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Enhancement of chemical activity in corrugated graphene

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Abstract

Simulation of chemical activity of corrugated graphene within density functional theory predicts an enhancement of its chemical activity if the ratio of height of the corrugation (ripple) to its radius is larger than 0.07. Further growth of the curvature of the ripples results in appearance of midgap states which leads to an additional strong increase of chemisorption energy. These results open a way for tunable functionalization of graphene, namely, depending of curvature of the ripples one can provide both homogeneous (for small curvatures) and spot-like (for large curvatures) functionalization.

1 Introduction

Graphene is considered as a prospective material for the electronics "beyond silicon"¹. Modern electronics is essentially two-dimensional, we use mainly just the surface of semiconductors and the bulk is, roughly speaking, a ballast limiting the perspectives of further miniaturization of electronic devices. It is not surprising therefore that the discovery of the one-atom-thick material with high electron mobility² has initiated a huge interest in this new field. At the same time, specific massless chiral character of charge carriers in graphene³ leading to the "Klein tunneling"⁴ is not favorable for some, potentially, the most interesting, applications such as transistors based on p-n junctions. Thus, creation of another two-dimensional materials based on graphene which would be conventional semiconductors is an important problem. Chemical functionalization of graphene is one of the most efficient ways to manipulate its physical properties⁵. Two-side complete hydrogenation of graphene reversibly transforming it into graphane has been predicted theoretically^{6,7} and realized experimentally⁸. Graphane is a broad-gap semiconductor, with the gap value more than 5 eV⁹. For the case of complete functionalization, replacement of hydrogen by other functional groups does not change the electronic structure essentially⁵. To tune the value of the energy gap, one should focus on the one-side functionalization; the metal-insulator transition for the case of one-side hydrogenation has been demonstrated experimentally for graphene on substrate⁸. The value of the energy gap is changed also at the reduction of graphene oxide as was predicted theoretically¹⁰ and confirmed experimentally¹¹. However, in both these cases strongly disordered semiconductors arise whereas to preserve high enough electron mobility one has to realize some regular structures of the adsorbates. For the case of hydrogenation, the disorder is related, the most probably, with ripples on graphene¹² which can bind hydrogen⁸. At the same time, it is possible to create artificially regular ripple structures with a given shape¹³. Ripples themselves can change drastically electronic structure of graphene resulting, e.g., in an appearance of midgap states¹⁴. Here we study the effect of the ripples on chemical activity of graphene, using hydrogenation as an example, which will allow us to formulate specific recommendations how to produce graphene with a desirable type of functionalization manipulating by inhomogeneities of the substrate.

2 Computational method

Our calculations have been carried out with the SIESTA code¹⁵ using the generalized gradient approximation (GGA)¹⁶ to DFT and Troullier-Martins¹⁷ pseudopotentials. We used energy mesh cutoff of 400 Ry, and $10 \times 10 \times 4$ k -point mesh in Monkhorst-Park scheme¹⁸. Graphene with ripples is not strictly two-dimensional system. Chemisorption of chemical species leads to additional deviation from the planar geometry. Therefore we have chosen several k -points (namely, 4) also in z direction. During the optimization, the electronic ground states was found self-consistently by using norm-conserving pseudopotentials to cores and a double- ζ plus polarization basis of localized orbitals for carbon and metals. Optimization of the bond lengths and total energies was performed with an accuracy 0.04 eV /Å and 1 meV, respectively. This technical parameters of the computations are the same as in our previous works^{5,7,10}. The supercell in our computations contains 128 carbon atoms.

