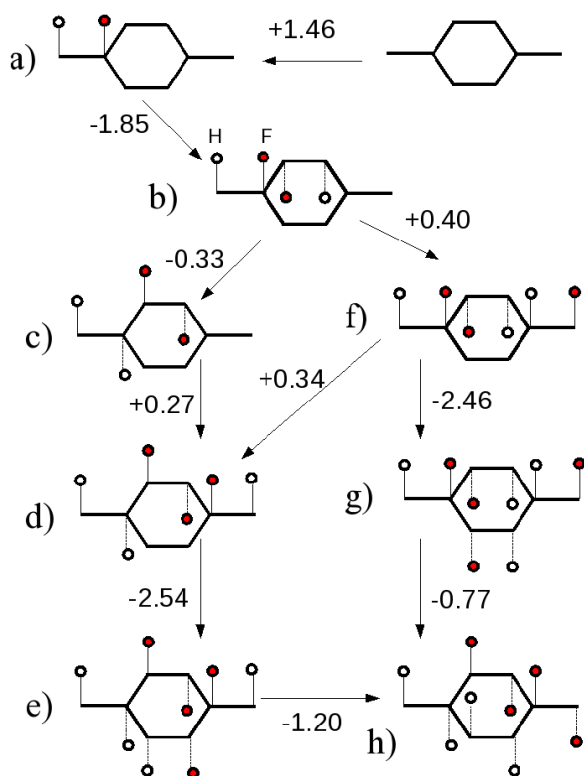
Figure 7. A sketch illustrating processes and energetics of different reactions of graphene with hydrofluoric acid. White and red (dark) circles are hydrogen and fluorine atoms, respectively; all energies are in eV.

Figure 8. Optimized geometric structure for step-by-step adsorption of oxygen molecule on graphene.

may be a problem for industrial use. Also, fluorine is used for ripping of nanotubes [141, 142] which means that, potentially, edges and defects of the graphene lattice interacting with the fluorine can be centers of its destruction. Actually, graphene samples are always rippled [143–148] or can be deformed as observed for graphene ribbons [74].

Let us consider now, step by step, the interaction of graphene with the inorganic acids HF and HCl. The process of functionalization of graphene by HF starts with the chemisorption of fluorine and hydrogen atoms at neighboring carbon sites at the same side of the graphene sheet (figure 7).

As a first step of chemisorption of hydrofluoric acid molecules we consider bonding of hydrogen and fluorine atoms with the neighboring carbon atoms at the same side of the graphene sheet (figure 7(a)). In contrast with molecular fluorine where the chemisorption energy is negative (see above) the energy of this step turns out to be positive, +1.46 eV, mainly due to strong distortions of the initially flat graphene at the one-side functionalization. As the next step, we consider chemisorption of one more H–F pair from another side of graphene (figure 7(b)). Similar to chemisorption of the second hydrogen atom (see above) this step is energetically favorable, with the formation energy −1.85 eV. Reconstruction of the structure shown in figure 7(c) diminishes the total energy by 0.33 eV, which makes this a possible third step of the process under consideration. After that, the chemisorption energy of a third HF molecule turns out to be much smaller than for the first one but still positive, +0.27 eV (figure 7(d)). Starting from the fourth molecule,
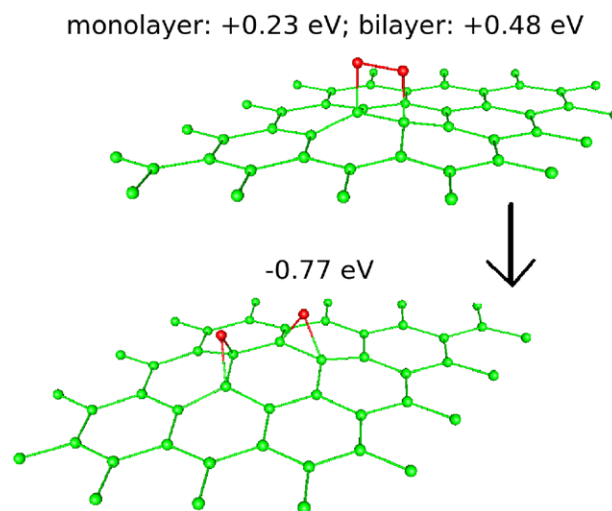
the chemisorption energies are negative so further reaction is exothermal. As a result, complete coverage of graphene by hydrofluoric acid is energetically favorable but requires high enough energy for the first step. This means that, most probably, bulk graphene without defects will be stable enough with respect to reaction with HF, at least at room temperature. It seems to be practically important since hydrofluoric acid is used to solvate an SiO_2 substrate when preparing freely hanging graphene membranes [150, 151]. One can expect in this case a formation of a chemically modified layer near edges with essentially different electronic structures (see below).

