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Engineering the electronic structure of zigzag graphene nanoribbons with periodic line defect

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ABSTRACT

By using first principle calculations we have studied the magnetic, electronic and transport properties of zigzag-graphene nanoribbon (zGNR) with a topological line defect (LD) composed of pentagons and heptagons (5-7). We show that one can engineer the magnetic and electronic properties of the edge passivated zGNR with 5-7 LD through the variation of either the width of the zGNR or the position of the LD. Thus, one can have ferromagnetic behaviour in zGNR by introducing 5-7 LD close to one edge of the ribbon. One can tune the zGNR with 5-7 LD from semi-metallic to semi-metallic semiconductor either by increasing the width of the ribbon or by changing the position of the LD. We have also studied the effect of the doping on the degeneracy of the spin states of 4-4-LD-zGNR. The calculation of transport properties of N-doped 4-4-LD-zGNR reveals that it has high spin filtering efficiencies. The tuning of the spin polarization through the formation of 5-7 LD in zGNR holds a promise for its application in spintronic devices.

1. Introduction

Graphene [1] is an infinite two dimensional single atomic layer of graphite composed of sp^2 hybridized carbon atoms, arranged in honeycomb-like hexagonal lattice. In the last few years, graphene has become an exciting area of research due to its novel physical [2], electronic [3], thermal [4] and mechanical [5] properties. Graphene shows its pertinence in spintronics and nanodevice application [6–8] owing to these properties. Despite intense interest, application of graphene in many fields gets restricted due to its lack of band gap.

The opening of band gap has found when graphene is patterned into a quasi-one-dimensional ribbon. Depending on the edge type, graphene nanoribbons (GNR) are classified as zig-zag GNR (zGNR) and armchair GNR (aGNR) [9,10]. Edge orientation shows considerable ascendancy on the electronic [11–13] and magnetic properties [14–16] of GNRs. aGNRs are nonmagnetic-semiconductors [17,18] whereas, zGNRs exhibit semiconducting property in antiferromagnetic ground state [19] where edge carbon atoms within the same edge are ferromagnetically coupled, but they are coupled antiferromagnetically across the edge [20]. zGNRs exhibit zero magnetic moment as well as degenerate spin states. As a result applicability of zGNR in spintronics device [21–23] is limited. Several techniques such as application of electric field/magnetic field [19,24,25], chemical doping [26–28] etc. have been used to tune the magnetic properties and lift the degeneracy of up and down spin states of zGNRs. In this context, the lattice imperfections such as structural defects [29,30], which may appear during crystal growth, can alter the electronic and magnetic properties significantly.

The insertion of defect, which is periodically repeated along periodic direction i.e. line defect within perfect zGNR has been the subject of recent interest [31–40]. The interest in this direction stems from the fact that the presence of periodic line defect can lift the spin degeneracy and thus one can tune the magnetic properties of graphene nanoribbon just by introducing various kinds of line defect in graphene. Thus, Lin et al. [41] studied the edge passivated zGNR with the periodic line defect composed of one octagon and a pair of pentagons (558-defect) in one unit cell and have shown that one can tune the magnetic properties from antiferromagnetic (AFM) to ferromagnetic (FM) by varying the width of the GNRs. The zGNR with 558-line defect has been successfully synthesized by Lahiri et al. [29] through the absorption of two graphene sheets on a Ni(111) surface with respect to fcc and hcp patterns. This zGNR with 558-line defect is shown to exhibit metallic conductivity thereby suggesting the potential application of this system in spintronics. By using first principle calculation Kan et al. [42] showed that zGNR with 558-defect can be tuned from AFM to FM state by either applying uni axial strain along the periodic direction or through substitutional doping with B, N, Al or P. The first principle study of Kou et al. [43] has predicted a

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ferromagnetic ground state for graphene with topological line defect with spin polarized electrons localized within the extended line defect region. These authors have shown that the weak magnetism of this system can be greatly enhanced by applying strain along the zigzag direction but is sharply reduced when the strain is over a critical value. Very recently, by using constant temperature ab initio molecular dynamics simulation Ghosh et al. [44] have studied the 5-8-5 and 8-8-8 extended line defect in graphene, BN and hybrid(graphene and BN) NRs. Tang et al. [45] have studied the electronic and magnetic properties of hybrid boron nitride nanoribbons and sheets with 5-7 line defects. Dai et al. [46] in their study beautifully demonstrated the engineering of electronic and magnetic properties of zigzag graphene nanoribbon with 585 line defect. There are many more studies on graphene with topological line defect available in the literature [47–56]. However, most of the studies consider mainly 5-8 or 5-5-8 line defect since it has been experimentally synthesized. But it is very natural that there is possibility of other kind of line defects in graphene NRs.

