Carbon 124 (2017) 228–237

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Magneto-electronic properties and carrier mobility in phagraphene nanoribbons: A theoretical prediction

P.F. Yuan, Z.Q. Fan, Z.H. Zhang*

Institute of Nanomaterial & Nanostructure, Changsha University of Science and Technology, Changsha 410114, China

A R T I C L E I N F O

Article history:
Received 10 June 2017
Received in revised form
12 August 2017
Accepted 29 August 2017
Available online 29 August 2017

Keywords:
Phagraphene nanoribbons
Bipolar magnetic semiconductor
Transverse electric field effect
Half-metallicity
Carrier mobility

A B S T R A C T

To explore the quantum confinement and edge state effects for phagraphene, a recently proposed new 2D material, we here consider to cut it along a certain direction, and six kinds of the nanoribbons with special A-, B- and C-type edge structures are achieved. Their structural stability with H passivation is verified by the calculated binding energy, phonon dispersion and molecular dynamics simulation. The nanoribbons with two A-type edge structures are nonmagnetic semiconductors with a periodically altered band-gap versus the width. While those with B-type and/or C-type edge structure for two edges are spin-degenerate/spin-splitting semiconductors in the antiferromagnetic ground state. Particularly, nanoribbons with A-type edge structure for one edge while with B-type or C-type edge structure for other edge only hold the ferromagnetic ground state and present the bipolar magnetic semiconducting nature. The further studies reveal that the nanoribbon is an excellent magnetoelectric material and its half-metallicity can be realized by the application of an electric field. More interestingly, the carrier mobility for the nanoribbon with two A-type edge structures is very high and strikingly size-dependent, from ~10^3 to 10^6 cm^2/V.S. This means that width control is a possible routine to effectively regulate the mobility of nanoribbons.

1. Introduction

Graphene, an allotrope of carbon with a symmetrical hexagonal honeycomb atomic structure, has attracted great research interest since its successful fabrication in 2004 due to the presented unique and excellent physical properties [1–4]. The wide investigation on this emerging material mainly focuses on its promising applications in the nanoelectronics and spin electronics [5–10] The other significance about the discovery of graphene is that it verifies the two-dimensional (2D) material to be able to exist stably in reality, as a result, this has spurred a surge to explore other types of 2D materials [11–13]. So far, more and more 2D materials have been synthesized or predicted to hold a good stability and become the research focus in scientific community, such as the monolayered h-boron nitride [14], silicene [15], transition metal sulfide [16], phosphorene [17], and so on. Because of the unusual electrical, optical, and mechanical properties of these 2D nanomaterials, their discovery and further research for realistic applications will produce a profound and significant impact for developing nanoelectronic and spintronic devices.

Recently, phagraphene, a new 2D nanomaterial, was predicted to be able to exist stably [20], which is a new carbon allotrope with a monolayered planar structure but composed of 5-6-7 carbon atom rings, namely, surrounded by 6-carbon rings, the pairs with 5- and 7-carbon rings invert to each other and are arranged in a rectangular fashion. Its plane group thus is Pmg, unlike P6m of graphene. This 2D nanomaterial is energetically comparable to graphene and more favorable than most of other carbon allotrope because all the internal carbon atoms are bonded with graphene-like sp^2-hybridized features and possess a high atomic packing density. Its distorted Dirac cone in first Brillouin zone indicates that phagraphene holds a high carrier mobility. However, the two Dirac bands in the proximity of the Fermi level is no band gap, as well as no magnetism occurs in phagraphene since the p_z orbitals for all neighbored C atoms form π-bonding to quenches magnetism. These makes its applications in logic operations and magnetic devices be severely limited. The simplest routine to functionalize phagraphene is to cut 2D layered nanomaterials to 1 D nanoribbons. Generally, 1 D nanoribbons have different behaviors from 2D morphology due to the quantum confinement and edge effects,

---

* Corresponding author.
E-mail address: cscuzzh@163.com (Z.H. Zhang).

http://dx.doi.org/10.1016/j.carbon.2017.08.068

typically for graphene nanoribbons [21–29], silicene nanoribbons [30], and phosphorene nanoribbons [31].

In this present work, as a promising structural modification to expand functions and applicability of phagraphene, we consider tailoring it along a certain direction, and six types of nanoribbons are achieved. The calculated binding energy, phonon dispersion and molecular dynamics simulation suggest that PHAGNRs are highly stable and might be able to exist in experiment. Lots of interesting properties arise because of the further quantum confinement and the new emerging edge states of ribbons. For example, PHAGNRs can be a nonmagnetic semiconductor, magnetic metal, spin-degenerate/spin-splitting semiconductors, or bipolar magnetic semiconductors, completely depending on their edge structures and the magnetic states. And also shown is that PHAGNR is an excellent magneto-electric material, whose magnetic properties are entirely tunable via electrical method. In particular, the half-metallicity can be realized for a nanoribbon by the application of a transverse electric field. As we know, the carrier mobility is a very important parameter to evaluate the electrical properties of materials for electronic application. Therefore, the carrier mobility for PHAGNRs are also investigated. The results show that they have a higher carrier mobility from ~2.9×10^3 to ~1.3×10^6 cm^2 V^{-1} s^{-1}, depending on the ribbon widths, which makes them promising for applications in nanoelectronics and optoelectronics.