To simulate the hydrogenation of rippled graphene the following procedure is used. First, we create some artificial ripple with a given height and radius, by a smooth out-of-plane distortion of a group of carbon atoms

at the centre of the supercell. As a trial geometric shape of the ripples a semisphere has been chosen (Fig. 1a), which is isotropic, in a qualitative agreement with the results of Monte Carlo simulations¹⁹ and experimental observations¹². The initial height (h) of the ripples varied from 0.01 to 0.3 nm, and the radius (R) from 0.8 to 1.5 nm. Then, we add two hydrogen atoms to two neighboring carbon atoms (see Fig. 1a) situated at the top of the ripple and after that optimize geometric structure. To calculate the chemisorption energy one needs to know also total energy of the ripple without hydrogen which is, of course, unstable. To this aim, we make the ripple stabilized by the pair of hydrogen atoms smooth by decreasing out-of-plane displacements only for two atoms which were bonded with hydrogen and keeping all other atomic positions fixed. To calculate the chemisorption energy we use the expression $E_{chem} = E_{graphene\ with\ ripple} + 2H - E_{graphene\ with\ ripple} - E_{H_2}$ where the last term is the energy of hydrogen molecule. This characterizes stability of bonding of hydrogen with the ripple since it will desorb from the ripple as molecular hydrogen. At the same time, it allows us to estimate energetics of one-side hydrogenation by molecular hydrogen; the hydrogenation by hydrogen plasma proceeds without barriers⁸.

3 Shape of the ripples

First, we confirm that ripples on graphene can be stabilized by the chemisorption of functional groups⁸. We have carried out calculations for the pair of fluorine atoms or the pair of hydroxyl groups, and the results are similar to what is presented here for the case of hydrogen. Without functionalization, the supercell relaxes to the flat state and the ripples disappear at the structure optimization. The functionalized ripples keep basically their original form except some geometric distortions in a close vicinity of the functional groups. This means that corrugations created initially by substrate and then decorated by chemisorption remain stable after elimination of the substrate.

Note that the ripples stabilized by chemisorption remain isotropic and have shapes not too far from semi-spherical ones (the real shapes are shown in Fig. 2). The radius of optimized ripples varies between 0.7 to 1.0 nm and their height from 0.04 nm to 1.6 nm. These radii are of the same order as a spatial scale of geometric distortions around hydrogen impurity on pristine graphene^{5,7}. The effect of the impurity on electronic structure and, thus, on the chemisorption energies of next hydrogen atoms, is essentially nonlocal. The final optimized sizes of the ripples lie in much narrower intervals than the initially chosen parameters so one can hope that they are, indeed, intrinsic characteristics of the ripples and not artifacts of computational procedure. Fig. 2 shows optimized shapes of the ripples for three essentially different values of the geometric parameters (B, D, and E, according to the Figure 3a). One can see that neither radius nor height of the ripples can be used for their characterization. Similar to earlier works¹⁴, we characterize the ripples by the ratio h/R which does correlate with the value of chemisorption energy, according to our calculations.

4 Energetics of chemisorption

Further, we investigate dependence of the chemisorption energy on the curvature of the ripples. First, it is worthwhile to notice an important difference of one-side functionalization of graphene with and without ripples. Whereas in the case of flat graphene the optimal configuration of the pair of hydrogen atoms is para (1,4) configuration (Fig. 1c), for the case of ripples with large enough curvatures ortho (1,2) position (Fig. 1b) becomes more energetically favorable. This is due to the fact that curved surface of the ripple is close initially to atomic distortions created by the pair of hydrogen atoms in ortho position⁷. This explains the initial decrease of the chemisorption energy for such pair of atoms (the part A-B in Fig. 3a), the energy gain in comparison with flat graphene is 0.5 eV for the point A. For stronger corrugations the chemisorption energy per pair drops to the values close to zero (the part C-D in Fig. 3a) and, at last, for further increase of the ratio h/R the chemisorption energy becomes negative (the part D-E-F). This means that molecular hydrogen will be decomposed and bonded at the ripples with large enough curvature stabilizing them. This sharp decrease of the total energy can be related with the formation of the midgap states at the corresponding ripples (midgap) as one can see in Fig. 3b. Hydrogen atoms destroy the midgap states providing the energy gain (see Fig. 3b). In such cases the chemisorption of six hydrogen atoms leads to the opening of the gap in electron energy spectrum which does not take place for less curvature of the ripples (Fig. 3c).

