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Spin and band-gap engineering in zigzag graphene nanoribbons with methylene group

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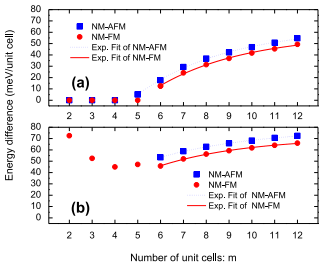
HIGHLIGHTS

- Zigzag graphene nanoribbons with different side-attached CH_2 groups exhibit various magnetic states.
- The CH_2 group saturates both σ and π bonds of ZGNRs, and thus opened the band-gap of them.
- The CH_2 group enhances the stability of the zigzag ZGNRs.
- Zigzag ZGNRs with side-attached CH_2 groups could be useful to design magnetic nano-devices.

GRAPHICAL ABSTRACT

The energy difference between different magnetic states for ZGNR with CH_2 attached at different sides.



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ABSTRACT

First-principles calculations have been used to investigate electronic and magnetic properties of zigzag graphene nanoribbon (ZGNR) with side-attached CH_2 groups. The CH_2 suppressed the magnetic states of pristine ZGNR within 12 Å. As the relative amount of CH_2 decreases, the ZGNR with CH_2 pairs located at each edge experiences a transition from a nonmagnetic state to an anti-ferromagnetic one. The energy gap opens in the nonmagnetic state. When only systems with a CH_2 attached at one edge, they exhibit ferromagnetic or ferrimagnetic states depend on number of CH_2. The CH_2 group saturates both σ and π bonds of ZGNR, and thus opens the band-gap of ZGNRs and enhances the stability of the ZGNRs. Therefore, the ZGNR provide a wide range of possible electronic and magnetic properties based on the same ribbon structure but different sites and numbers of CH_2 groups.

1. Introduction

Carbon nanostructures have unique properties that make them interesting materials from the point of view of fundamental physics and as potential candidates for applications in nanotechnology [1–3]. The case of magnetism in these compounds is illustrative; under certain conditions, magnetic ordering has been predicted to occur even in the absence of transition metal impurities. These conditions involve situations in which electronic localization takes place, such as at zigzag edges or defects in graphene sheets and ribbons [4–7]. Among them, zigzag-edged graphene nanoribbons (ZGNRs) have edge localized states, which lead to spin-polarized states and open a band gap [8]. Such ZGNRs have attracted particular attention. Theoretical studies have shown that the spins on each edge are ferromagnetically coupled but antiferromagnetically coupled between two edges [9,10]. A number of spintronics applications have been suggested based on the spin control of the edge states by using transverse electric field [2,11,12], magnetic field [13], and chemical decoration at the edges [14–17].

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In addition, it is well-known that the intrinsic properties of GNR depend on their sizes and edge shapes. Distinguished by the directions of the cutting edges, two unique types of edges can be obtained: zigzag and armchair [18]. The size of the energy gap of a GNR was found to depend on the width of the ribbon and the hydrogen passivation on edges [19,20]. However, the width of controllable path has no influence on the spin of ZGNRs, and the armchair GNRs are nonmagnetic. GNRs combined with the nature of zigzag and armchair edge maybe arise some novelties in electronic structure and magnetic properties [21–23]. According to theoretical calculations, the zigzag-armchair GNR heterojunctions converted from nonmagnetic semiconductors into magnetic semiconductors by increasing the length of zigzag segments. Therefore, for GNR heterojunctions, it suggests that armchair segment will not affect the electronic and magnetic properties of zigzag GNR [21]. These results imply that magnetic properties of the heterojunctions engineering are limited by the size of zigzag length.

In this paper, using first-principles methods, we demonstrate that radical CH_2 groups can tune the electronic and magnetic properties of ZGNRs by controlling the length of zigzag unit cells and the sites adsorbed by CH_2. These carbon nanostructures in our study can be considered as CH_2 groups attaching ZGNR or ZGNRs heterojunctions as shown in Fig. 1. As the length increases, we find that the system with one CH_2 pair located at each edge experiences a transition from a nonmagnetic state to the antiferromagnetic state. Only the system with a CH_2 attached at one edge shows ferromagnetic or ferrimagnetic features, while the energy gap opening in nonmagnetic state. The diversity of the electronic and magnetic properties of ZGNRs with CH_2 radial can be used to develop electronic and spintronic devices in future.

