First-principle Studies of armchair graphene nanoribbons

N. M. Wang, G. J. Zhao, X. X. Liang and T. L. Song
Department of Physics, School of Physical Science and Technology, Inner Mongolia University, Hohhot, 010021, P. R. China

E-mail address: stzhaogj@imu.edu.cn

Abstract. In this article, by using the first principle calculations based on the density functional theory, we present a detailed investigation of the energy band and density of states of armchair graphene nanoribbons (AGNRs) with bare and H-terminated edges. Based on the structural optimization results, we compute the energy band and density of states of considered nanoribbons. The results show that there is a direct band gap for bare and H-terminated edges AGNRs, and indicate AGNRs have semiconductor properties for both cases our calculated. There are localized states turns up at -2.520eV for the case of bare edges, after modification of hydrogen atoms, the localized states disappeared, the band gap is widened form 0.535eV for the bare edges to 0.722eV for H-terminated edges, at the same time, and the energy band degeneracy appeared.

1. Introduction

From the end of the 20th century, carbon-based materials have attracted researchers attentions, due to their unique structural and physical properties[1, 2]. Graphene is one of them, it is a monolayer honeycomb lattice of sp2-bonded carbon[3]. Because of the unique properties, graphene has the potential application in many fields. And it is an important on nanoelectronics and renewable energy storage[4]. However, researches focus more on graphene nanoribbons (GNRs). The graphene nanoribbon is a related type to carbon based quasi-one dimensional systems. According to the feature of edge, the GNRs include zigzag edge graphene nanoribbons (ZGNRs) and armchair edge graphene nanoribbons (AGNRs) [5]. Armchair edged (AGNRs) show semiconductor behaviour, and all zigzag edged (ZGNRs) are known to be metallic [6]. GNRs intrinsically have dangling bonds at the edges, and thus cause instability and reduce carrier mobility. Usually, a carbon atom on the nanoribbon edge is terminated by H atom which is used to be a termination[7]. The structural and electronic properties of F-terminated GNRs with different widths are investigated using density functional theory by Lu D B *et al*[7]. They found that the band gaps for the F-terminated AGNRs are smaller than those of the H-terminated AGNRs. Jaiswal N K and Srivastava P studied the electronic properties of bare and

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H-terminated ribbons using *ab-initio* approach[8]. It found that H-termination enhances the stability and band gap of nanoribbons whereas dangling bonds in bare ribbons reduce the band gap.

In this paper, we investigate the electronic energy band and density of states of bare AGNRs and H-terminated AGNRs, using first principle calculations based on density functional theory.

2. Modeling and computational details

In the calculations, we employ the local density approximation (LDA) within the Perdew-Zunger exchange correlation functional. In order to achieve accurate results, the plane-wave cut off energy was set to 135Ry, with 540Ry for the charge density. The numerical integration of the Brillouin zone (BZ) was performed using a k-mesh of dimensions 1×1×21. The periodic boundary condition of nanoribbons was maintained along the *z* axis. In order to neglect the interaction of ribbon with its periodic images, a vacuum padding of 6.8Å and 20Å was also modelled along x and y axis. The modeling was done with XCrySDen [9]. Figure 1(a) shows the bare AGNRs model.The C-C bond length is 1.42Å for experiment value of bare AGNRs. Figure 1(b) shows the H-terminated AGNRs model. All calculations are implemented by using the code of Quantum ESPRESSO[4].

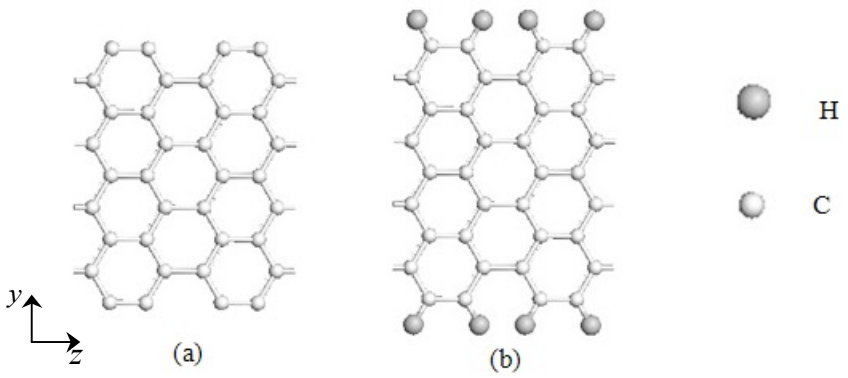


Figure 1. Schematic diagram of AGNRs figurations: (a) bare AGNRs; (b) H-terminated AGNRs.

3. Results and discussion

The total energies of bare and H terminated AGNRs are calculated by using self-consistent calculation, we found that the total energy of H terminated AGNRs is lower than the bare AGNRs. It can be predicted that H terminated AGNRs is more close to the practical situation than bare AGNRs. This conclusion is similar to other theoretical calculations [8].

The energy band structures of bare AGNRs and H-terminated AGNRs are presented in Figure 2. Figure 2 (a) show that the bare AGNRs and H-terminated AGNRs are all direct band gap semiconductor with energy gap of 0.535eV and 0.722eV respectively. These results are different with early work by Wang and Zhao[3]. In that work, the bare AGNRs is an indirect band gap semiconductor with 1.58eV band gap and H terminated AGNRs is a direct band gap semiconductor with 1.68eV band gap. The band gap of H terminated AGNRs is enhanced due to elimination of the dangling bonds which is unstable.