Our calculations show that the first step of the functionalization of graphene by hydrochloric acid is essentially different, due to a larger interatomic distance (1.27 Å for the HCl pair, instead of 0.97 Å for HF) which is close to the carbon–carbon distance in graphene (1.42 Å). As a result, there is no breaking of bonds between hydrogen and chlorine but, instead, the HCl molecule hangs over the graphene layer, bonding with it by only a weak van der Waals bond and there is no chemical reaction. Thus, hydrochloric acid can be safely used to clean bulk graphene.Regions near edges or defects in graphene can in principle be functionalized by HCl, similar to the case of hydrogen considered in [41].

Let us consider now, using an oxygen molecule as an example, a chemisorption of a diatomic molecule with a *double* chemical bond. In this case, at the first step the double bond will transform into the single one, with formation of single bonds with neighboring carbon atoms (figure 8). This reaction requires overcoming some energy barrier which is, however, rather low since the flexibility of graphene allows it to minimize the energy costs due to lattice distortions. Bilayer graphene is much less flexible (out-of-plane distortions of the graphene layer are 0.53 Å and 0.11 Å for the cases of single layer and bilayer, respectively), due to interlayer coupling, which makes the chemisorption energy higher, in agreement with the experimental data [154].

If we would calculate the chemisorption energy with respect to not the singlet but the triplet state of O_2 molecules

it would increase all chemisorption energies by 1.12 eV (see section 2). The resulting energies are so high that it seems in contradiction with the experimental fact that graphene is relatively easily oxidized already at temperatures up to 200 °C [154]. Also, the 'unzipping' process at the oxidation of graphite observed experimentally [71, 152] will involve energetically unstable states. Graphene oxide turns out also to be unstable with respect to triplet oxygen [46, 155]. Probably these discrepancies mean that formation of singlet oxygen plays some role in these processes. This issue requires further investigation. A similar problem was discussed earlier for nanotubes [110].

Oxidation energy for graphene turns out to be lower than for the case of nanotubes [110, 111]. In the latter case, π-orbitals are rotated with respect to each other [7] which makes formation of oxygen bridges between carbon atoms more difficult.

Previous computational results for oxidation of graphene [153] are qualitatively similar to ours. However, the energy of cyclo-addition there is higher than achieved in our calculations. There are two possible reasons for this difference: the use of LDA in [153] instead of GGA in our calculation (overestimation of covalent bonding energy for hydrogen on graphene within LDA is discussed in [24]) and the use of very narrow armchair graphene nanoribbons (three hexagon width) instead of an infinite system with periodic conditions here.

Let us consider now another important issue, the simulation of the reduction of graphite oxide (GO). We have proposed earlier [46] models of this compound with different degrees of reduction. In [155] a process of the reduction has been studied and the scheme of the corresponding reactions has been proposed. Using our model and this scheme, we have simulated three possible ways for the chemical reduction of GO depending on degree of preliminary reduction and calculated the corresponding energies (figure 9). To compare, we have calculated also energy costs of direct reduction (e.g. by heating). One can see from the figure that for high degrees of coverage of GO (weakly reduced) energy costs of chemical reactions are smaller than those of the direct reduction whereas for the case of strongly reduced GO, and vice versa, direct total reduction turns out to be more energetically favorable. Similarly, other reactions of real [49, 47] and potential functionalization of GO can be simulated which may be important in searching for ways for its complete reduction to pure graphene.