In this work we have studied a particular type of periodic line defect (LD) embedded within perfect zGNR. The line defect is composed of pentagonal and heptagonal sp^2 hybridized carbon rings i.e. 5-7 defect, periodically repeated along x-direction. In this context, it is to be noted that pristine zGNR embedded with periodic pentagonal-heptagonal (5-7) edge defect is experimentally reported by Girit et al. [57]. However, our 5-7 line defect is different from that and as per suggestion of Jia et al. [58] theoretical as well as experimental exploration of zGNR with such 5-7 line defect is very much important. There are many studies reporting the different aspects of 5-7 LD in different carbon nanostructures such as quantum Hall plateaus, Fano interference, scattering etc. [32,33,59–62]. However, theoretical studies addressing the electronic structure of zGNR with 5-7 LD are still lacking. The 5-7 line defect segregates the zGNR into two parts with zigzag edges, upper and lower part with respect to LD region, respectively. We have described the zGNR with line defect as N_1-N_2-LD-zGNR, where N_1 and N_2 represent the number of perfect zigzag chains above and below the line defect region, respectively. In this paper, we first investigate the electronic and magnetic properties of different zGNRs with 5-7 line defect using first principle approaches. The variation of electronic properties of LD-zGNR is explored as a function of ribbon width as well as position of line defect within ribbon for a certain ribbon width. The effect of doping with B and N atoms on the nature of spin polarization in zGNR with 5-7 LD has been explored. Finally, we have investigated spin-transport properties of N-doped 4-4-LD-zGNR.

2. Computational methods

All first-principles calculations were performed using density-functional theory (DFT) as implemented in SIESTA package [63]. We have considered norm-conservative Troullier–Martins pseudopotentials [64] and double-ζ plus polarization (DZP) basis set for representing core and valance electrons, respectively. The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof [65] (PBE) form is applied to account for electron–electron interactions. The ribbon is periodic along the x direction and a large vacuum space is added in both y and z directions in order to avoid interaction between neighbouring cells. The conjugate gradient method is used to fully relax all the atomic positions without any geometrical constraints until the maximum force becomes less than 0.01 eV $Å^{-1}$. A real space mesh cutoff of 200 Ry is used throughout the entire calculation and the electronic temperature is set to 300 K. The tolerance for energy convergence is 0.001 eV. The k-point sampling for unit cells was performed with a $8 \times 1 \times 1$ Monkhorst–Pack grid [66], respectively. To investigate the magnetic coupling between the two edges of N_1–N_2-LD-zGNR, we have calculated and compared the energies corresponding to ferromagnetic (FM) and antiferromagnetic (AFM) states.

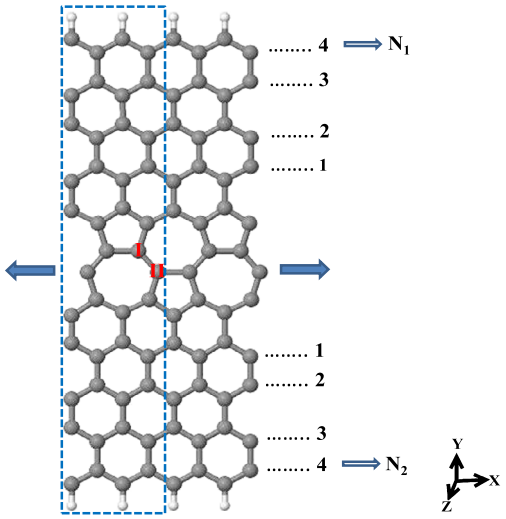

Fig. 1. Optimized structure of 4-4-zGNR with 5-7 line defect. Unit cell is represented within the box. Gray and white balls represent the C and H atoms, respectively. I and II represent two different doping positions.

The spin transport properties are simulated using the TranSIESTA module within the SIESTA package, which is based on the combination of density functional theory and non-equilibrium Green's function (NEGF) [67]. We have used the same basis functions, the exchange-correlation functional and convergence criteria as our first-principles calculation. In the NEGF self-consistent loop, the charge density was integrated over 200 energy points along the semicircle in the complex plane. We used doped ribbons as left (LE) and right (RE) electrodes thereby sand witching the central scattering region (SR) and the spin polarized current is calculated using the Landauer–Buttiker formula, which can be expressed as:

$$I_{\uparrow(\downarrow)}(V_b) = \frac{e}{h}\int_{\mu_L}^{\mu_R} T_{\uparrow(\downarrow)}(E, V_b)[f_L(E-\mu_L) - f_R(E-\mu_R)]dE. \quad (1)$$

3. Results and discussion

The optimized structure of one representative zGNR with 5-7 line defect namely 4-4-LD-zGNR is shown in Fig. 1. We first determine the geometric and magnetic properties of 4-4-zGNR with 5-7 line defect. To accomplish this we have relaxed the geometry of 4-4-zGNR with 5-7 line defect starting from both AFM and FM alignment between local magnetic moments. The geometry optimization reveals that at optimum lattice constant (l.c.) 4.9325 Å, it attains planar structure. The width of 4-4-LD-zGNR is 24.7144 Å. The line defect is composed of fused pentagon and heptagon, similar to the structure of nonbenzenoid aromatic compound azulene, which is an isomer of naphthalene. Azulene is particularly a 10 π electron system and it has aromatic property with similar peripheral bond length. Similarly, in our investigated system the average C–C bond length of pentagon and heptagon of LD is 1.45 Å, which is very close to C–C bond length (1.42 Å) in benzene. This obviously indicates the delocalization of π bonded electrons to attain aromaticity. We have modelled systems like 3-2, 3-3, 4-1, 4-2, 4-3, 5-1, 5-2, 5-3, 5-5, 6-1 and 6-2 LD-zGNRs from original relaxed structure of 4-4-LD-zGNR. The energy difference between the AFM and FM ground state (Table 1) of different LD-zGNRs shows that 4-1 zGNR is more stable in FM configuration whereas, 4-4, 4-3, 4-2-LD-zGNRs are stable in AFM configuration. Further studies, under the