2. Computational details

All results presented here were performed using the SIESTA package [24] which employs norm-conserving pseudo-potentials and linear combinations of atomic orbitals as basis sets. The wave function was expanded with double-ξ polarized (DZP) basis set and the exchange correlation potential was generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) [25,26]. The numerical integrals were performed on a real space grid with an equivalent cutoff of 200 Ry. In order to eliminate the interaction between adjacent ZGNR, a slab with vacuum layer larger than 12 Å was used. A periodic boundary condition was set along x direction and the Brillouin zone was sampled by a $20 \times 1 \times 1$ k-point grid. Each configuration was fully relaxed to reach the force tolerance of 0.01 eV/Å.

Following the customary notation to describe ZGNR, the model denoted as (m, n)-ZGNR, where m and n are the numbers of rows and columns across the ZGNR length and width, respectively. Here we choose the (m, 8)-ZGNR as the prototype models and simply name them as m-ZGNR, as shown in Fig. 1. To illustrate the effect of CH_2 groups, two types of CH_2 function have been considered: one is the m-ZGNR with a couple of CH_2 attached at each edge with mirror symmetry, labeled as P_m, and the other is the m-ZGNR with a CH_2 located at one edge, marked as T_m. As an example, the optimized structure of P_5 is given in Fig. 1(a). In this model, the CH_2 groups parallel to the ZGNR plane and the dangling bonds of the ZGNR completely are saturated by H atoms. We also considered another highly symmetric case that is the CH_2 vertical to ZGNR plane. After full relaxation, the energy of the vertical structure is larger than the parallel model by 4.0 eV, indicating the parallel structure is more stable than the vertical structure. In order to avoid direct interaction between the CH_2 groups, the number of the unit cell (m) is greater than or equal to two cells.

3. Results and discussions

First, we performed calculations for various magnetic states, including nonmagnetic (NM), anti-ferromagnetic (AFM), and ferromagnetic (FM) states. The energy difference between the NM state and the magnetic states, namely, AFM and FM states, and between the AFM state and FM state, as shown in Fig. 2. The results for configurations P_m and T_m are presented in Fig. 2. We found that the energy difference is zero in the range of $2 \leq m < 5$, and the ZGNR with CH_2 on both sides becomes NM. Consequently, the model of $m=5$ is critical case where the system transits from the NM state to AFM or ferromagnetic state. Increasing the m, the energy of AFM state is lower compared to the corresponding FM state in P_m models, suggesting that AFM is always the ground state for long length system. As shown in Fig. 2(b), the FM state is occurs in T_m models in the range of $2 \leq m \leq 5$. We find the initially constructed AFM state finally converges to the FM state upon optimization, and the energy difference between NM and FM state

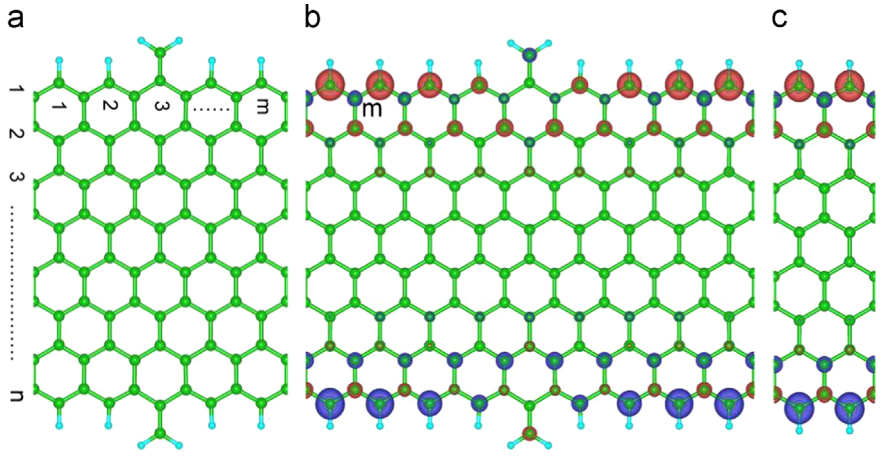

Fig. 1. Structures of ZGNRs (a) with two side-attached CH_2 groups ($n=8$, $m=5$), (b) with two side-attached CH_2 group ($n=9$, $m=5$), and (c) without CH_2 group. Big and small sapphire balls denote carbon and hydrogen atoms, respectively. The n and m are the width and length of ZGNR, respectively. The blue and wine isosurfaces show the up and down-spin densities, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)