Graphene quantum dots and antidots: possible ways to preparation

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ABSTRACT

The formation process of graphene quantum dots surrounded by hydrogenated carbon atoms are studied using tight-binding (TB) approach implemented with dOXON code. To study the electronic properties of such material, we compared the tight-binding method with a more accurate density functional method. Was shown that for such objects tight-binding method gives good agreement with the DFT method to study the electronic properties. Using TB method theelectronic properties and their dependence upon the concentration of the hydrogen on the surface was studied.

INTRODUCTION

Graphene which was obtained only few years ago, attract a lot of attention from scientific community and it would be no exaggeration to say that authors of pioneering Nobel Prize awarded work Kostya Novoselov and Andre Geim are founders of new exciting scientific field of two-dimensional materials [1]. The appeared interest to graphene is bounds with it unique properties that potentially can be used in the future nanotechnology.

Today's challenge in investigation of graphene is connected mainly with attempts of opening of the band gap in graphene's semimetallic electronic structure. It will allow it to use in semiconducting field and design new low-dimensional nanoelectronic devices based on quantum dots [2]. Now researchers have been especially interested in the possibilities of the controlled creation of graphene quantum dots (GQDs) and antidotes (GADs) based on graphene nanoislands [3-5] because these objects have wide prospects of their applications. Therefore, we face the problem of finding the simplest ways of the formation of GQDs and GADs with controlled properties.

There are two promising possibilities of manufactures opening of the band gap in GQDs and GADs in the controlling way: the functionalization or the cutting of the grapheme surface and surface. In the first case the main driving force of the semimetal-semiconductor transition is changing of sp^2 to sp^3 type of bonding of carbon atoms with new adatoms (hydrogen [6, 7] or fluorine [8]) and formation of diamond-like regions on the graphane surface. In the second case, the cutting of graphene to small ribbons with QD of nanometer [2] width will push apart the conduction and valence bands due to the quantum confinement effect [9].

In this work we suggest novel schemes based on the creation of graphane CH nanodomains. Such two CH domains separates graphene nanoportion are formed on graphene nanoribbon (GNR) a quantum dot, where the quantum effects transform the continuous spectrum of the GNR to a system of energy levels had place. Periodically organization of graphane nanodomains on a graphene sheet can be transform their semimetal spectrum into semiconductor one.

Two simple schemes of experiments of controllable creation graphene quantum dots on a GNR are offered by using favorable adsorption of atoms of hydrogen on the convex GNR sites (methods of “knife” action and “sinusoid” GNR under stress).

We consider also the technique of imposing of one layer of GNR array on another under certain angle [3] which allow to prepare GQDs in mass quantity (adsorption of H-atoms will lead to ribbon "splitting" on two zones: a free site from "mask" graphane type, and a site with one open party of be-graphene, unprofitable for adsorption of hydrogen. Here we use the data of experiments [4] - difference between processes of hydrogen absorption on single layer and bilayered graphene. The similar effect we use in order to prepare GAD arrays on graphene by applying graphene nanomesh mask.

METHODS AND CALCULATIONS

Here we studied the structures combining both effects mentioned above: the graphene ribbons functionalized by hydrogen. We investigated the electronic properties of such material and their dependence upon the concentration of the hydrogen on the surface and focused on the formation of graphene quantum dots surrounded by hydrogenated carbon atoms.

Firstly, we studied the specific graphene nanoribbons with varying width and with smoothly changed shape (Fig. 1). We used TB and more accurate density function theory (DFT-LDA implemented in Siesta package (Ref. 10)) methods for calculating the electronic structure of such object. From the figure it is possible to make the following conclusion: the variation of the ribbon width leads to confining of the electrons in the larger graphene region and formation of quantum dots which can be seen from the linear electronic spectrum (Fig. 1). Also one can conclude that results from the calculation by TB and DFT methods are close to each other and therefore tight-binding approach can be applied for the solution of the problem.