5. Functionalization of graphene nanoribbons

Polyaromatic hydrocarbons (PAH) [173] are quite close to graphene nanoribbons (GNR), and their chemistry, in particular, hydrogenation of their edges, is rather well studied [160]. Other nanoobjects which can be considered as predecessors of GNR are nanographite and nanographite intercalates which were studied, in particular, in connection with their magnetism [156, 157]. Model calculations of their magnetic properties are presented in [156, 157] whereas first-principles calculations, using a fragment of graphene sheet as a model of nanographite, have been performed in [159]. In
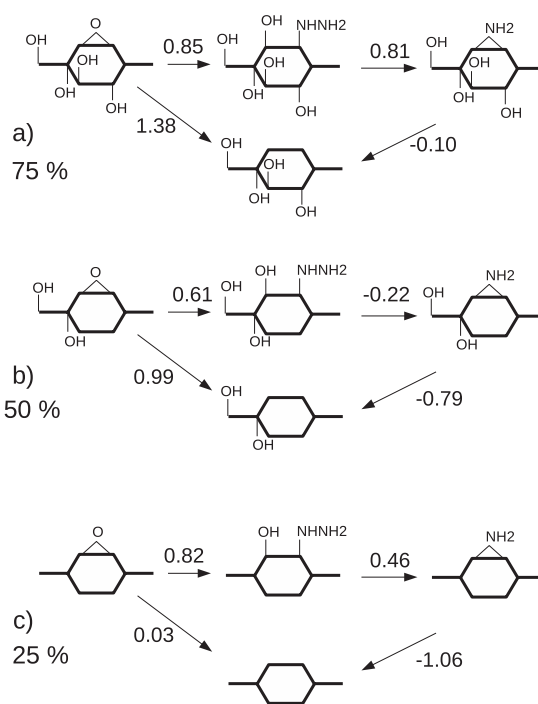

Figure 9. Sketch of chemical reduction of graphene oxide [155] for various degrees of its functionalization. All energies are in eV.

that paper, functionalization of the graphene edges by a single hydrogen atom has been considered, as well as suppression of magnetism by fluorination, in relation with the experimental data [158].

Starting from the first work by Louie and co-workers [52] predicting, on the basis of DFT calculations, a half-metallic ferromagnetic state of zigzag graphene edges, this problem attracts serious attention [54, 64]. Later, the first results have been reconsidered by the same group using a more accurate many-body GW method [55]. Chemical functionalization of GNR is currently one of the most popular subjects in graphene science.

Hod *et al* have considered the effects of the shape of semiconducting GNR on their stability and electronic structure [57], electronic structure of graphenic nanodots [58] (similar calculations of magnetism and electronic structure have been presented also in [62]), effects of geometry of graphene nanosheets on their electronic structure [59] and enhancement of half-metallicity due to partial oxidation of the zigzag edges [60]. Interesting effects which can arise in graphene nanoflakes are discussed in [53]. Usually, it is supposed in these calculations that edges of nanoflakes are passivated by hydrogen atoms [58, 59, 53, 161–164] but sometimes pure edges are considered [165, 166]. The real structure of some graphene nanoflakes was discussed in [167]. In general, the state of real graphene edges is not well understood yet and this very important problem needs further investigation.

In [61] the effect of vacancies at the edges of the electronic structure of GNR were studied. Influence of chemisorption of different chemical species on the electronic structure of GNR

was investigated in [56, 63]. Reference [65] considered the chemisorption of molecular oxygen on GNR and its effect on their magnetism. Various configurations of hydrogenated [69] and self-passivated [70] GNR were studied; in both cases the nonmagnetic state of GNR turned out to be the most stable. References [41, 68] demonstrated suppression of magnetism at the zigzag edges by oxidation. Since the latter is a natural process in the production of GNR [74, 75, 168] some special measures to protect the magnetism chemically are probably necessary.

Thus, works on the functionalization of GNR can be divided into three groups. First, there are investigations of electronic structure and physical properties (especially magnetism) of the edges themselves. This group includes most of the theoretical works. Second, there are works studying the functionalization of the nanoribbons between the edges. It seems that the effect of the edges on the electronic structure of GNR is long range enough and, as a consequence, the chemistry of GNR can be essentially different from that of bulk graphene. Research in this direction is just starting. Third, there are attempts to find optimal geometric and chemical structures of GNR taking into account realistic technological processes of their formation. As a preliminary, there is an impression that some structures considered theoretically before can be very different from the real ones, so we are, indeed, only at the beginning of the way. On the other hand, a lot of experimental and theoretical information is available for related compounds such as arynes [169], polyhexacarbons [170] and polycyclic aromatic hydrocarbons [171] which may also be relevant for GNR.

