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Theoretical exploration of the half-metallicity of graphene nanoribbons/boron nitride bilayer system

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ABSTRACT

The geometrical and electronic structures as well as stabilities of zigzag GNR (ZGNR) stacked on zigzag BN nanoribbon (ZBNNR) or BN sheet have been theoretically studied at the DFT-LDA level for the first time. It is shown that the most stable structure for 4-GNR/5-BNNR is AB (boron) stacking configuration with equilibrium distance at 0.320 nm and formation energy (E_f) at −605.39 meV. At the same time, the ZBNNR changes the ZGNR from spin-degenerated semiconductor to spin-polarized semiconductor with the up- and down-spin gaps of 0.38 and 0.28 eV, respectively, due to the spontaneous polarization of ZBNNR. Most importantly, we found that the band structures of ZGNR on ZBNNR or BN sheet can be tuned into half-metal simply by two methods including applying appropriate vertical electric field and interlayer compression due to the enhanced interlayer polarization and significant changes in the charge densities at the edge atoms of ZGNR. Correspondingly, the calculated critical electric fields from semiconductor to half-metal are 2.11 and 1.70 V/nm for 4-GNR/5-BNNR and 4-GNR/BN sheet, respectively, which are smaller than that of 2.31 and 1.80 V/nm for the ZGNRs sandwiched between BNNRs or BN sheets at the same PWC/DNP level of theory. Note that the interaction between ZGNRs and ZBNNRs can be significantly enhanced under the appropriate vertical electric field. The calculated critical interlayer distance of compression-induced semiconductor-to-half metal transition for 4-GNR/5-BNNR is 0.245 nm. Moreover, it is shown that the wider stacking system can realize its half-metallicity more easily. These findings may provide new ways in fabricating new spintronic devices that are compatible with the current technology of the semiconductor industry, and may be helpful for the synthesis of nanoelectronic devices experimentally.

1. Introduction

Graphene, as a single layer of graphite, has attracted considerable research interests owing to its novel thermal, mechanical and electrical properties [1–12], such as massless Dirac Fermion behavior [4,5], high electron mobility [2,9], excellent thermal conductance [11,12], and the largest strength [8]. The two- dimensional (2D) graphene sheet itself is a semimetal, when it is cut into long rectangle slices, namely the graphene nanoribbons (GNRs), it can exhibit markedly different properties from graphene [13–21]. Theoretically, it has been predicted that H-terminated GNRs with either armchair or zigzag edges have non-zero band gaps [13–15], which has been experimentally confirmed [18,19]. It is shown that the armchair GNRs (AGNRs) are nonmagnetic, while the ZGNRs are magnetic because the localized edge states are ferromagnetically ordered at each edge but antiferromagnetically coupled between the two edges [13,14,17,20,21].

Great endeavors have been made, both experimentally and theoretically, on functionalizing ZGNRs to tune the electronic and magnetic properties of pristine ZGNRs for their applications for multi-functional nanodevices [14,22–45]. Among these, the most intriguing discovery is probably the realization of half-metallic behaviors in ZGNRs. Generally, half-metallic materials hold the promise for spintronic applications [23–26,34–37], such as spin filter, memory devices and computer processors [46,47] due to one channel of electron spin is semiconducting or insulating, while the other one is metallic. It is theoretically found that an electrostatic potential difference will be generated between the two ZGNR edges with an external electric field across the nanoribbon width,

