

Strong Influence of Graphane Island Configurations on the Electronic Properties of a Mixed Graphene/Graphane Superlattice

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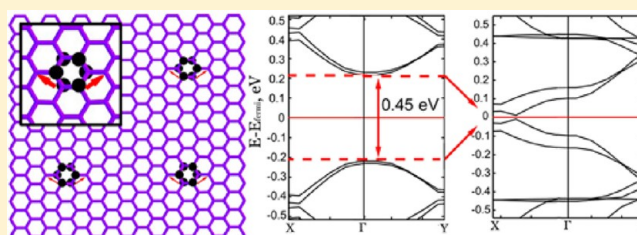
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ABSTRACT: We focus on the description of a complex mechanism whereby the graphene electronic properties vary in the case of graphene hydrogenation as periodic graphene/graphane structures are formed. Two nonmonotonic dependences of the band gap on the hydrogen concentration and on the arrangement of adsorbed hydrogen atoms on the graphene surface were obtained. The origin of this effect is discussed and explained from an atomistic point of view. We discuss how one can possibly form the superlattice by using a graphene nanomesh.



INTRODUCTION

Graphene is one of the most interesting materials synthesized in the recent years. Its two-dimensional nature, along with fascinating electronic properties, attracts great attention of the scientific community. Graphene displays unique electronic properties, such as a linear dispersion law leading to zero effective mass for electrons and holes. It has already been considered as a promising candidate for the basis of future nanoelectronics¹ and applied as a base of a solar cells,^{2,3} liquid crystal devices,⁴ molecular sensors,^{5,6} nanosized transistor prototypes,^{7,8} and touch screens.^{7–9}

Despite many fascinating properties, the semimetallic nature of graphene complicates its application in semiconductor nanoelectronics. In recent years, a number of ways to open a gap in graphene were proposed. For example, cutting graphene into thin strips (so-called graphene nanoribbons) leads to a band-gap opening owing to the quantum confinement effect, but the requirements of the nanometer strip width along with a fine structure of the edges do not allow efficient ribbon fabrication in today's technology.^{10,11} Another promising method is to modify the graphene surface by introducing vacancy defects^{12,13} or by chemical adsorption of adatoms.¹⁴ It has been predicted that the total hydrogenation of graphene would lead to a change in the conductivity from a semimetal to an insulator,^{15,16} and this has generally been confirmed experimentally.¹⁷ Moreover, the graphene electronic properties can be changed drastically even by partial hydrogenation. It has been found that adsorption of a single hydrogen atom onto a graphene area of about 2 nm² could open a band gap of 0.45 eV.^{14,18} Furthermore, the adsorption of hydrogen into periodically arranged lines changes the graphene properties in

the same way as formation of graphane ribbons:^{19–21} graphene confined by the hydrogen lines displays a band gap depending on the distance between the lines and their direction. We point out that the experimental graphane synthesis¹⁷ resulted in a structure whose resistivity was lower than expected; this can be explained by incomplete graphene hydrogenation. In a recent paper,²² partially hydrogenated graphene (PHG) was fabricated, whose band gap was lower than the band gap in graphane as well.

There are a number of theoretical papers explaining the behavior of the electronic properties of PHG. It was assumed that, as graphane grows on graphene (by increasing the amount of adsorbed hydrogen atoms on the graphene surface), the band gap in the structure increases monotonically.^{23–25} However, a more complex behavior of the band gap, whose physical origin is still unclear, is suggested in a recent series of papers.^{19–21,26,27}

We present a systematic study of the electronic properties of graphene with adsorbed hydrogen atoms in various combinations. We show that the electronic properties of PHG display a complex dependence on the shape and size of the formed graphane nanoislands. We obtained two characteristics dependences of the PHG band gap on the adsorbed hydrogen atom concentration and discussed their origin. We show that, depending on the particular location of the hydrogen atoms in the formed islands, the structure can display two types of semiconductor behaviors.

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METHODS AND CALCULATIONS

To obtain a qualitative description of the evolution of the electronic properties of hydrogenated graphene, a tight binding method based on the *DOXON* code with the periodic boundary conditions was used. The reason that the semiempirical approach was used is that our calculations involve structures with a large number of atoms. The TB method well describes both the atomic geometry and the electronic properties of hydrocarbon systems and shows good agreement with the results of accurate *ab initio* calculations.²⁸ The relaxation was carried out only at the Γ -point due to the large unit cell ($\sim 30 \times 30 \text{ \AA}^2$) of the structures to be studied. In the course of the atomic structure minimization, structural relaxation was carried out until the change in the total energy was less than 10^{-2} eV , or forces acting on each atom were less than 10^{-2} eV/\AA .

