Non-hexagonal-ring defects and structures induced by healing and strain in graphene and functionalized graphene

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Abstract

We perform ab initio calculations for the strain-induced formation of non-hexagonal-ring defects in graphene, graphane (hydrogen-functionalized graphene) and graphenol (hydroxyl-functionalized graphene). We find that the simplest of such topological defects, the Stone–Wales defect, acts as a seed for strain-induced dissociation and multiplication of topological defects. Through the application of inhomogeneous deformations to graphene, graphane and graphenol with varying initial concentrations of pentagonal and heptagonal rings and small-sized voids, we obtain several novel stable structures that possess, at the same time, large concentrations of non-hexagonal rings (from fourfold to elevenfold) and small formation energies.

(Some figures may appear in colour only in the online journal)

1. Introduction

The intense interest in the physics of graphene over the last few years derives in large part from the exceptional electronic properties of the pristine material [1–4]. While pristine samples obtained by exfoliation of graphite have allowed exploration of a rich variety of phenomena connected with the Dirac-fermion nature of the electronic excitations in graphene, current large-scale synthesis protocols have reached the point where polycrystalline or highly inhomogeneous samples are being produced [5–9]. In very recent experiments, graphene layers resulting from reduction of graphene oxide (GO) show conductivities that are one or two orders of magnitude smaller than those of pristine graphene [10–16], possibly due to residual dopants and intrinsic defects. Better conductivities can be obtained in exfoliated graphene by electron-beam irradiation [6] and by irradiation under extreme temperatures [7]. The occurrence of areas with a high density of extended topological defects (ETDs) observed in the samples of [5] was attributed to the process of oxidation and further reduction of the GO, since such large defective areas do not appear in mechanically exfoliated graphene from the same graphite source. Moreover, in these samples residual functional groups were found to concentrate primarily on regions with ETDs, surrounded by pristine (non-functionalized) graphene areas.

Defective graphene systems have also been produced in the process of healing of sub-nanometer and nanometer-sized holes, produced by etching under an electron beam, as a result of interaction with metal impurities. Such healing processes lead, in many instances, to the formation of clusters of non-hexagonal defects in the sample, as observed with scanning TEM [8].

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Given this current interest in defective graphene systems, in the present work we employ ab initio density functional theory (DFT) calculations to study the morphological evolution of the following graphene structures: (i) homogeneously strained graphene sheets containing Stone–Wales (SW) defects [18]; (ii) pristine and functionalized graphene sheets containing initial distributions of isolated topological defects (TDs) [19], after introduction of sub-nanometer holes and highly inhomogeneous bond deformations. Our calculations address the morphological evolution of graphenes with a large initial concentrations of TDs, such as present over large areas in the above mentioned experiments [5–8, 17].

We find that stress relaxation of a graphene sheet containing large initial concentrations of SW defects may lead to the formation of ETDs, with morphological units that are very similar to those observed in the aforementioned experiments [5–7, 9]. We uncover the role of the SW defect as a stress-accumulation site which induces the bond rotation events that generate the ETDs. Furthermore, we find that healing of sub-nanometer-sized holes coupled with the relaxation of inhomogeneously strained regions also leads to the formation of ETDs, revealing a rich variety of morphological patterns and plastic deformation mechanisms in pure and functionalized graphene structures. Our results indicate that the marked tendency of graphene to form TD clusters under stress is aided by functional groups, since the formation energies of such defective structures are considerable smaller in graphane (a graphene sheet fully functionalized with hydrogen atoms) and in graphenol (a graphene sheet fully functionalized with hydroxyl groups) than in graphene, in agreement with the experimental evidence in [5].

2. Methodology

Our calculations are performed using Kohn–Sham density functional theory (KS-DFT) [20], the generalized-gradient approximation [21] for the exchange–correlation functional and norm-conserving Troullier–Martins pseudopotentials [22], to describe the electron–ion interactions. We use the LCAO method implemented in the SIESTA code [23], with a double-zeta pseudo-atomic basis set augmented with polarization orbitals, with an energy cutoff of 0.01 Ryd.

