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Electronic band structure of carbon honeycombs

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ABSTRACT

In this article, we present the electronic properties of various carbon honeycombs (C-honeycombs) with different cell sizes and junction types based on *ab initio* calculations. Among the three typical C-honeycombs with junctions connected via the zigzag edge, the armchair edge, or the hybrid edges of graphene nanoribbons, it is found that the zigzag C-honeycombs and the hybrid ones exhibit metallic properties. However, the armchair C-honeycombs are metallic only if the number of atomic planes N of the graphene nanoribbon in the C-honeycomb sidewall follows $N = 3p+1$, with p as an integer and are semiconducting for other N. For those semiconducting ones, the bandgap of the C-honeycomb is about 1.19 eV with the narrowest sidewall (5.2 Å) and monotonically decreases to about 0.15 eV when the width is increased to 34.8 Å. The semiconducting nature of such C-honeycombs with nanometer size pores may be used for lightweight semiconductor in electronic devices or supercapacitor energy storage. As a comparison, we show that all boron honeycombs are metallic, and their electronic properties are independent of sidewall widths.

Graphene has extremely high strength [1], high electrical and thermal conductivity [2,3], and many other appealing physical and chemical properties [4]. Owing to its nature with zero bandgap [5], different strategies have been proposed to open the electronic bandgap of pristine graphene. For example, the substrate-induced bandgap opening method [6,7] and tensile straining [8] may lead to a small bandgap in pristine graphene. By cutting large-area graphene into nanoribbons, distinct electronic properties were observed in contrast to the pristine graphene sheets. Further studies indicate that both the edge-type and ribbon width may affect the electronic properties of graphene nanoribbons (GNRs) [9–17]. The bandgap is a primary effect of large number of defects in such GNRs. Indeed, grain boundaries in polycrystalline graphene could also introduce a small bandgap per the first principle calculations [9–17]. With the success of carbon honeycomb (C-honeycomb) synthesis [18] and the identification of stable three-dimensional (3-D) structures [19,20], it would be of interest to examine the electronic properties of those stable 3-D C-honeycombs constructed by graphene sheets of different chirality since they inherit both the GNR structures and the grain boundary defects. In this article, we show how the sidewall width and junction type may influence the electronic properties of C-honeycombs. Borophene is another two-dimensional material, which might form honeycomb structures as well. Here, we also study the electronic properties of boron-honeycombs (B-honeycombs) and compare them with C-honeycombs.

As detailed in the study by Pang et al [19], a C-honeycomb is composed of GNRs by forming junctions with hybrid sp^2 and sp^3 bonding. Stable zigzag GNRs form 5-5-8 junction of C-honeycomb (ZZ-CH), while the armchair GNRs form 6-6-6 junction of C-honeycomb (AC-CH). A hybrid C-honeycomb structure, with alternative 5-5-8 junction and 6-6-6 junction can also be formed. Two types of combination, with sp^2 bonding in the sidewall and sp^3 bonding in the junction exist not only in the zigzag and armchair C-honeycomb structures but also in the hybrid structures. To analyze how the bonding hybridization may influence the electronic properties, we denote the junction atoms (in red color) as C1 and the sidewall atoms (in blue color) as C2, as shown in Fig. 1a.