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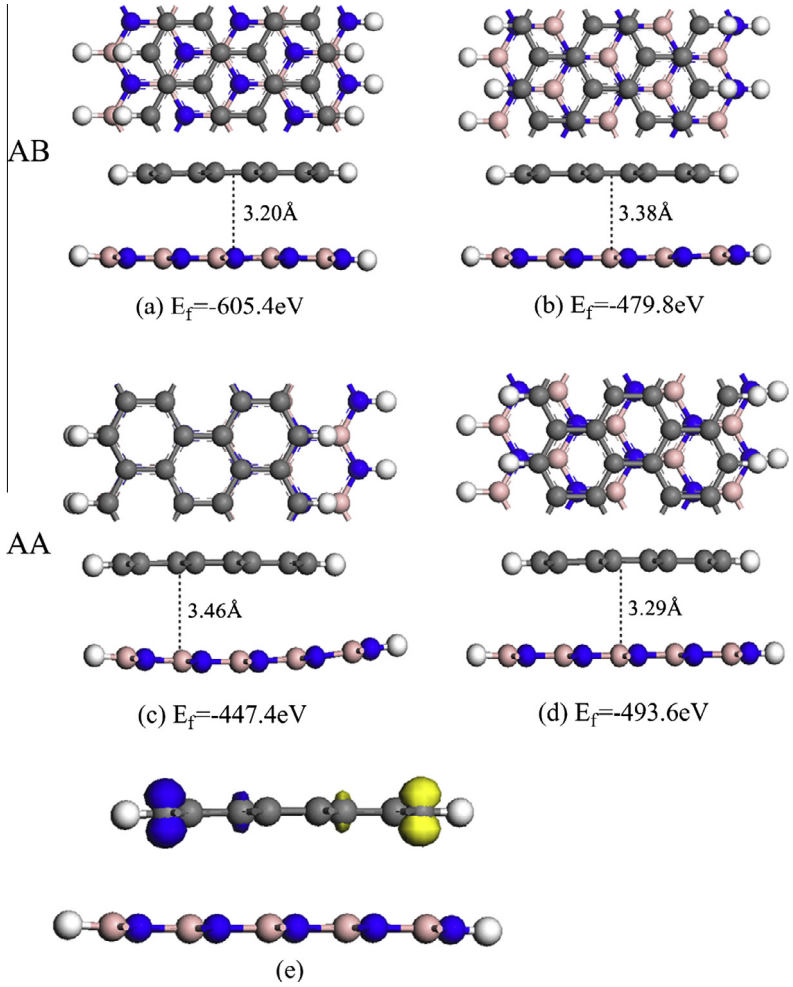

Fig. 1. Top and side view of the optimized geometrical structures and formation energies (E_f) of four stacking patterns including (a) AB (boron) (b) AB (nitrogen) (c) (AA-I) and (d) (AA-II) for the 4-GNR/5-BNNR. (e) The spatial spin distribution of the 4-GNR/5-BNNR in AB (boron) stacking configuration. The isosurface level is set to 4.2 e nm^{-3}. Note that the pink, blue, gray and white balls represent boron, nitrogen, carbon and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which converts the ZGNR to half-metal from semiconductor [14,26,48]. However, in contrast to the technology of widely applied bias voltage, the required transverse potential difference for the half-metal transition increases rapidly with increased ribbon width, thus its realization is challenging. To circumvent this difficulty, many alternative routes have been proposed theoretically to break the symmetry of the two edge states of the ZGNR, such as being chemically edge functionalized [22–24,27,34] or embedded in a polar boron nitride (BN) sheet to form hybrid systems [22,25,45]. Furthermore, some appealing properties of graphene/boron nitride stacking structures have also been reported, such as tailored band gaps [33,42] and superior capacitor properties [49,50]. It is especially recognized that graphene supported on a hexagonal boron nitride (h-BN) substrate exhibits much higher mobility compared to any other substrate [30,39]. Kan et al. [51] pointed that the symmetry of the ZGNR band structure near the Fermi energy can be broken by introducing a segment of BNNR. Yu et al. [52] recently have demonstrated that ZGNRs sandwiched between ZBNNRs or BN sheets can be tuned into half-metal simply by a bias voltage or a moderate compressive strain. However, to the best of our knowledge, no study can be found on the configurations, stability, and half-metallicity for the similar but much simpler bilayer stacking structure, that is, just the monolayer ZGNR stacked on ZBNNR or BN sheet.

Therefore, it is natural for us to raise the following questions: (1) what are the geometrical and electronic structures of ZGNR stacked on ZBNNR or BN sheet? (2) how about the stability of such stacking systems? (3) could we tune such stacking systems into half-metal by applying electric field even interlayer compression? If so, what are the critical values for electric field and interlayer compression? Surely, without systematic theoretical calculations, we cannot answer the above questions. So, we decide to perform quantum chemistry calculations to answer above questions about the unknown bilayers of GNR/BNNR and GNR/BN sheet based on density functional theory (DFT).

2. Computational methods

All geometry optimization and electronic structure calculations are based on spin-polarized DFT as implemented in the DMol^3 code [53,54]. The local density approximation (LDA) with the Perdew–Wang (PWC) method is utilized as the exchange–correlation functional with the double numerical plus polarization (DNP) [54] basis set [55]. Although neither LDA nor generalized gradient approximation (GGA) functional fully accounts for van der Waals (vdW) interactions, the LDA has been proven to perform well for the adsorption of weakly bound systems [56]. Moreover, it has been shown that the LDA calculation for the band gap of bilayer