Full structural optimization of atomic positions and supercell vectors is performed. For the relaxed structures the total force on each atom is less than 0.02 eV Å⁻¹ and the pressure on the supercell is less than 1 kbar. The supercells employed are periodic in the graphene plane, being surrounded by a 30 Å vacuum region in the transverse direction, with negligible interactions between each layer and its periodic images.

For the majority of the results presented below, a non-spin-polarized KS-DFT approach is employed. In order to ensure that the bond dissociation and bond reconstruction processes involved in the formation of the TD clusters we consider are well described within this approximation, we have also performed spin-polarized calculations for a selected set of structures. All of our results for the resulting ETD morphologies and respective formation energies remain the same when a spin-polarized approach is employed. Below, we comment on the specific cases where spin-polarized calculations were performed. We can safely conclude that the non-spin-polarized wave functions provide an accurate description of the formation of TD clusters in our study.

3. Results and discussion

3.1. Homogeneous shear deformations of graphene containing Stone–Wales defects

3.1.1. First-principles results. We consider initially a scenario where homogeneous shear deformations are imposed upon a graphene sheet containing SW defects. SW defects are commonly found in graphene and nanotubes, and can be generated by irradiating the material with an 80 keV electronic beam, just below the knock-on threshold for sp² bonded carbon materials [6, 24, 25]. The impinging electrons give out the energy needed for the 90° rotation of a carbon–carbon (C–C) bond (as indicated in figures 1(a) and (b)) that transforms four hexagons of the pristine graphene matrix into a SW defect. Since a SW is an incipient dislocation dipole in graphene (each pentagon–heptagon pair is one of two dislocations with opposite Burgers vectors comprising the SW defect [26]), at first sight one expects shear deformations either to undo the C–C bond rotation, and thus lead to self-annihilation of the two pentagon–heptagon pairs, or to lead to dissociation of the dislocation pair into its individual components.

In order to investigate this, we consider the two graphene supercells, each containing a SW defect, shown in figures 1(a) and (b). They differ by the orientation of the SW defect

![Figure 1. Morphological transformation of a graphene sheet under strain. (a), (b) Two images of graphene supercells containing a Stone–Wales defect. The bond rotation that generates the defect is indicated. The two cases differ by the orientation of the defect with respect to the x and y axes of the cell. (c) Transformation of the supercell in (a) with relaxation of internal atomic coordinates, under homogeneous shear strain. (d) Fully relaxed stress-free state of the structure in (c), after relaxation of cell vectors.](image-url)
with respect to the $x$ and $y$ axes of the cell (indicated in the figure). We find that the critical shear for morphological transformation depends on the orientation of the imposed shear with respect to the SW defect. In our calculation for the supercell in figure 1(a), the transformation occurs when the imposed shear strain reaches 30%, while no plastic deformation occurs for an applied shear strain of 30% on the supercell shown in figure 1(b). The morphological transformation of the configuration in figure 1(a) leads to the formation of the ETD shown in figures 1(c) and (d), containing clusters of fivefold and eightfold rings. We should point out that previous works have found pristine graphene to sustain deformations of up to 25% without yielding [27–29], a result that we also find in our calculations, for graphene with SW defects. The morphological pattern observed in figure 1(c) is obtained by allowing the system to fully relax all the internal atomic coordinates, while maintaining the imposed homogeneous strain. No further changes in morphology are observed when full relaxation of both atomic coordinates and strain (i.e. the supercell vectors) is allowed, as shown in figure 1(d).

These results highlight a fundamental aspect of the plastic response of a graphene sheet to imposed stresses or strains: a tendency for the formation of ETDs as a stress-relaxation mechanism, spawned by bond rotation events, in the above example with the formation of clusters of fivefold and eightfold rings. We note also that the transformation depends on the orientation of the shear deformation with respect to the preexisting SW defect, which acts as stress-accumulation seed for the topological transformation.

Note that the concentration of SW defects in the supercells shown in figures 1(a) and (b) is large, and comparable to the concentrations of TD observed in the aforementioned experiments [5, 17, 6–8]. We cannot claim that ETDs of exactly the same morphology as that we obtain in the above numerical experiment should result from shear in the limit of much smaller initial concentrations of SW defects. We do, however, expect the mechanism of strain–energy concentration on the SW to hold, on the basis of the fact that formation of incipient dislocation dipoles is one of the fundamental processes of plastic deformation in materials.

