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THEORETICAL INVESTIGATION OF THE ELECTRONIC PROPERTIES OF ZIGZAG GRAPHENE NANORIBBONS WITH PYRIDINE AND PORPHYRIN-LIKE DEFECTS

Michael Mananghaya

Abstract—Defects can alter the properties of zigzag graphene nanoribbons (ZGNRs). A ZGNR segment containing 120 C atoms with pyridine (3NV-ZGNR) and porphyrin (4ND-ZGNR) defects was investigated with the aid of spin-unrestricted density functional theory (DFT). It is found out that the incorporation of pyridine and porphyrin defects resulted in half metallic behavior. The formation energies and electronic properties were also reported. The results provide comprehensive strategies in obtaining well-defined N-doped ZGNRs and realizing their novel intrinsic electronic and magnetic properties in the nonodevices.

Index Terms— Binding Energy, Density Functional Theory, Porphyrin Defects, Pyridine Defects, Zigzag Graphene Nanoribbons.

1 INTRODUCTION

Single layer of graphite called graphene has attracted considerable research interests owing to its novel properties. Physical properties such as massless Dirac fermions behavior [1-5], room-temperature quantum hall effect [6, 7] and high mobility and coherence [8] open up new perspectives and future research. The two-dimensional (2D) graphene sheet itself is a semi-metal. However, when the 2D sheet is cut into rectangle slices, namely, graphene nanoribbons (GNRs), they can become one-dimensional (1-D) semiconductors with their energy band gap depending on the width and crystallographic orientation of cutting edge of the nanoribbons. The GNRs could exhibit different edge geometries including zigzag and armchair, which will determine their electronic structures. In particular, the confinement of the electronic wave functions and the presence of the edges will open a band gap, which will make them suitable for the applications in semiconductor devices. Therefore, GNRs appear to be excellent candidates for the design of novel semiconductor devices [9-20].

Several recent theoretical studies have also revealed that zigzag edged GNRs (ZGNRs) can be converted into a half metal by either applying an external electric field or through chemical modification of the edges. Half metals hold the promise for spintronic applications [18, 21-27] as the electric current can be fully spin polarized when going through half metals. This is because for a half metal, one electron spin channel is insulating while the other channel is metallic. The spin density of states of functionalized GNRs doped with nitrogen (N) atoms was calculated using unrestricted density functional theory (DFT) and it was found out that that the edge substitutions at low density do not remarkably change the band gap, whereas the bulk substitution of N atoms will promote the onset of semiconductor–metal transitions. Aside from edge substitutions N dopants can also be substituted into the C network with a vacancy formation. Porphyrin-like (labeled as 4ND) and pyridine-like defects (labeled as 3NV) are formed in ZGNR as verified through spectroscopic measurements. ZGNR decorated with NO_2 chemical function group could become half metallic [26]. Chemical modification can elevate certain spin-polarized bands crossing the Fermi level. However, the large steric interactions between neighbor groups make the system distorted. Hence, our design is mainly focused on single-atom for the chemical functionalization.

2 METHODOLOGY

The electronic properties were studied using first-principles density function theory (DFT) calculations are carried out via *Dmol*^{3} package [27-29]. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and an all-electron double numerical basis set with polarized function (DNP basis set) were chosen for the spin-unrestricted DFT computation [30] set with atomic cutoff at 5.5 Å. To simulate ZGNRs, a cuboid supercell was used with a wall-to-wall distance of at least 20 Å sufficient enough to avoid in-plane interactions between adjacent cells. For geometric optimization, the Brillouin zone was sampled by 3 k points using the Monkhorst-pack scheme [31], the forces on all atoms were optimized to be less than 0.005 eV/Å using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm.