It was shown in our previous work [41], using hydrogen as an example, that the edges of GNR are centers of chemical activity and their functionalization can be just a first step to the functionalization of the whole nanoribbon. Here we will consider step by step the oxidation process of GNR. The computational results are presented in figure 10. Thus, oxidation of GNR is a chain of exothermal processes. This result may be relevant also for a better understanding of burning and combustion of carbon systems. These issues, as well as more detailed results concerning oxidation and unzipping [71] of graphene and related compounds, will be discussed elsewhere.

Let us consider now a reaction of GNR with hydrofluoric acid. A scheme of this reaction for a nanoribbon of width 2.2 nm is shown in figure 11(a) and dependence of the energy as a function of coverage is presented in figure 11(b). In contrast with the case of ideal infinite graphene for narrow enough GNR are *two* steps with positive chemisorption energy. This energy cost is so small that the process of hydrofluorination of this nanoribbon can take place even at room temperature. The situation is essentially different for a nanoribbon of width 6.6 nm. The steps with positive chemisorption energy just disappear, due to the larger distance between the regions of the reaction. Thus, the hydrofluorination of a broad enough GNR is easy and complete.

One can see that, similar to the case of hydrogenation [41] (see also section 4), GNR are very chemically active which
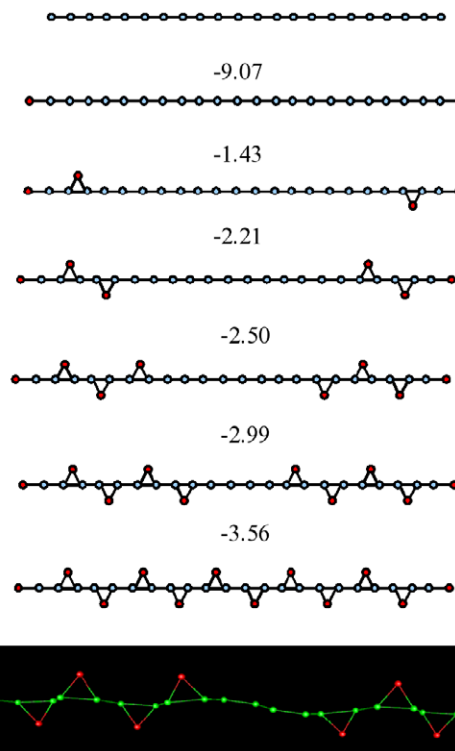

Figure 10. A scheme of step-by-step oxidation of GNR of width 2.2 nm. All energies are in eV (top panel). Optimized geometric structure for partially oxidized GNR (lower panel).

probably means that at least some of their applications will require an inert atmosphere.

6. Conclusions and perspectives

In section 3 we discussed, using hydrogenation as an example, three main principles of chemical functionalization of graphene: (i) broken bonds are very unfavorable energetically and, therefore, magnetic states on graphene are usually very unstable; (ii) graphene is very flexible, and atomic distortions influence strongly the chemisorption process; and (iii) the most stable configurations correspond to 100% coverage for two-side functionalization [24] and 25% coverage for one-side functionalization [25]. Based on these principles one can model the functionalization of not only perfect graphene [24, 25, 46] but also graphene with intrinsic and extrinsic defects which are centers of chemical activity [41].

In section 4 we have studied chemical functionalization of graphene by fluorine and hydrofluoric acids. They can provide complete coverage and, thus, a semiconducting state with large enough electron energy gap and weak disorder. Alternatively, non-covalent functionalization can be used to create the gap.