3.1.2. Analysis of elastic energy using a Keating model.

The latter point can be illustrated by following the evolution of the elastic energy of the cell during the deformation, as shown in figure 2. In the figure, we show a map of the elastic energy of the supercell at three different stages of the plastic relaxation process, computed using a Keating model [30]. Figure 2(a) shows the elastic energy for the initial strained geometry. Note that, in this configuration, the strain energy is distributed nearly uniformly over the whole system, with a larger magnitude at the SW defect. This pattern is preserved up to the point where a morphological transformation takes place. Figure 2(b) shows the strain energy right after the transformation: the important feature here is that a change in the distribution of the elastic energy takes place, from nearly uniform before the transformation to a pattern where the energy is concentrated on the ensuing

![Figure 2. Keating-energy analysis of stress relaxation by extended topological defect formation.](image1)

ETD, and where the bulk portion of the cell relaxes to a configuration of much smaller elastic strain. Relaxation of internal atomic coordinates, after the transformation, leads to further reduction of the strain in the cell. Finally, in figure 2(c) the imposed homogeneous strain is lifted and the system relaxes to a stress-free state, where the elastic energy in the bulk portions of the cell nearly vanishes, and most of the residual strain is located on the defect.

3.2. Deformations of graphene containing small holes and topological defects

We consider now more complex deformations of a graphene sheet, including small-sized holes generated by irradiation or by partially ripping a graphene sheet, coupled with strongly inhomogeneous bond deformations. These can be considered a model for severely strained and ripped graphene samples, such as those obtained by reduction of GO [5], by irradiation under extreme temperatures [7], or by etching under an electron beam [8]. In the following, we show that self-healing of such small graphene voids, combined with relaxation of the inhomogeneous deformations, also leads to the formation of ETDs, in some cases with morphologies similar to those that have been observed in recent experiments [5–8, 17].

![Figure 2. Keating-energy analysis of stress relaxation by extended topological defect formation.](image2)
3.2.1. Inhomogeneous deformations of graphene containing Stone–Wales defects. We start with the supercell shown in figure 1(b). By imposing a homogeneous shear strain, coupled with lines of strained C–C bonds (elongated by 27% to ~1.8 Å) as indicated by dashed segments in figures 3(a) and (c), and allowing for full relaxation of both internal coordinates and homogeneous strain, the system reaches a stress-free state where the dislocation dipole is dissociated into two individual dislocations separated by a lattice constant, as shown in figure 3(b). When the strained bonds combine with a homogeneous shear oriented with respect to the SW defect as shown in figure 3(c), the SW defect induces the nucleation of an ETD consisting of two side-sharing octagons connected to two pairs of pentagons, each on one of two opposite sides of the octagon pair, shown in figure 3(d). This ETD is similar in extent to those resulting from the 555–777 and 585 reconstructions of a divacancy in graphene [6].

3.2.2. Inhomogeneous deformations of topological defect networks in graphene. In order to further investigate the morphologies of deformed graphene, and to access the role of functionalization and preexisting topological defects, we choose as starting configurations the three TD graphene networks [19] shown on the left in figure 4, which were labeled $S_{12}$, $S_{31}$, and $S_{22}$ in [19]. We also consider the graphane [31–33] (hydrogen-functionalized) and graphenol (hydroxyl-functionalized) versions of these structures, both at full coverage, with graphenol taken as a simple model for GO [34]. A variety of deformation patterns, including small holes, as well as compressed and/or elongated bonds were initially imposed on these structures, and each system was allowed to relax (with optimization of both atomic coordinates and supercell vectors) onto a stress-free metastable local minimum of the total-energy surface.

Figure 3. Combination of homogeneous and inhomogeneous deformations of a graphene sheet: (a) and (c) show two images of homogeneously sheared supercells with a Stone–Wales defect and inhomogeneous deformations generating lines of strained bonds. (b) Relaxation of the deformations in (a) leads to dislocation–dipole (Stone–Wales defect) dissociation. (d) Relaxation of the deformations in (c) leads to formation of an extended topological defect.