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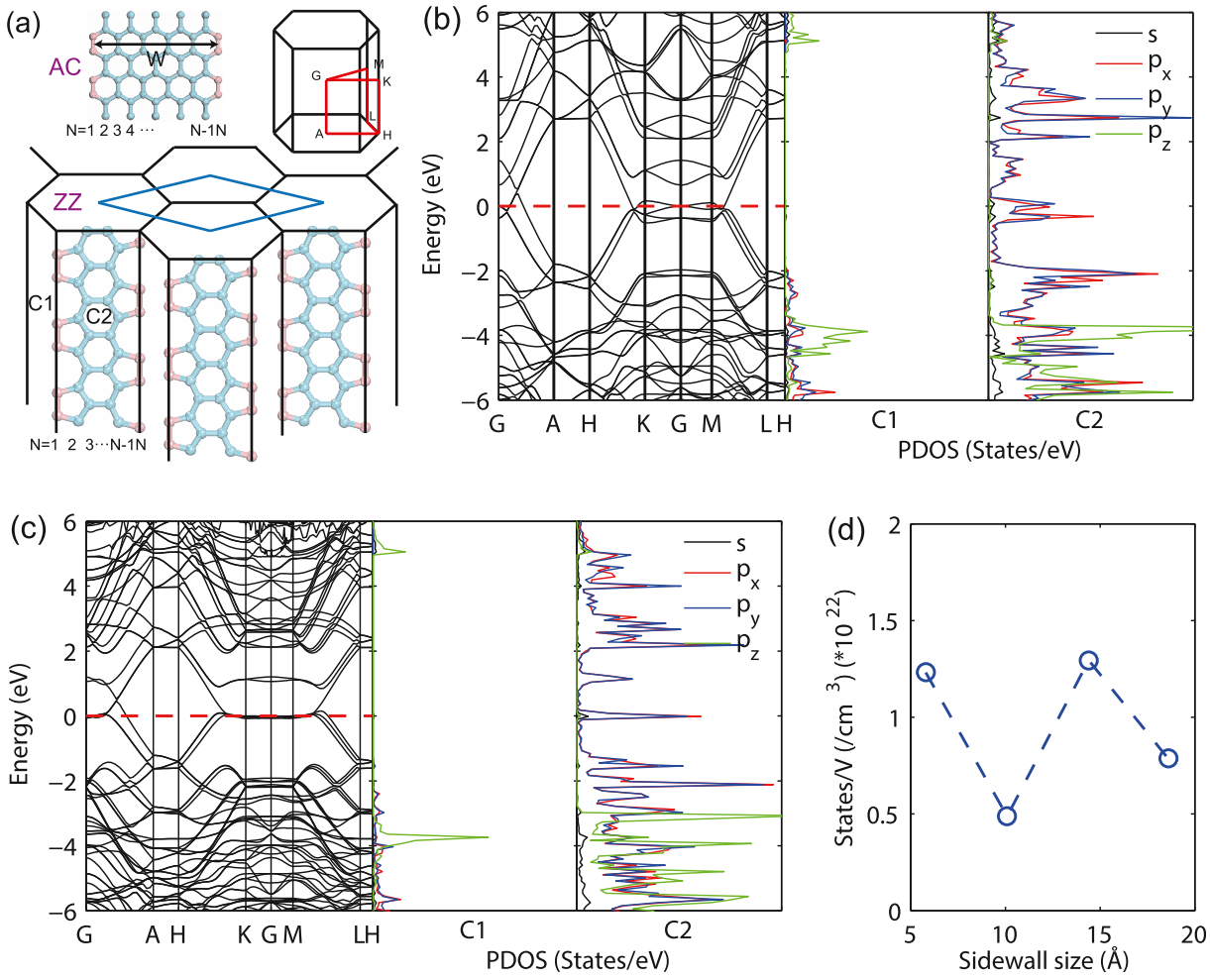

Fig. 1. Electronic band structure of zigzag C-honeycombs of different sizes. (a) Atomistic structure of sidewall in ZZ-CH and AC-CH. The inset at the top-right corner is the first Brillouin zone used to present the electronic band structures. Electronic band structures ($E-E_F$) and projected density of states of different kinds of atoms in the zigzag C-honeycombs with different sidewall widths: (b) 5.8 Å; (c) 10.1 Å. (d) States of the Fermi level average in the volume as a function of sidewall size. PDOS, projected density of states.

As illustrated in Fig. 1a, the size of C-honeycombs is identified by the width of the sidewall which is a GNR. The width W of a GNR is obtained as

$$W = \frac{(N-1)\sqrt{3}}{2}a_0 \tag{1}$$

for GNRs with armchair edges along the ribbon direction (armchair GNRs), and

$$W = \left(\left[\frac{N}{2}\right] + \frac{1}{2}\left[\frac{N-1}{2}\right]\right)a_0 \tag{2}$$

for GNRs with zigzag edges along the ribbon direction (zigzag GNRs), where N is the number of atomic planes of the graphene ribbon, and a_0 is the length of C-C bonds. The bracket [x] in Eq. (2) represents the integer function, which means the largest integer smaller than x.

We use the Vienna *ab* initio simulation package [21,22] to calculate the electronic band structures. Calculations are based on the projector augmented wave pseudopotentials [23] and the generalized gradient approximation of the Perdew–Burke–Ernzerhof functional [24]. The kinetic energy cut-offs for the plane-wave basis set are 520 eV for C-honeycomb and 400 eV for B-honeycomb. A 3×3×6 Monkhorst–Pack k-mesh is used for the reciprocal space of a primitive unit cell of ZZ-CH and AC-CH (width $W < 20$Å others, the atomic force convergence bar is set as $1e^{-2}$ eV/Å). The stability calculation of the hybrid C-honeycombs is completed by phonon dispersion analysis using the supercell method by Phonopy package [25]. The system is relaxed by setting the atomic force to be $1e^{-5}$ eV/Å to satisfy the required accuracy in phonon dispersion calculations.

We show in Fig. 1, the electronic band structures of ZZ-CHs of different sidewall widths. It is rather obvious that ZZ-CHs are metallic. To understand the origin of these electronic properties, we calculated the projected density of states of two types of carbon atoms (C1 and C2). As shown in Fig. 1b and Fig. 1c, there is negligible contribution from C1 atoms to the density of states (DOSs) around the Fermi level. Major contribution comes from the $2p_x$ and $2p_y$ orbitals in C2 atoms. These two projected DOS contribute equally to the metallic property. The band structures of the ZZ-CH with the sidewall width 10.1 Å (Fig. 1c) resemble those in GNRs [16,17] but differ greatly from that of the zigzag nanotubes [26]. These electronic band structures indicate that there will be a peak at the Fermi level for ZZ-CHs. The electrical conductivity is mainly dominated by the DOS $3k_BT$ close to the Fermi level, where k_B is the Boltzmann constant and T is the temperature in Kelvin. Fig. 1d shows the average electronic density (per atom) in those C-honeycombs. Although carrier concentration does not change