RESULTS AND DISCUSSION

The graphane growth process displays a nucleation nature:²⁹ the adsorption of hydrogen atoms on both sides of the graphene surface locally breaks graphene's π system and increases the chemical activity of the neighboring carbon atoms, which will tend to bind hydrogen further.³⁰ It is important to note that every nucleus can equiprobably start to grow from sites A or B of the graphene lattice, which can lead to discontinuation in the junction of the neighboring islands. Such discontinuities can significantly affect graphene electronic properties, because the adsorption of hydrogen on graphene is not likely in the region.¹¹ Graphane islands that started to grow from A and B graphene sublattices were defined as A and B graphane islands, respectively. In our work, we consider the simplest configuration of the islands $\begin{matrix} A & B \\ B & A \end{matrix}$ in a rectangular graphene cell.

The obtained structures were denoted by PHG-*X*, where *X* is the concentration of H atoms on the graphene surface. Various concentrations of the adsorbed hydrogen atoms from 2% to 56.3% were considered. Note that the hydrogen content is not an absolute parameter determining the electronic properties of the structures, because the electronic properties of a structure also depend on the particular location of the adsorbed atoms. In Figure 1, the atomic geometry and electronic structure of graphene with the same content of adsorbed hydrogen and various geometric arrangements are shown.

We start our study from structures with far-arranged ($\sim 2 \text{ nm}$) adsorbed pairs of hydrogen atoms. Considered graphene superlattices with rectangular C_{384} unit cells consist of four graphane $\begin{matrix} A & B \\ B & A \end{matrix}$ islands. Even at such a low hydrogen concentration, we can observe the opening and change of the band gap depending on hydrogen pair positions (Figure 1a,b). A similar effect has been obtained in ref 19. Following the classification given in this paper, the structure in Figure 1a can be represented as (7,0,3) PHG-2.1 showing a zero band gap. As the nucleation continues, the hydrogen pairs transform into graphane islands consisting of aromatic rings (6H-hexagons (Figure 1c) or 6H-chairs (Figure 1d)). The shape of the formed graphane areas already drastically affects the conductivity of the structure, which can directly be seen from Figure 1, where the electronic properties of PHG with the same concentration, but various distributions of hydrogen, are shown.¹⁹ The breaking of the CH hexagon in Figure 1c decreases the band gap on 0.4 eV and transforms the

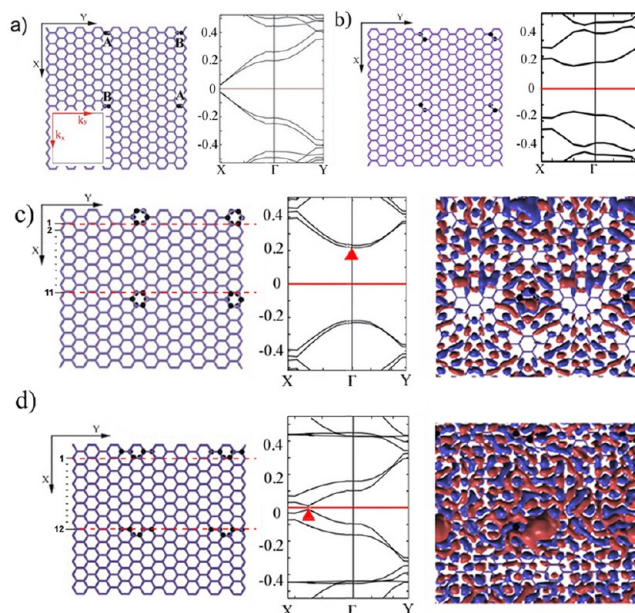


Figure 1. Evolution of electronic properties of partially hydrogenated graphene. Unit cells and band structures of the graphene superlattice with a concentration of hydrogen of 2.10%: (a) $E_{\text{gap}} = 0.02 \text{ eV}$, (b) $E_{\text{gap}} = 0.25 \text{ eV}$. A concentration of hydrogen of 6.25%: (c) graphane hexagon, $E_{\text{gap}} = 0.43 \text{ eV}$ and (d) graphane chair, $E_{\text{gap}} = 0 \text{ eV}$; the black points are H atoms. The Fermi energy is marked by the horizontal lines. The HOMO orbitals (isovalued 0.015) at the Γ -point (c) and at the point in $2/3$ of the Γ -X direction (d); see at the triangles.

semiconducting material into a semimetal (Figure 1d). The origin of the effect can be explained on the basis of the distribution of the electron wave function at the bottom of the conductive band of the structure, which is responsible for conductivity. In the case of a CH hexagon (Figure 1c), the electron wave function is concentrated around the island, which leads to opening of the band gap, whereas, in the case shown in Figure 1d, the electrons are nearly uniformly distributed on the surface.