Figure 4. Lowest-energy extended topological defects obtained from regeneration of holes and response to inhomogeneous deformations. The left column shows the parent geometry. The middle column shows imposed deformation. The right column shows the resulting stress-free metastable ETD after full relaxation of internal atomic coordinates and cell vectors. (a) Pristine (without functionalization) showing clusters of five to seven pairs as well as an 8558 unit. (b) Hydrogen-functionalized and (c) hydroxyl-functionalized graphene show a morphological pattern where a tetragon is surrounded by four heptagons, with pentagons connected to its perimeter.

Figure 4 shows starting configurations before and after introduction of holes and inhomogeneous compressions, and the resulting relaxed ETD configuration. In our calculations, these are, respectively, the lowest-energy ETD for each of the following three cases: (a) pristine graphene, (b) graphane and (c) graphenol. The two functionalized cases in figures 4(b) and (c) show the formation of a morphological pattern in the shape of a flower, where a square ring is surrounded by four heptagons, with pentagons connected at the perimeter. In the case of pristine graphene, the lowest-energy ETD we obtained in our calculations contains pentagon–heptagon clusters connected to pentagon–octagon units of the same morphology as the one that has been recently observed as the periodic unit of a domain boundary in a graphene layer deposited on a nickel substrate [35–37].

Further morphologies are obtained by considering the various deformation patterns described above. While the formation of the ETDs observed experimentally is largely dictated by kinetics, the thermodynamic stability of such structures can be analyzed by computing their formation energies, $E_f$. In the following, we describe a total of 12 ETD configurations with $E_f \leq 0.30$ eV/atom. To put these formation energies into perspective, we quote the formation energy per atom of a fullerene molecule, 0.40 eV/atom with respect to a graphene sheet, and the energy of the pentaheptite, a theoretical allotrope of graphene composed entirely of pentagons and heptagons, 0.24 eV/atom [38, 19], both computed with the same methodology as the ETD energies in this work.

3.2.3. Formation energy and energetics. In the present study, the formation energies per atom of the structures without
deformed versions of the S
common morphological pattern emerging from small-hole
formation of pentagon–heptagons clusters is clearly the most
unreconstructed (UNREC).
the RGO samples in [5]. These are indicated in table 1 as
is consistent with the presence of holes in the final state of
cases, regeneration of holes did not take place, a feature that
22
and S
are defined as
as the reference, such that the formation energies per CH unit
systems with hydrogen functionalization, we take graphane
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total energy per atom of an
systems with hydrogen functionalization, we take graphane
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energy per atom in graphene, and define
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energy per atom in graphene, and define
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energy per atom in graphene, and define
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for the energy per COH unit, where again we keep
µ
for the energy per atom of an N-atom bulk graphene cell. For
with and without functionalization. In some
cases, regeneration of holes did not take place, a feature that
is consistent with the presence of holes in the final state of
the RGO samples in [5]. These are indicated in table 1 as
unreconstructed (UNREC).
Figure 5(a) shows the six structures derived from
deformed versions of the S_{12} structure (shown in the center).
(b) Low-energy extended topological defects derived from
deformed versions of the S_{31} structure (shown in the center on
the top row). Color coding for topological defects, ranging from
tetragons to hendecagons, is indicated.

Table 1. Formation energy \( E_f \), in eV per formula unit, of extended
topological defects in graphene. All structures without
functionalization are metallic, with the exception of the S_{31}. Except
for the SE geometry, all functionalized structures are
semiconductors or insulators. For these, the electronic band gaps \( E_g \)
in (eV) are included in the last two columns.