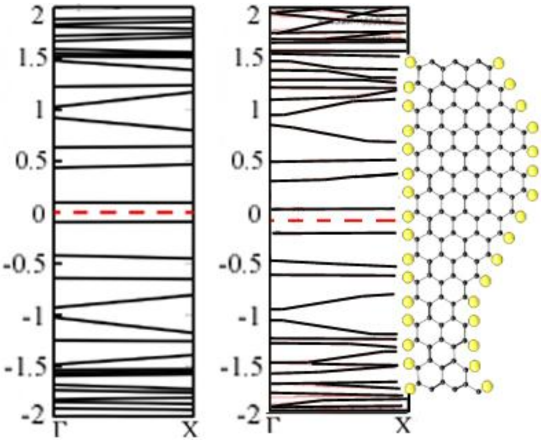

FIG. 1. The electronic spectrum of graphene ribbon with varying shape calculated by TB (on the left) and DFT (on the right) methods.

The tight-binding (TB) approach with periodic boundary conditions implemented in dOXON package was used in present study. This method was chosen because it allows makes the qualitative studies of the electronic properties of structures consists of a large number of atoms (more that 1000 atoms). Also, tight-binding approximation allows computing electronic structure and atomic geometry of hydrocarbons with good qualitative accuracy. Due to the large length of the unit cell (from 19 Å to 25 Å) only Γ-point was used during the relaxation. For the calculation of the electronic structure 10 k-points in periodical direction was used.

A classical molecular dynamics simulation for these cases of the favorable bonding for hydrogen atoms at specially prepared places of a GNR was performed using the GULP (General Utility Lattice Program) code [11]. The energy spectra for the obtained GQDs and GAD patterns were calculated using the tight-binding approach with periodic boundary conditions within the framework of the dOXON program package. Earlier, this approach exhibited a good agreement with more accurate *ab initio* calculations [12].

RESULTS AND DISCUSSIONS

The firts step of out investigation is the study of the formation process of graphane nanoribbons from graphene nanoribbons using TB (Fig. 2). Nanoribbon 4ZGNR was considered for investigation in which hydrogen atoms were added. For each new hydrogen atom the four possible configurations (each connection with all neighboring carbon atoms) were calculated. At high hydrogen concentrations has been included for consideration the compression of the ribbon by varying the unit cell parameter. For a cluster of n chemisorbed H atoms, the average binding energy $E_b(n)$ is

$$E_b(n) = \left(E_{gr} + nE_H - E_{ribb}\right)/n\,,$$

where E_{gr} is the energy of either graphene ribbon or its fragment, E_H is the energy of single H atom, and E_{ribb} is the total energy of hydrogenated graphene ribbon [13].