Another interesting and important effect related to such structures with the small hydrogen concentration is observed when we change the distance between the graphane nanoislands. The band gap appears and disappears depending on the distance between the islands along the zigzag direction (X direction), which obeys the rule $N = 3p + 2$ (p is an integer number) in the classification, like for armchair graphene nanoribbons (NZGNRs).³¹ We consider such structures as the intersection of zigzag and armchair GNRs. If the index of the zigzag ribbon between the graphane islands satisfies that rule (in our case, the index N is equal to 11; see Figure 1c), then the structure shows semiconductor properties. Although the structure in Figure 1d does not satisfy the $3p + 2$ rule, it shows metallic properties (the index N is equal to 12). Whether the rule is satisfied does not depend on the shape of the graphane islands and depends only on the width of the ribbons between the graphane nanoislands. It is also important to know that there are no such rules and dependences for the distance changing between graphane nanoislands along the armchair direction (the Y direction). This interesting effect has already been observed in studies of antidot graphene structures in a recent paper.³²

The effect also influences the electronic properties of PHG with higher concentrations of hydrogen, but in this case, the

confinement effects should be taken into account. We studied this effect in detail by considering graphene with a 56.25% concentration for various distributions of the adsorbed hydrogen atoms on the surface (Figure 2). At this concentration, the adsorbed hydrogen formed islands on the graphene surface, whose interaction affects the electronic properties of the structure.

Graphane islands are viewed as potential barriers for conduction electrons, and therefore, the electronic properties (mainly, the band-gap value) of such PHG structures display behavior similar to that of graphene antidot superlattices with

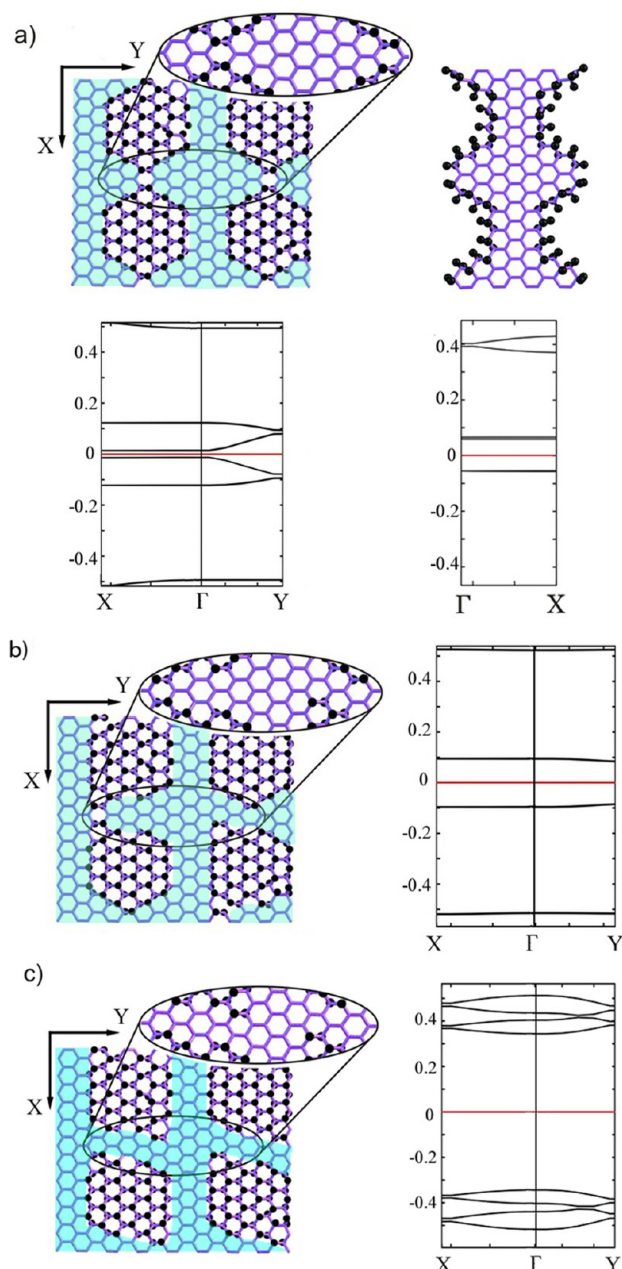


Figure 2. Impact of the positional change of the adsorbed hydrogen atoms on graphene on the electronic properties of PHG shown by the example of PHG-56.25. The atomic geometry (on the left) and the band structure (in the center) of PHG with a 56.25% hydrogen concentration. Hydrogen-free regions are filled with blue (gray) for clarity. The band gap is (a) 0.02, (b) 0.91, and (c) 0.17 eV. The Fermi level is taken as zero.