| Structure | +H | +OH | +H | +OH |
|-----------|----|-----|----|-----|
| Graphene  | 0.00 | 0.00 | 0.00 | 4.70 | 2.48 |
| S_{12}    | 0.40 | 0.27 | —   | 4.83 | —   |
| S_{22}    | 0.26 | 0.16 | —   | 4.67 | —   |
| S_{31}    | 0.36 | 0.29 | 0.36 | 5.15 | 0.51 |
| SA        | 0.27 | 0.22 | UNREC | 4.97 | —   |
| SB        | 0.26 | 0.18 | 0.25 | 5.05 | 2.98 |
| SC        | 0.37 | 0.21 | 0.20 | 5.20 | 3.04 |
| SD        | 0.32 | 0.26 | 0.35 | 5.14 | 2.94 |
| SE        | 0.43 | 0.30 | 0.29 | —   | —   |
| SF        | 0.28 | 0.27 | UNREC | 5.29 | —   |
| SG        | 0.59 | 0.32 | 0.22 | 0.82 | 1.44 |
| SH        | —   | 0.24 | 0.47 | 1.05 | 2.59 |
| SJ        | —   | 0.34 | 0.28 | 2.71 | 0.43 |
| SK        | 0.33 | 0.26 | 0.27 | 1.80 | 0.84 |
| SL        | 0.24 | —   | —   | —   | —   |

where \( E_{ETD} \) is the \textit{ab initio} total energy of the N-atom
supercell containing the ETD and \( \mu_C = E_{\text{graphene}}/N \) is the
total energy per atom of an N-atom bulk graphene cell. For

\begin{equation}
E_f = \frac{E_{ETD}}{N} - (\mu_C + \mu_H);
\end{equation}

where we keep \( \mu_C \) as the energy per atom in graphene, and
define \( \mu_H = \mu_{CH} - \mu_C \), where \( \mu_{CH} = E_{\text{graphene}}/N \) is the total
energy per CH molecule for a bulk graphene calculation. For
the hydroxyl-functionalized cases, we have

\begin{equation}
E_f = \frac{E_{ETD+OH}}{N} - (\mu_C + \mu_{OH}),
\end{equation}

for the energy per COH unit, where again we keep \( \mu_C \) as the
energy per atom in graphene, and define \( \mu_{OH} = \mu_{COH} - \mu_C \),
where \( \mu_{COH} = E_{\text{graphenol}}/N \) is the total energy per COH
radical in a bulk graphenol calculation.

Table 1 shows the formation energies of the 12 ETDs,
along with the energies of the parent geometries, S_{12}, S_{31},
and S_{22}, both with and without functionalization. In some
cases, regeneration of holes did not take place, a feature that
is consistent with the presence of holes in the final state of
the RGO samples in [5]. These are indicated in table 1 as
unreconstructed (UNREC).

Figure 5(a) shows the six structures derived from
deformed versions of the S_{12} geometry [19]. From the figure,
formation of pentagon–heptagons clusters is clearly the most
common morphological pattern emerging from small-hole
regeneration and relaxation of deformed graphene sheets,
as found in recent experiments, but other morphologies are also
manifest. We observe polygons ranging from tetragons to
hendecagons, with color coding indicated in the figure. The
ETD in structure SA, with a nonagon connected to pentagons,
is very similar to that present in the model of amorphous
graphene recently proposed as a high-specific-area material
for supercapacitor applications [39]. The five structures
resulting from deformations of the S_{31} geometry are shown in
figure 5(b). Linear polyacetylene-like chains are observed
in the SG and SJ hydrogenated clusters, in structures with a
strong sp^{3}-hybridization content, which are stabilized by the
functional groups. Such polymer-like carbon chains were also
obtained in molecular dynamics models of RGO. Removal
of functionalization in the SI geometry leads to the recovery
of a threefold connected network of pentagon–heptagon
clusters, in the form of a climbed dislocation dipole of the
type observed in irradiated graphene samples [24]. Another
striking geometry is SI, which shows the presence of tetragons
connected to decagons, with a reasonably low formation
energy of 0.3 eV/atom when functionalized with hydrogens.
Note the presence of a network of large pores, which would
make defective graphene sheets with such morphologies
candidates for applications such as supercapacitors [39] and selective permeable membranes [40, 41].