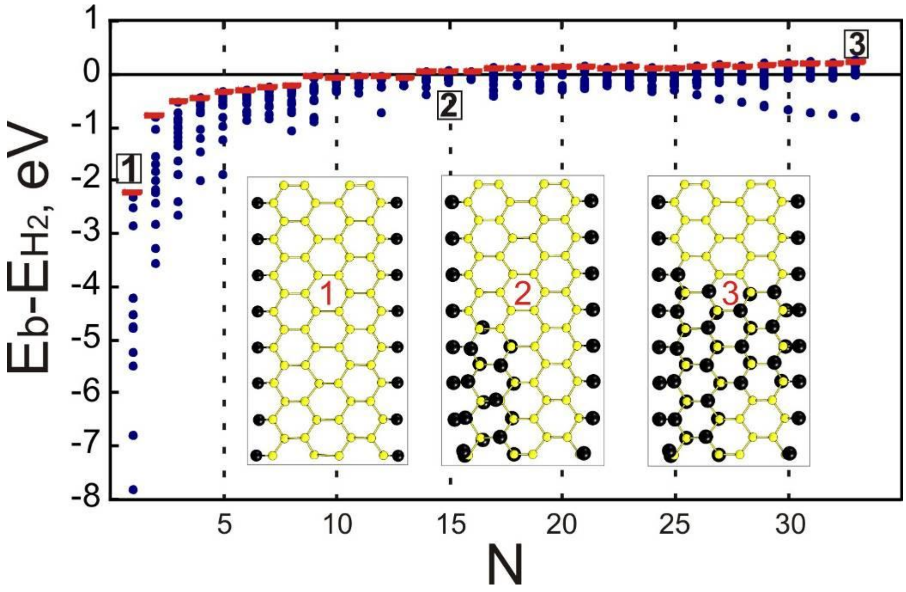

FIG. 2**.** Binding energy per hydrogen atom for all ribbons considered as a function of hydrogen concentration.The insets show 0, 15, and 33 adsorbed H atoms. The red lines corresponds the most stable configurations.

Dependence of binding energy on hydrogen concentarion. For zero binding energy was used the binding energy of hydrogen molecule per atom E_H=2.3 eV (Ref. 13). It can be seen that the addition of each new hydrogen atom increases the binding energy of the structure.

Next, the electronic properties of different hydrogenated ribbons (HR) were investigated. It was found that the hydrogenation of the graphene ribbon leads to blocking of ballistic transport in the structure and increasing of the band gap in the spectrum. The alternating of pure and hydrogenated graphene regions leads to confinement of the electrons with formation of graphene quantum dot (Fig. 3). We studied the dependence of electronic properties of the structures upon the hydrogen concentration as well as shape of the hydrogenated regions.

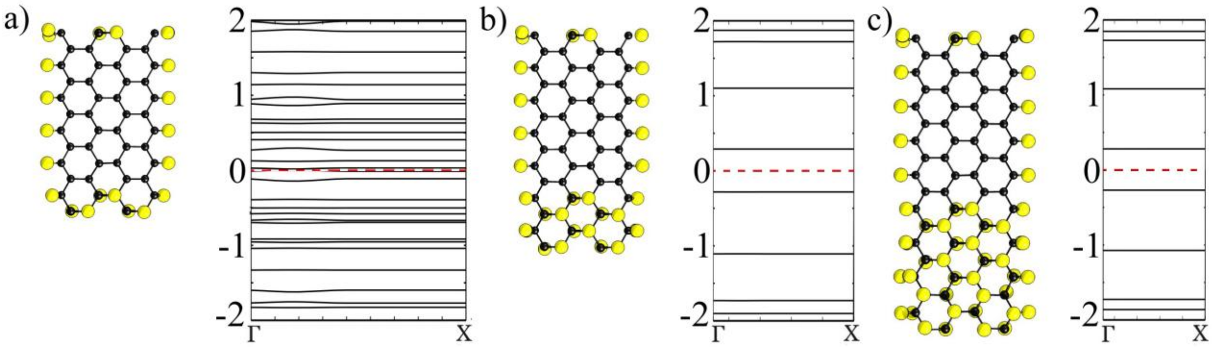

FIG. 2. The dependence of the electronic structure of HR upon the width of the hydrogenated region. Values of the band gap: (a) 0.13 eV, (b) 0.59 eV, (c) 0.61 eV.

We studied the dependence of the electronic structure of the HR upon the width of the hydrogenated region to find the minimal width of the region, which suppress the electron movement throw the ribbon (Fig. 2). It was found that the width of hydrogen region from 4 Å is blocking the movement of electrons (two graphene unit cells), which is clearly seen from the Figure 2. The electron dispersion of the ribbon with hydrogenated region of one graphene unit cell display electron dispersion (Fig. 2a), whereas two or more hydrogenated unit cells change the electron dispersion to linear one (Fig. 2b and Fig. 2c).