We tried to create initially ripples with the ratio h/R uniformly distributed between 0.01 and 0.17. However, after optimization of the structure three ranges have appeared (A-B, C-D, and D-E) with breaks between them, with average values of h/R equal to 0.08, 0.12, and 0.16, respectively. Interestingly, for chemisorption of the pair of hydrogen atoms at flat graphene the height of out-of-plane atomic distortions is about 0.04 nm, with the

radius of the distorted region ≈ 1 nm, so, $h/R \approx 0.04^5$. Thus, the regions of stable ripples are characterized approximately by integer numbers of this ratio. For $h/R < 0.07$ the ripples disappear at the optimization of atomic positions and graphene with the pair of hydrogen atoms remains flat. The value $h/R \approx 0.12$ (part C-D) is typical for fullerenes, therefore, the chemisorption energies for this range is close to that for chemisorption of the pair of hydrogens at C_{60} ²⁰. Further increase of the curvature (the part E-F) when the midgap states appear corresponds to the ripples (for our choice $R \approx 1$ nm) where the length of C-C bonds reaches its maximal value 0.155 nm. Further increase of the curvature will lead to breaking of the chemical bonds and formation of vacancies and other types of defects. It was noticed earlier²¹ that appearance of the midgap states requires so strong stresses that formation of dislocations becomes possible. Chemisorption of hydrogen destroys the midgap states stabilizing such ripples which may be an alternative to vacancy or dislocation formation.

5 Conclusion

To conclude, we have demonstrated that ripples in graphene effect drastically on its chemical activity. Functionalization can stabilize ripples with very strong strains, close to the breaking of carbon-carbon bonds. However, if original corrugations are small enough, such that typical h/R is smaller than 0.07, the ripples will disappear after elimination of the substrate even in the presence of hydrogen. In this situation one can hope to provide a regular structure shown in Fig. 1c.

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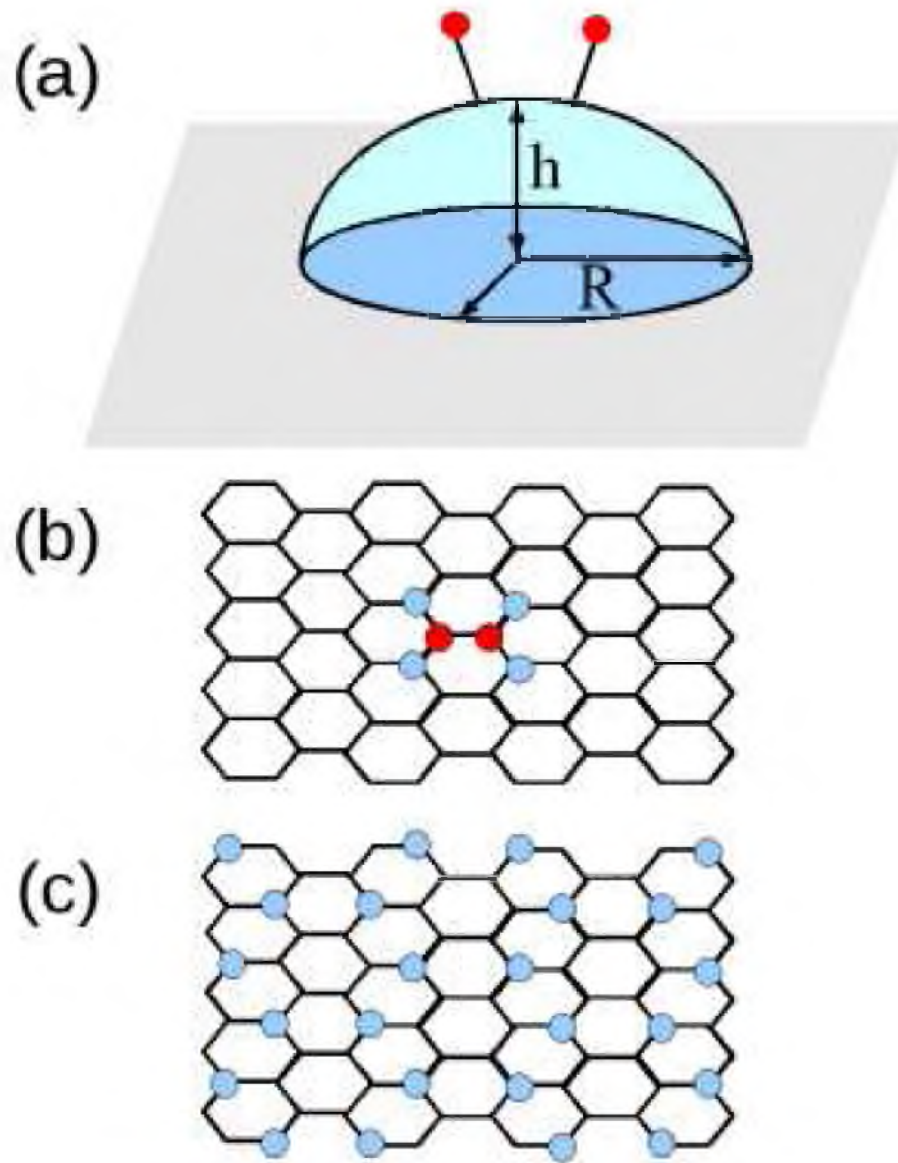