The $E_f$ values in table 1 were computed with a non-spin-polarized GGA functional in the KS-DFT approach. As a check, we computed the entire process of ETD formation, starting from the same initial configuration, using a spin-polarized GGA functional for the SA, SA + H, SB, SB + H, SC, and SC + H geometries. All of the resulting geometries and formation energies remain the same, which indicates that spin polarization is not relevant for the relaxation processes in our study.

3.2.4. Role of functionalization in energetics. Regarding the role of functionalization, we observe in table 1 that the formation energy decreases with functionalization in all cases, with the exception of the hydroxyl-functionalized S$_{31}$, SD and SI, which have slightly higher values of $E_f$ than their pristine counterparts. For the hydrogen-functionalized ETDs, an average reduction of 95 meV/formula unit (fu) is observed in table 1, while for the hydroxyl-functionalized ETDs, we obtain an average reduction of 125 meV/fu. In both cases rather sizable maximum reductions of $E_f$ of 0.27 and 0.37 eV/fu occur, respectively, for the H- and OH-functionalized SG morphologies, where functionalization leads to stabilization of polymer-like carbon chains.

3.2.5. Rippling and corrugation. Formation of ripples or corrugation associated with out-of-plane deformations are possible relaxation mechanisms in two-dimensional crystals. In the present study, no constraints preventing such out-of-plane distortions were imposed. Among the non-functionalized structures we consider, only the SK and the SL geometries underwent ripple formation from the starting planar geometries (constrained to wavelengths commensurate with the corresponding supercells), with maximum out-of-plane distortions of 0.43 Å and 1.00 Å, respectively. The non-functionalized SB geometry shows a rugged structure with maximum out-of-plane distortions of 0.2 Å. The remaining non-functionalized geometries are metastable in the planar form.

In the functionalized structures, incorporation of an sp$^3$ component in the electronic bonding leads naturally to corrugation in all cases in our study, and to electronic band gaps, as discussed below. As examples, figures 6(a) and (b) show a view of the ripples in the non-functionalized SL geometry and the rugged landscape of the H-functionalized SB geometry, respectively.

3.3. Electronic structure

Functionalization also changes the electronic structure: while all pristine ETDs are metallic, with the exception of the S$_{31}$ parent geometry, the functionalized ETDs are all semiconductors or insulators, with the exception of the SE. This change in the electronic structure is connected with the incorporation of an sp$^3$ component in the electronic bonding of these graphene materials, associated with the binding of the functional groups to the graphene sheet.

Among the reference systems, graphene is a null-gap semiconductor, while graphane and graphenol are insulators with gaps of 4.70 eV and 2.48 eV, respectively. In table 1 we include the values of the electronic band gap for all non-metallic structures. The S$_{31}$ semiconductor structure, with a gap of 0.61 eV, remains a semiconductor with a smaller gap of 0.51 eV when fully functionalized with hydroxyl groups, but its 100% H-functionalized form is an insulator with a gap of 5.15 eV.

Looking in detail at the exceptional case of the SE geometry, which shows a finite density of states (DOS) at the Fermi level (FL) in the graphene, graphane and graphenol configurations, we observe the presence of a dangling bond (in the absence of functionalization) in each octagonal carbon ring. This leads to a broad structure in the DOS in the region of the Fermi level in the pristine case, as shown in the upper panel in figure 7. While the DOS in the FL remains finite after functionalization with both hydrogen (middle panel in figure 7) and hydroxyl (lower panel in figure 7), the dispersion of the DOS peak at the FL is reduced in both cases.

4. Conclusion

In conclusion, ab initio calculations indicate that stress relaxation of a graphene sheet containing TDs may lead to the formation of ETDs showing morphological units that have been observed in recent experiments. We uncover the role of TDs as stress-accumulation sites which induce the bond rotation events that generate the ETDs. Furthermore, we find that healing of sub-nanometer-sized holes coupled with the relaxation of inhomogeneously strained regions also lead to the formation of ETDs, revealing a rich variety of morphological patterns and plastic deformation mechanisms in pure and functionalized graphene structures. Our results indicate that the tendency of deformed graphene sheets to form ETDs is enhanced in the presence of functional groups, with a systematic reduction of the formation energies of such defective structures in graphane and in graphenol,
when compared to graphene, in agreement with the available experimental evidence.

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