Let us consider now possibly a more advanced technique for producing a GQD at a long nanoribbon by formation of a “sinusoid” in the course of compressing the ribbon [14]. For this purpose, we chose the 7AGNR ribbon (59.6 × 13.5 Å^2). Under the effect of the force equal to 2 nN acting on its ends, the ribbon took a nearly sinusoidal shape (Fig. 3a). A step by step deposition of hydrogen atoms onto the energetically favorable locations at the bends of GNR gave rise to the stable shape with three C–H nanodomains (see Fig. 3b and Fig. 3c). The energy calculation of the superlattice generated owing to this shape demonstrated that the graphene portion (17 × 13 Å^2) located between C–H nanodomains has the line spectrum characteristic of a quantum dot (Fig. 3d). We also considered the adsorption of hydrogen atoms at the inflections of the “metallic” 14ZGNR ribbon. We obtained similar results concerning the energetically favorable formation of graphane nanodomains at such a ribbon. In experiment, we should expect the elongation of such domains with an increase in the exposure time for hydrogen atoms acting on the GNR.

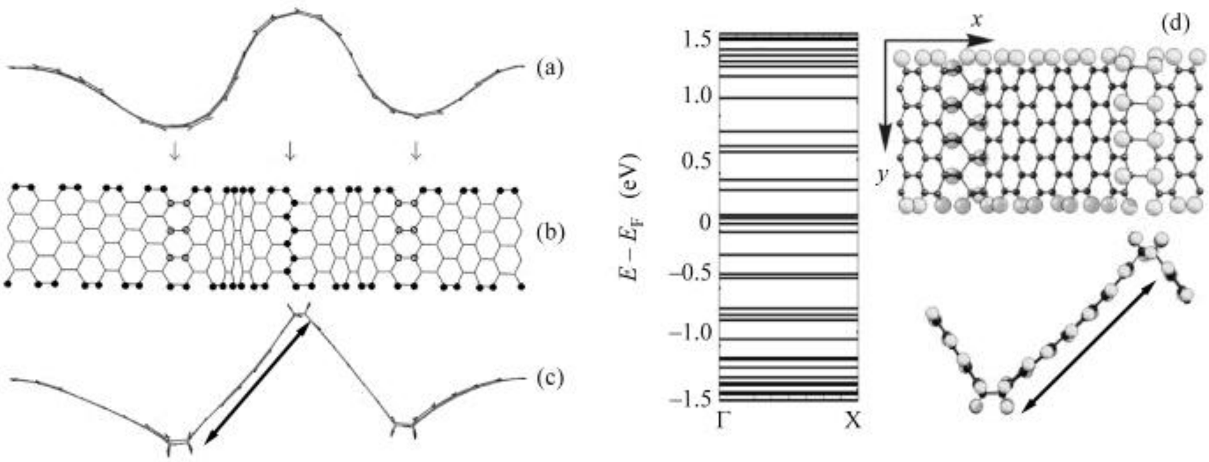

FIG. 3. Schematic view of the sinusoidal bending of the 8AGNR ribbon arising owing to its compression; (b) and (c) the same ribbon after the hydrogen adsorption at more favorable convex regions; (d) spectrum of the optimized superlattice of the quantum dot type with nanographene consisting of 64 sp^3 atoms between the diamond like C–H domains at this nanoribbon. The optimized structure is shown on the right. (Half-periods are shown by arrays).

We have also considered the scheme of “knife” action method using a wedge tip influence on the graphene ribbon. Two types of boundary conditions such as completely fixed ends of GNR and ends fixed only in two directions were applied. These conditions allow the ribbon to change the shape and length and make the ribbon surface is not planar [3]. Such way can permit to form the structure similar to structure, shown at Fig.3c.

Let us consider now possibly a more advanced technique for producing a GQD at GNR based on the difference in the hydrogen adsorption on graphene and bigraphene [16]. For this purpose, we suggest a mask type experiment with a pattern of nanoribbons applied on each other. For simplicity, we consider the intersection of nanoribbons at an angle of 90° (“upper” GNR array- mask on “down”GNR array Fig. 4).