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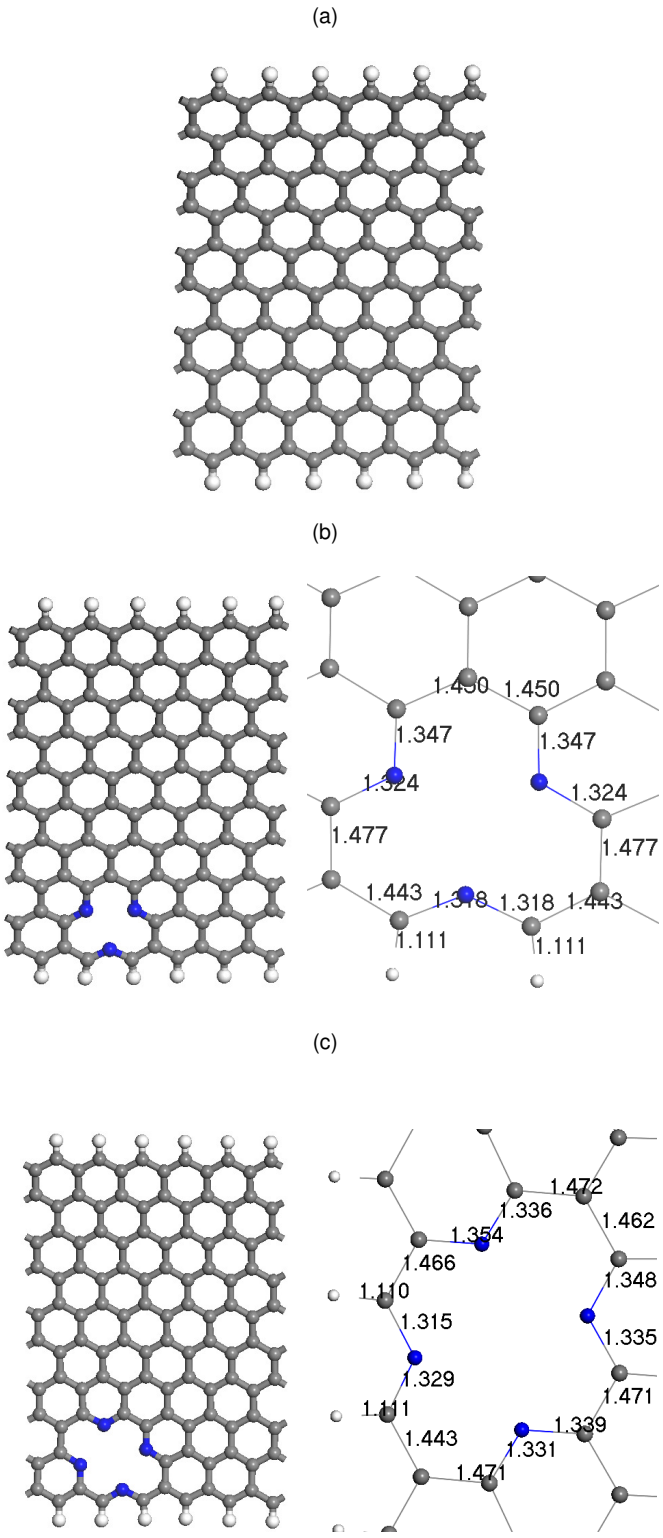

Fig.1. Optimized geometry of (a) the infinite ZGNR, (b) ZGNR with pyridine defects (c) ZGNR with porphyrine defects. Gray color depicts carbon atoms blue is Nitrogen and white is Hydrogen.

Two types of modified ZGNRs were considered: Pyridine and porphyrin defects usually occur in graphene-based systems. 3NV defect can be constructed by removing a C atom and substituting the three nearest neighbor C atoms with N atoms (3NV-ZGNR) as seen in Fig. 1(b), substitution of nitrogen dopants with vacancy formation, by removing two C atom among four hexagons and replacing the four surrounding C atoms with 4 N atoms (4ND-ZGNR) as seen in Fig. 1(c)