It can be see that, for the bare AGNRs, there are localized states turns up at -2.520eV, but localized states despaired, and the energy band degenerate from the conduction band at 1.439ev and 1.807eV for H terminated AGNRs. This is due to the dangling bonds in bare AGNRs.

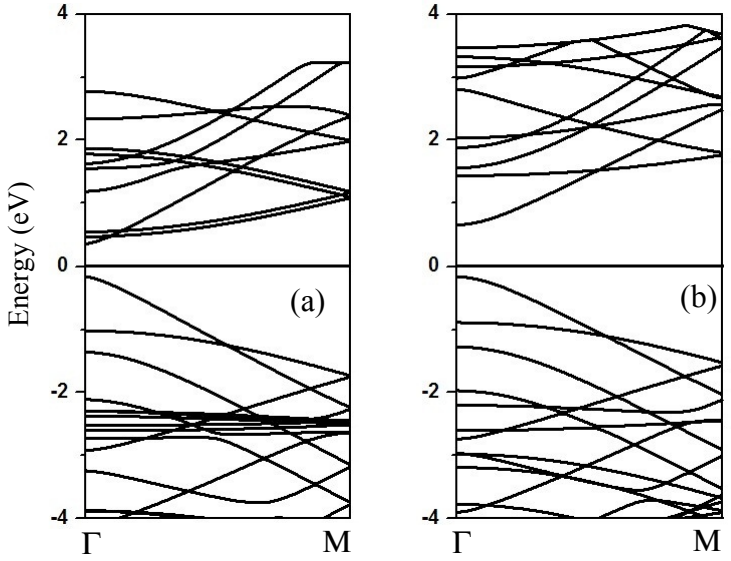


Figure 2. Calculated band structures of AGNRs: (a) bare; (b) H-terminated.

In order to understand the distribution of electronic states and the contribution of individual atomic orbitals, we calculated the total density of states(DOS) and the projected density of states(PDOS) near the Fermi level as shown in Figure 3, the Fermi level is located at 0eV.

Figure 3(a), the localization state at -2.52 eV for bare AGNRs is caused by the C-2p electronic states due to dangling bonds. The peak of total DOS appeared at around -2.568eV. From Figure 4(a), we can see that C-2p states mainly dominate at the top of the valence bands and the conduction bands.

For H-terminated AGNRs, the DOS and PDOS indicates that C-2p electrons and H-1s states contribute to the lower valence-band and conduction band. At the same time, by modification of hydrogen atoms, localized states are disappeared and the structure is more stable.

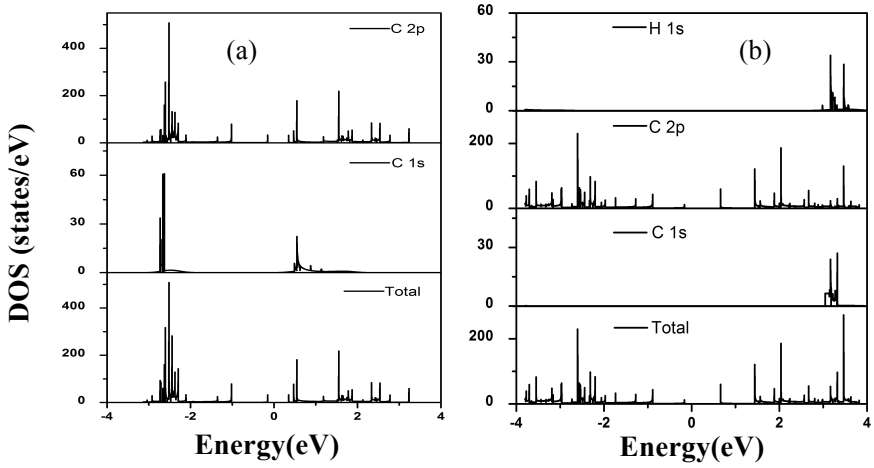


Figure 3. Total and projected density of states of AGNRs: (a) bare; (b) H-terminated.

4. Conclusions

In this article, we compute the energy band and density of states of considered nanoribbons for bare and H-terminated. It is revealed that the H terminated has the lowest total energy. Both bare and H-terminated AGNRs are direct band gap semiconductors. After modification of hydrogen atoms, the localized states disappeared, the band gap is widened form 0.535eV for the bare edges to 0.722eV for H-terminated edges, at the same time, and the energy band degeneracy appeared.

5. Acknowledgments

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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 Science **306** 666

[2] Hass J, Feng R, Millan-Otoya J E, Li X, Sprinkle M, First P N, de Heer W A, Conrad E H, Berger C 2007 Phys. Rev. **B75** 214109

[3] Wang W H, Zhao G Z 2013 Solid State Commun. **166** 6

[4] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, et al, 2009 J.Phys.:Condens. Matter, 21, 395502

[5] Jia X T, Campos-Delgado J, Terrones M, Meunier V, Dresselhaus M S 2011 Nanoscale **3** 86

[6] Chauhan S S, Srivastava P, Shrivastava A K 2013 Solid Stat Commun. **154** 69

[7] Lu D B, Song Y L, Yang Z X, Li G Q 2011 Appl. Surf. Sci. **257** 6440

[8] Jaiswal N K, Srivastava P 2011 Physica **E44** 75

[9] Kokalj A, 2003 Comp. Mater. Sci. **28** 155