The current situation seems to be a bit controversial. In some papers [27, 26] an energy gap opening due to physisorption of various molecules has been found, in contrast with other results [76, 77, 16, 78, 17]. It is difficult to compare these works directly since they are, in general, done for different chemical species and concentrations. However, keeping in mind that in some cases [77, 78, 26] the same case
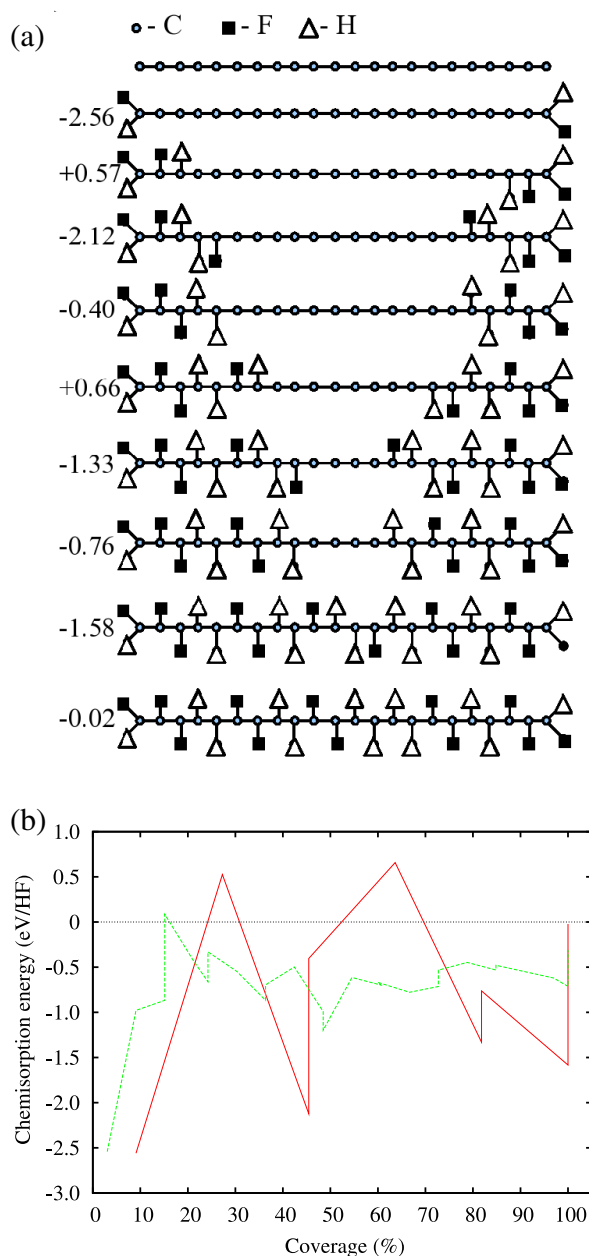
Figure 11. A scheme of step-by-step reaction of GNR of width 2.2 nm with HF; the energies are in eV (a). The same energies as functions of coverage for the case of GNR with width of 2.2 nm (red solid line) and 6.6 nm (green dashed line).

We have demonstrated using HF as an example that it is important to simulate the chemisorption process step by step since it allows us to estimate accurately chemisorption energies relevant for each step of the process. It turns out that for perfect infinite graphene the energy cost of the first step for the case of HF is rather high whereas for HCl this reaction is practically impossible. This means that these acids can be safely used for cleaning of graphene samples. At the same time, the energy cost of oxidation is rather low, which makes even moderate annealing of graphene in oxygen-contained atmosphere not a very safe procedure.

We have shown also, in the last section, that the graphene nanoribbons are chemically active enough to be oxidized and to interact with hydrofluoric acid with relatively low chemisorption energy of the first step of reaction. It means that to prepare the graphene nanoribbons with a given chemical composition alternative ways should be used, e.g. its synthesis from polyaromatic hydrocarbons [173, 174, 167] or even use of microorganisms as is used already for biogenic growth [175, 176] and cleaning [177].

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of water has been studied one can conclude that the electronic structure is very sensitive to the specific concentration and specific geometric configuration of water on the graphene surface. At the same time, one should keep in mind that a very specific structure of water [172] and other hydrogen-bonded substances may not be very accurately reproduced in the DFT calculations. Probably, only a combination of the DFT, quantum chemical calculations and molecular dynamics can clarify the situation.

Anyway, since the cohesive energy at physisorption does not exceed 20 kJ mol^{-1} the physisorbed graphene cannot be very robust, which may result in some restrictions of its use in electronics.

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