2. Structure model and theoretical method

Fig. 1(a) shows the 2D phagraphene atomic structure, which consists regularly of 5-6-7 carbon atom rings [20]. To achieve PHAGNRs, there exist many crystallographic orientations for tailoring. The structural configurations for differently derived PHAGNRs are distinct discriminatively, even some of them are relatively complicated and the corresponding unit cell is too large for calculations. Here, only the PHAGNRs derived from cutting phagraphene along the x-direction are considered, as shown in Fig. 1. One can see that there are three types of different edge structures (carbon chain formations) upon such a tailoring orientation, named as A-, B-, and C-type, and denoted by red, green, and blue, respectively. Both A- and B-type edges are a mixture of zigzag and armchair shaped segments, the difference is the outward armchair shape for the A-type edge but the inward armchair shape for the B-type edge, which are indicated by the arrow in the armchair part of the ribbon edge. C-type edge is the zigzag-like edge. Based on the combination of three types of edge structures, six possible subgroups for PHAGNRs can be classified, as displayed in Fig. 1(b)–(g). According to the types of their opposite edges, we name these 1D structures as nanoribbons AA, AB, AC, BB, BC, and CC, respectively. This point is significantly different from graphene nanoribbons whose two edges always possess the same edge shape. In addition, the width of PHAGNRs, *w,* is defined as the total number of carbon chains (A-, B-, and C-type chain chains) across the nanoribbons. As example, Fig. 1(b)–(g) show nanoribbons AA, AB, AC, BB, BC, and CC with different width *w.* To avoid the existence of dangling bonds and ensuring the stability of the edge structure, we saturate the edge of the nanoribbons uniformly with hydrogen atoms. The red dashed box denotes one unit cell, namely, the smallest repeatable units of each periodical structure along the ribbon-length direction. The suppercell convergence test shows that such one unit cell is suitable for calculations in this work.

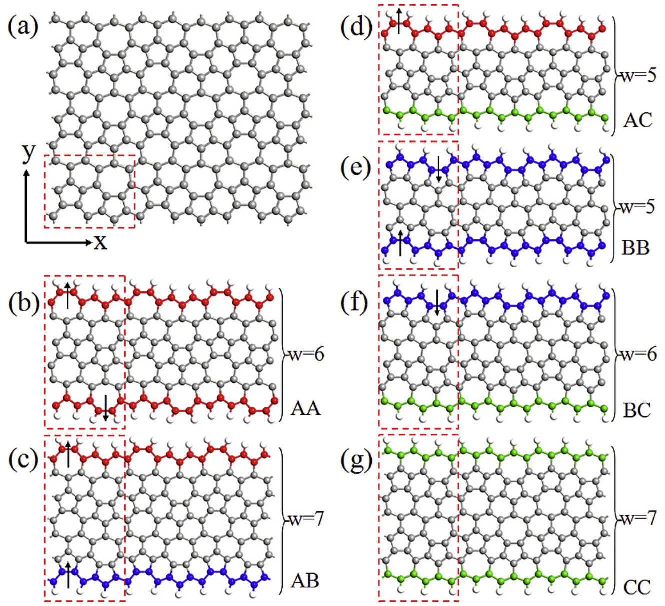

Fig. 1. Structural models. (a) Schematic of 2D phagraohene. Tailoring it along the x-direction, six typical nanoribbons are achieved, which are denoted as (b)AA, (c)AB, (d) AC, (e)BB, (f)BC, and (g)CC, respectively. The rectangular red box denotes one unit-cell of the nanoribbons, and *w* stands for the width of nanoribbons. (A colour version of this figure can be viewed online.)

To study the structural stability, magneto-electronic properties and carrier mobility of the nanoribbon structures, the ATK (Atomistix ToolKit) software package based on the first-principles method of density functional theory is adopted [32–35]. The spin-dependent generalized gradient approximation (SGGA) is selected as exchange correlation potential and the valence electron state is expanded by the local orbitals to solve the Kohn-Sham equation. Considering the influence of the atom polarization, the wave function was expanded by using the DZP (double ζ + Polarization) basis for all atoms, and $1 \times 1 \times 300$ k-point sampling in one-dimensional Brillouin zone are selected for x, y, and z direction, respectively, where the z axis is the direction of nanoribbon length. The energy cut-off is taken as 150 Ry to control the real space integral network partitioning and solving the Poisson equation for the balance of calculation efficiency and accuracy, The quasi-Newton method is used to optimize the geometrical model, and the residual stress between each atoms is reduced to less than 0.01 eV/Å, the nanoribbons with different widths are studied respectively. The interaction between adjacent nanoribbons was eliminated by using a vacuum layer at least 15 Å. For simplicity, the Fermi level was set to zero in all the ribbon systems.

3. Results and discussions

3.1. Structural stability

After optimization, all atoms, including carbon and edge hydrogen atoms, in various PHAGNRs stay the same plane. To assess their energetic stability, we calculate the binding energy $E_{BE,}$ defined as $E_{BE} = (E_{NR} - n_C E_C - n_H E_H)/(n_C + n_H)$, where E_{NR} denotes the total energy for one unit cell, E_C (E_H) and n_C (n_H) are, respectively, the energy of one isolated C (H) atom and the number of corresponding atoms in one unit cell. The obtained results for AA, AB, AC, BB, BC, and CC, respectively, with width w = 6, 4, 5, 5, 6, and 4 are summarized in Table 1. Clearly, all the binding energies fall between −8.93 and −9.62 eV per atom, with the highest value for nanoribbon AB and the lowest one for nanoribbon BB. According to the definition, the negative binding energy suggests that the corresponding structure is energetically favorable, and the lower value means more stable structure. Therefore, all nanoribbons are highly stable. For comparison, we also calculate the binding energy of the zigzag graphene nanoribbons (ZGNRs) with the width w = 6, it is −9.51eV per atom. Obviously, the binding energy for PHAGNRs is