Figure 1: Schemes of chemisorption of pair of hydrogen atoms on the top of the ripple with the height h and radius R (a), of step-by-step hydrogenation of the top of the ripple (red pair is the first step and the blue pairs is the second one) (b), and of complete homogeneous one-side functionalization of flat graphene (c).

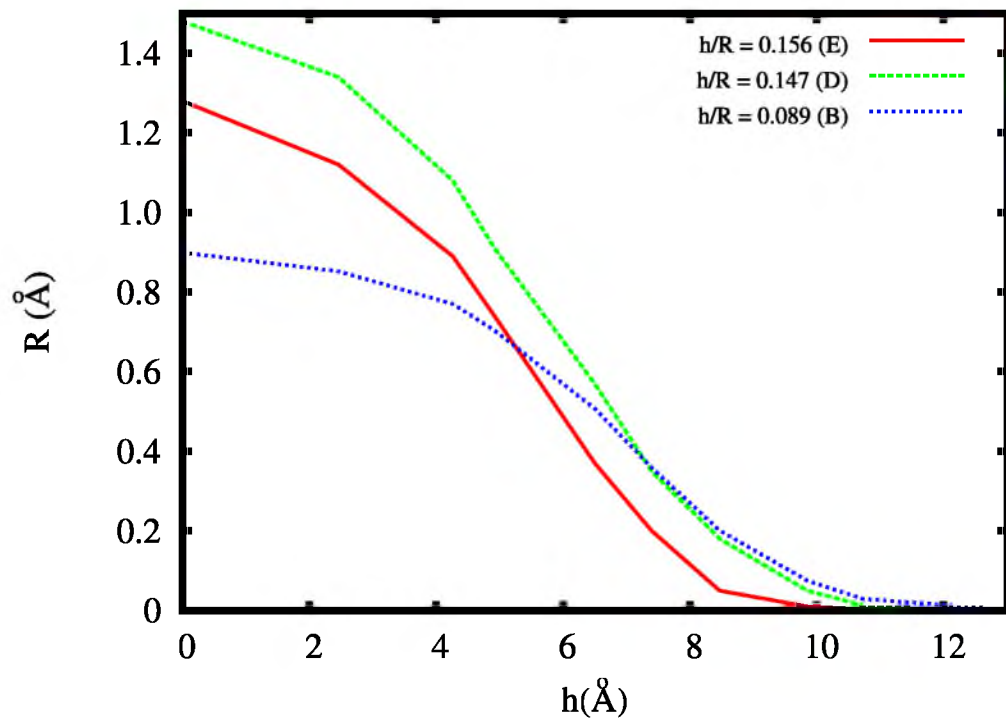


Figure 2: Optimized shapes of the ripples stabilized by hydrogenation, for special points B, D, E in Fig. 3a.