For the case of adsorption between the mask and the ribbon the potential energy surface of a system with one hydrogen atom as a function of distance (R) between the edge of the mask and the hydrogen atom and height between the plane of the ribbon and the position of hydrogen atom was constructed (Fig. 4b). Potential energy surface is a powerful tool to estimate local values of the energy system. By these values we can determine the most favoriable adsorption position for hydrogen. It is shown that with decreasing distance between the hydrogen atom and the "mask" the barrier of hydrogen adsorption increases, making this process impossible. The molecular dynamics computations demonstrate that the adsorption at bilayer graphene is less favorable than that at single layer grapheme and that H-atom can not move under the mask. This confirms the previously obtained experimental data [16]. Hydrogen can not penetrate between the layers in the bigraphene. So, possible way to obtain graphane (fully hydrogenated from both sides of a graphene sheet) is a process of hydrogenation of monolayer of graphene. These calculations are completely confirmed by experiments concerning the hydrogen adsorption on graphene and bigraphene.

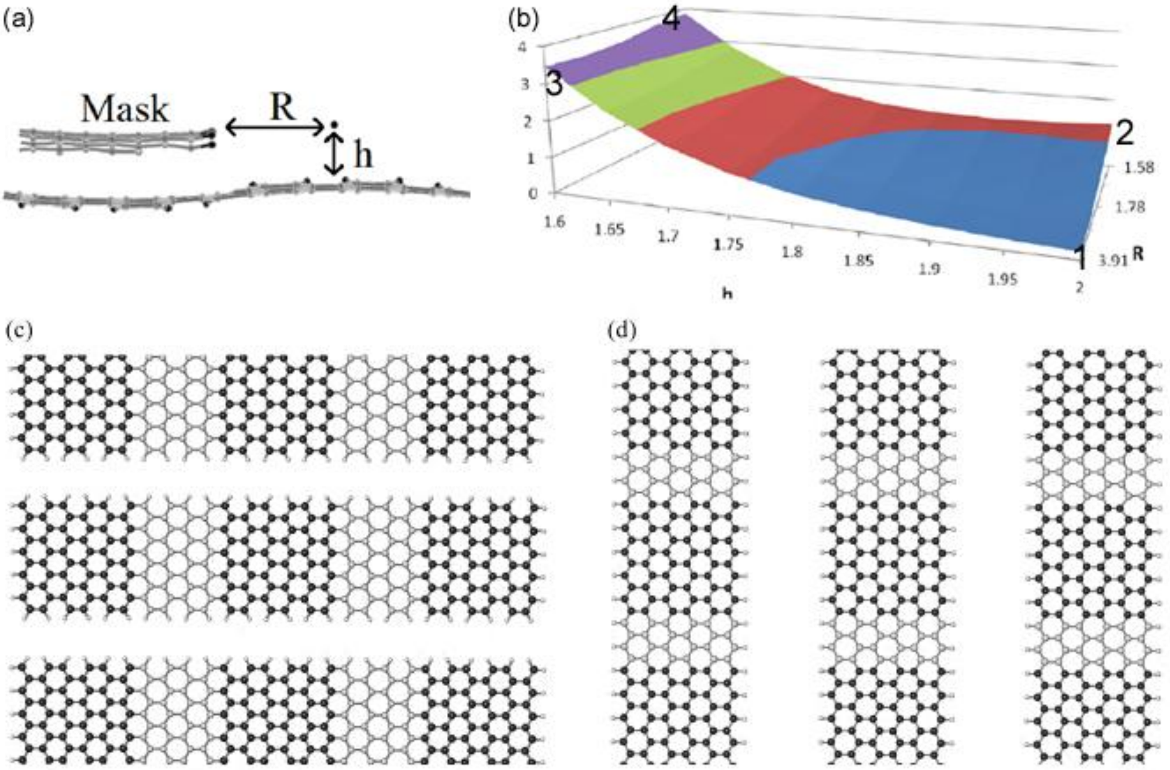

FIG. 4. Layout of the experiment on the creation of GQDs at the 9AGNR(3.84)/AZGNR(2.13)/90° system of GNR rows inter secting at an angle of 90°. (a) The principac scheme of the method; (b) Potential energy surface. Position “1” corresponds to R=3.9 Å, h=2 Å, E_b= 0.19 эВ, 2: (R=1.5 Å, h=2 Å, E_b=0.89 эВ), 3: (R=3.9 Å, h=1.6 Å, E_b=3.46 эВ), 4: (R=1.5 Å, h=1.6 Å, E_b=3.98 эВ) (c) and (d) rows of 10AGNR and 6ZGNR graphene ribbons (black circles denote C atoms at “empty” domains II) and graphane (gray circles demote C atoms with H atoms attached from both sides of graphene domains I) after their separation after the termination of the hydrogen adsorption process at the 10AGNR(1.72)/6ZGNR (2.27)/90° system in hydrogen plasma.

We construct the notation for such a system based on the well known notation for armchair and zigzag GNR (AGNR and ZGNR). As an example, we have consider the structure 10AGNR(1.72)/6ZGNR (2.27)/90°, which denotes that the row of longitudinally located 10AGNR with a period of 1.72 nm is applied to the row of transversally located6ZGNR with a period of 2.27 nm.