the same shape of the holes. A special case of such a structure is a graphene road implemented in graphane,³³ whose electronic properties correspond to those of graphene ribbons. Figure 2a compares PHG and graphene nanoribbon with a periodically varying width. The linear electronic spectrum in the Γ -X direction of both structures can be explained as the existence of quantum dots in the widened graphene regions. If we connect such nanoribbons periodically in the Y direction and completely fill out the empty space between the ribbons by graphene islands, we obtain the same PHG structure shown in Figure 2a. Owing to the periodicity of the structure and the effect of tunneling through the CH barriers, the energy bands are formed along the Γ -Y direction. Therefore, for this PHG structure, we have the appearance of electron motion along the Y axis.

The difference between parts a and b in Figure 2 is only in the location of hydrogen pairs at the edges of the islands, which leads to breaking the symmetry of the quantum dot and increasing the value of the band gap from 0.02 to 0.17 eV.

In the structure presented in Figure 2c, the pairs of hydrogen atoms are shifted from the edges of the widened graphene region in opposite directions along the Y direction. Such a small shift leads to changing the electronic properties of the structure drastically and increases the band gap from 0.17 eV (Figure 2b) to 0.69 eV (Figure 2c).

A similar effect of band-gap variation depends on various motions of hydrogen pairs and has also been obtained for other hydrogen contents, such as PHG-49.5 (see Figure 3).

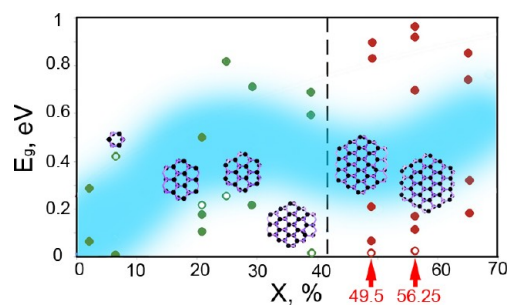


Figure 3. Dependence of the band gap of PHG on the concentration X consisting of two parts with two significantly different values of the band gap. The structures consisted of magic hexagonal graphene islands marked by empty circles. The distance between the circles from two parts is about 0.4 eV; it is marked by the blue region. Red arrows represent this dependence for the structures PHG-49.50 and PHG-56.25 shown in Figure 2. The insets in the figure display the shapes of graphene islands only for structures with magic hexagons.

Note that all of the studied structures with the same concentration of hydrogen atoms from the energy point of view differ by only 10^{-2} eV/atom; and therefore, the probability of formation of all of the presented structures is practically the same.

We investigated two different configurations of $\begin{matrix} A & A \\ A & A \end{matrix}$ and $\begin{matrix} A & B \\ B & A \end{matrix}$ graphene islands and did not find a significant difference between their electronic structures. The band gaps are practically the same; for example, the band gaps in PHG-6.25 and PHG-56.25 are nearly equal to 0.4 and 0.9 eV, respectively, within the accuracy of 10^{-2} eV regardless of the types of graphene island configurations.

In Figure 3, the summary of the calculation of the band gaps of all the studied PHGs is presented. This graph can be divided into two conditional parts. At the high hydrogen concentration on the surface (>40%, marked by the vertical dashed line), the graphane nanoislands begin to connect, and the motion of electrons in the Y direction is closed. The obtained data can be approximated by two areas with two significantly different values of the band gap. The main purpose of this graph is to show the complex behavior of the dependence of the band gap on the concentration of the adsorbed hydrogen on the graphene surface. For the same hydrogen concentrations, the various band-gap values can be obtained. These gaps differ from each other several times. As one can see, a concentration of 40% changes the criterion of estimating and predicting the band gap owing to the strong change in the symmetry of the graphane islands. However, if we can control the formation of periodic structures with controlled CH-island shapes, we will obtain a semiconductor with a determined energy gap.