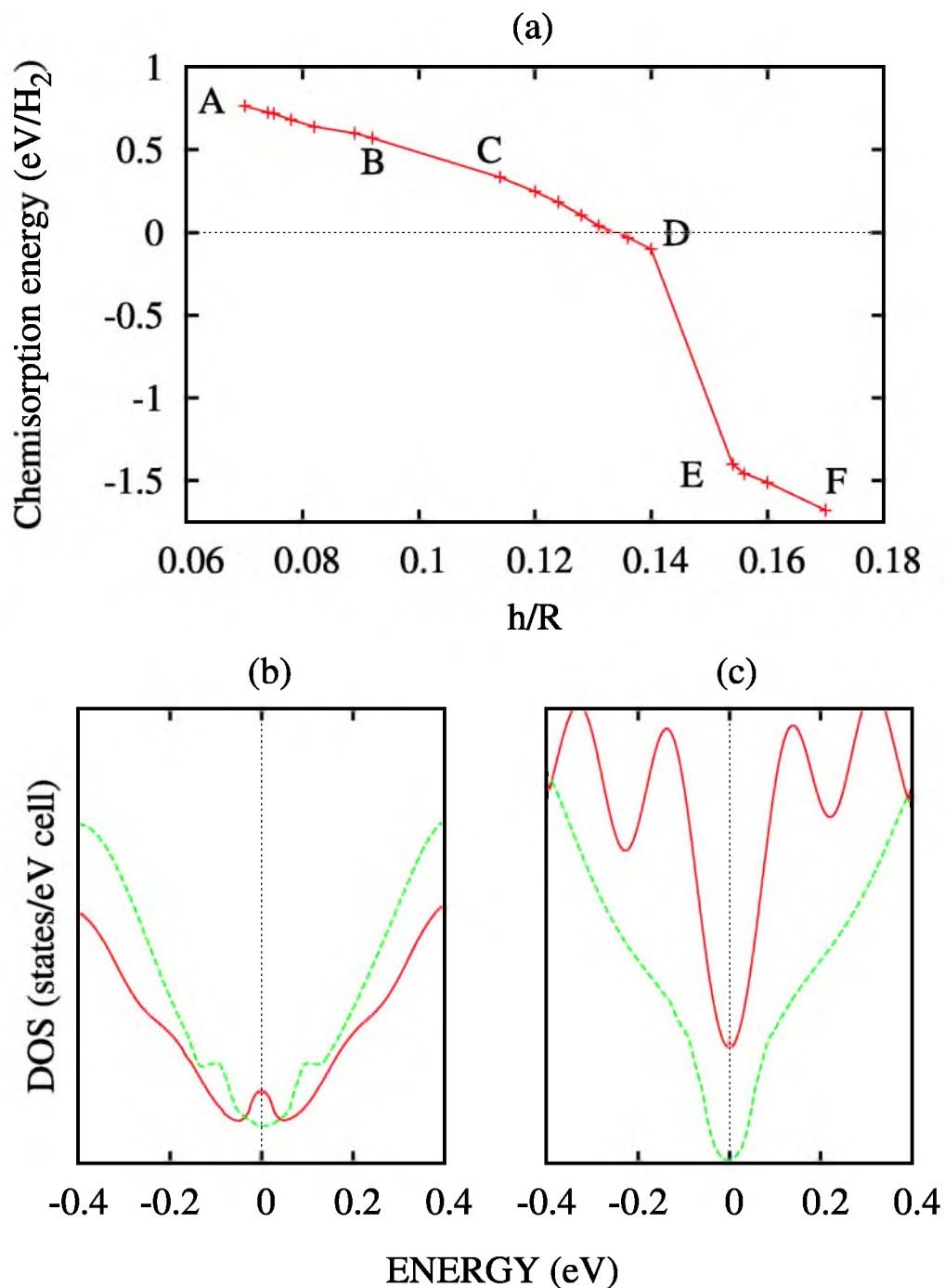


Figure 3: Dependence of the chemisorption energy on curvature of the ripple (the radius was of order of 1 nm, more detailed data see in the Supporting Information) (a); density of states for the point E with (dashed green line) and without (solid red line) the pair of hydrogen atoms (b); density of states for six hydrogen atoms per ripple (see Fig. 1b) for the points D (solid red line) and E (dashed green line) (c).