The molecular dynamics computations demonstrate that the adsorption at domain II is less favorable than that at domain I. Figure 4b shows the energy difference $\Delta E\left(D_{C-H}\right)=E_I-E_{II}$ as a function of the C–H distance if a hydrogen atom moves perpendicularly (along the z axis) toward a carbon atom at sites I or II. For domain II, the barrier for the covalent bonding appears to be higher by 0.03–0.05 eV (x = 1.4–1.5 Å). The step by step planting of five hydrogen atoms around the first C–H pair for both domains demonstrated the following things. For each subsequent H atom planted at domain II, the energy barrier grows significantly. In this domain, the adsorption of hydrogen atoms is possible only from one side of each ribbon in bigraphene. For graphene domain II, the adsorption is favorable from both sides. The difference ΔE_5 between the barriers at a distance of 1.3 Å from the surface grows to 0.1 eV in the case of planting the fifth hydrogen atom.

In addition, it was demonstrated that, if the location of the C–H bond approaches the mask (domain II), the barrier for the hydrogen adsorption at a carbon atom grows significantly. The difference ΔE ($x = 1.5$ Å) between the barriers at the center of domain II and near the dashed line in the vicinity of domain II (Fig. 4a) equals already 0.3 eV. For this reason, the penetration of hydrogen atoms between the layers of bigraphene is impossible even at 1000 K. Thus, H atoms from the incident hydrogen flow can be adhered, giving rise to a graphane region, only to domains I open from both sides, which are free of the applied ribbons of the second layer. At the intersection, where bigraphene domains II are formed (Fig. 4a), the hydrogen adsorption is impeded. Such domains remain “bare.”

Figure 4c and Figure 4d exemplify the possible formation of the rows of graphene quantum dots with periods of 1.72 and 2.27 nm at 10AGNR and 6ZGNR ribbons after their separation following the termination of the hydrogen adsorption at the 10AGNR(1.72)/6ZGNR (2.27)/90° system. Combining the arrangement of the GNR rows, one can controllably create various GQD combinations at the chosen nanoribbons.

In summary, we have proposed three types of experiments on the controlled production of graphane strips at graphene nanoribbons leading to the creation of quantum dots. Two of them are based on the preparation of curved surfaces, the convex portions of which are favorable according to our calculations for hydrogen adsorption. The third technique involves the application of one GNR layer on another layer at certain angles, which is promising for mass production of GQDs. The examples of the calculations for specific GQD structures formed at the conventional stable nanoribbons of the zigzag and armchair types demonstrated the possibility in principle of varying the inter level distance in the range from 0.1 to several electron volts by changing the length of graphene nanodomains.