In the age of nanotechnology, we should not only predict new nanostructures but also suggest ways for their manufacturing. Therefore, we suggest a method of experimental implementation of partially hydrogenated graphene with graphane islands arranged in a regular way. The scheme of the proposed experiment is shown in Figure 4: a matrix composed of graphene nanomeshes (GNMs) with periodically

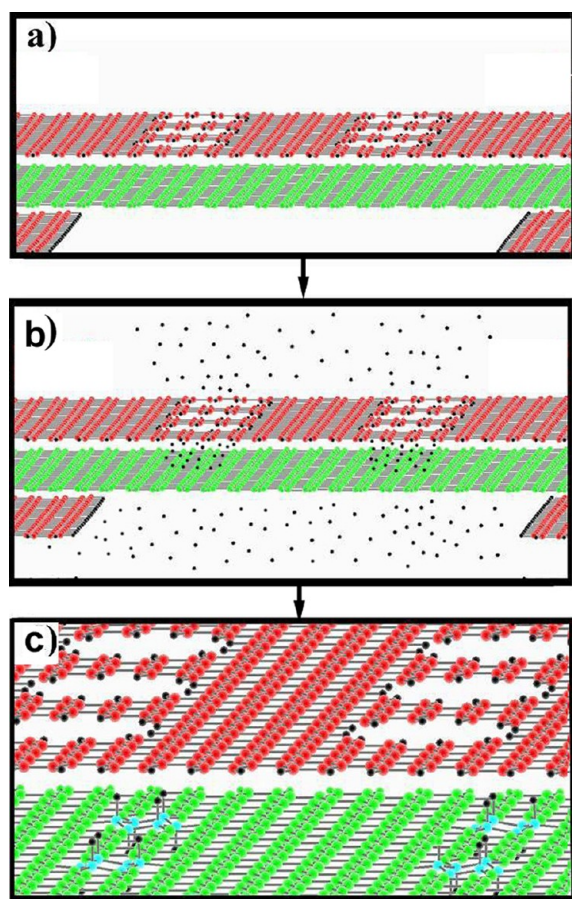


Figure 4. A possible way of PHG structure fabrication. Hydrogen gas passes through the matrix (marked as the dark gray or red line) and is connected with the upper side of the graphene (marked as the light gray or green line) directly under the holes. The hydrogen situated under the graphene supports the hydrogenation process.

hexagonal or round holes covers the defectless graphene on which we will form a semiconductor graphene/graphane structure. In addition to the proposed method of making graphene structures with periodically arranged graphane nanoislands (or antidots³⁴), one can also use a mask made of a porous aluminum substrate.³⁴ Recently, such GNMs have been produced with various periodicities and nanohole diameters.^{35–37} This system should be placed into the chamber with hydrogen plasma. During the hydrogenation process, hydrogen gas will pass through the matrix and adsorb on the upper side of the graphene directly under the holes. At the same time, hydrogen atoms will adsorb on the same places on the lower side of the graphene (Figure 4b,c). It is known that hydrogenation from only one side of graphene is an energetically unfavorable process.¹⁷ Therefore, during the adsorption of hydrogen on the upper side, the hydrogen from the bottom side will connect to the neighboring site, and in such a way, a graphane nanoisland will be formed.

Such a system represents the bilayered structure with the upper layer of the graphene nanomesh. The process of hydrogen adsorption on one layered and bilayered graphene has been previously investigated (Supporting Information of ref 17) and theoretically explained in ref 36. It has been shown that the hydrogen adsorption on the single-layered graphene is preferable to adsorption on the bilayered graphene. That is a reason why the hydrogen adsorption would be in the spots under the holes rather than in the areas nearby the holes. After that, we can obtain the required PHG structure when we have separated the upper layer from the lower one.

In the proposed experiment, it is possible to control the conductivity of PHG structures by the variation of the size and shape of the holes in the GNM.^{37,38}

Similar semiconductor structures can be fabricated by F-atom passivation with the same geometric arrangement on the graphene. Recently, a number of reports about the study of and obtaining such objects have been published; see, for example, ref 33.

CONCLUSION

Systematic studies of partially hydrogenated graphene superlattices are presented. The dependence of PHG electronic properties on the concentration of the adsorbed hydrogen on the graphene surface was obtained. Our results on the energy gap behavior of considered structures could be separated conditionally into the two parts corresponding to different H-atomic configurations. Also, it was found that, at the high hydrogen concentration (>40%), the electronic properties of PHG superlattices are dictated by the close proximity of the formed graphane islands to each other. Finally, the method of experimental realization of partially hydrogenated graphene with graphane islands arranged in a regular way was proposed.

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Notes

The authors declare no competing financial interest.

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