Note that the experiment for the latter technique can be improved by placing GNR onto a pattern of silicon nanowires (this scheme was implemented for the formation of narrow GNR [17]). Upon the adsorption of hydrogen atoms, this will again lead to the separation of the ribbon (as in Fig. 4) into two domains: the domain free of the mask of the graphane type (domain I) and the domain with one open graphene side unfavorable for the adsorption of hydrogen (domain II) [16]. Note that the schemes of these experiments are undoubtedly applicable also in the case of fluorine (or oxygen) adsorption for the formation of GQDs with the nanodomains made of graphene fluoride (FG) or oxide (OG). Such a conclusion is based on rich experimental and theoretical material concerning the preparation of FG and OG structures [18].

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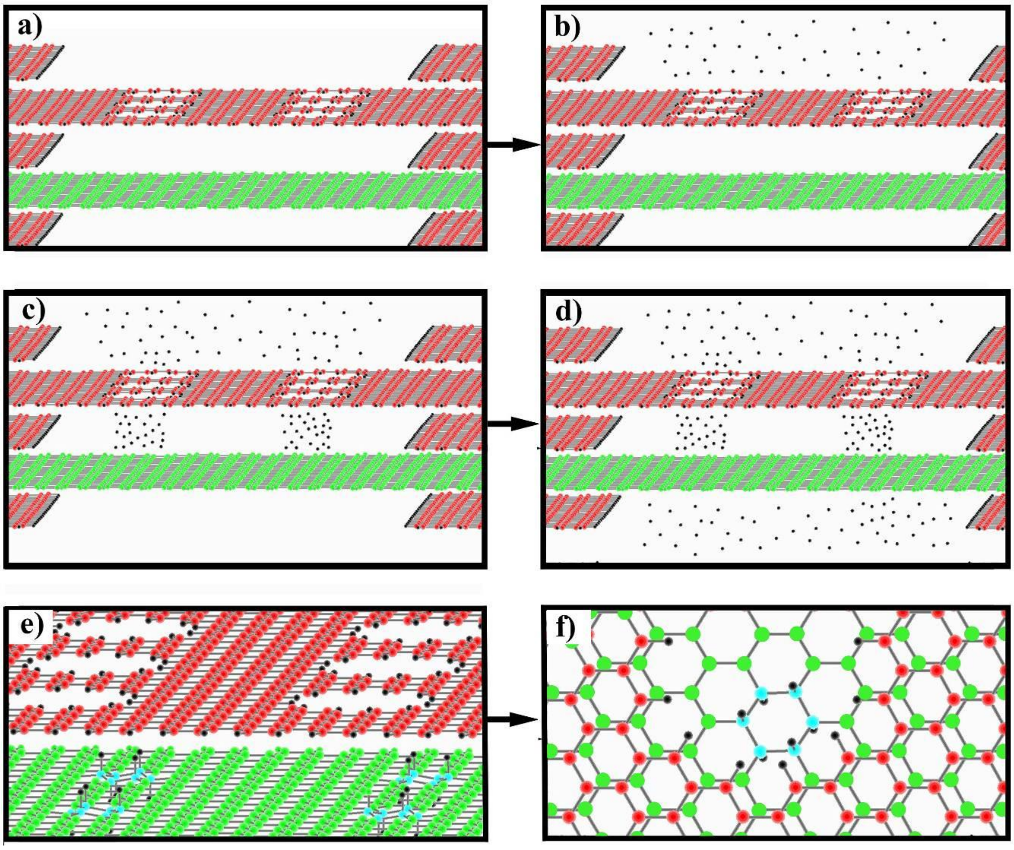

FIG. 5. A possible way of graphane CH nanodomains fabrication. Hydrogen gas passes through the matrix (marked as the dark gray or red line) and is connected with the upper side of graphene (marked as the light gray or green line) directly under the holes. The hydrogen situated under the graphene supports hydrogenation process.

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