3 RESULTS AND DISCUSSIONS

3.1. Structure of 10-ZGNR, 3NV-ZGNR and 4ND-ZGNR

Fig. 1(a) shows the relaxed geometries of the nanoribbon, which was chosen as a typical semiconducting model for investigation. The width of the pure ZGNR was defined with the width parameter N_z of zigzag grapheme nanoribbons as the number of zigzag lines across the ribbon width, as exemplifyied by 10-ZGNR was chosen in the present work. The edge carbon atoms of the nanoribbon are all saturated with H atoms to avoid the dangling bond states. The total energies for different magnetic phases of 10-ZGNR, including nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) were calculated to determine the ground state. The total energy of the FM phase is lower than that of the NM phase but higher than that of the AFM phase. Therefore the AFM phase is the most favorable for 10-ZGNR. The results are in agreement with literature, indicating that the methods in this work are reliable to describe fully the electronic properties of ZGNRs.

Due to the two missing C atom(s), the C–N bond lengths of pyridine-like and porphyrin-like doping are determined to be ~1.318–1.347 Å (see Fig. 1(b)) and ~1.315–1.354 Å (see Fig. 1(c)) respectively, depending on the orientation, as compared to ~1.407-1.443 Å for the C–C bonds. Thus, N impurities in ZGNR s produce their own local strains and deformation.

3.2. Electronic properties of 10-ZGNR, 3NV-ZGNR and 4ND-ZGNR

The formation energies (E_f) defined as:

$$E_f = E_{tot} - n_{C(}\mu_C - n_H\mu_{H)}/120 - n_N\mu_N - n_H\mu_H, \quad (1)$$

where E_{tot} is the total energy of the 10-ZGNR with 3NV or 4ND defects, n_C n_N and n_H are the number of C, N and H atoms, respectively. μ_C is the chemical potential of C obtained from the corresponding pure 10-ZGNR, and μ_N with μ_H is the chemical potential of N, H obtained from nitrogen and hydrogen in gas phase. There are many possible configurations since the defect can exist in different locations but computation shows that the configuration with defects close to the edge is energetically favored. The formation energy of the 3NV defect is lower than that of the 4ND defect indicating that 3NV defect is more likely to form in 10-ZGNR. The calculated formation energy of the 3NV-ZGNR is on the average of 2.78 eV and 3.70 eV for the 4ND-ZGNR.

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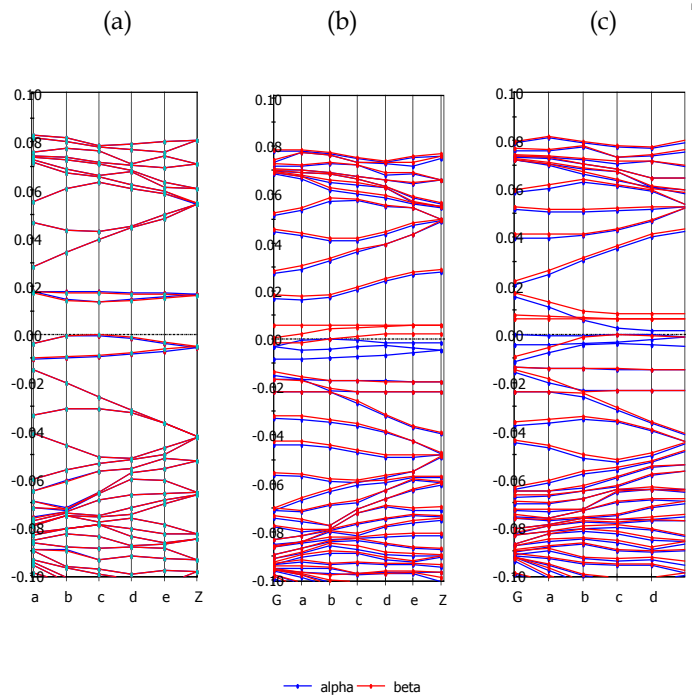

Fig.2. The band structures of (a) pure 10-ZGNR, (b) 10-ZGNR with pyridine-like defect and (c) 10-ZGNR with porphyrin-like defect, Fermi level is set as zero and plotted with a broken line.

To clarify the issues on the effects of the formation of 3NV and 4ND defects have on the electronic properties of ZGNR the band structures of the ZGNR with 3NV and 4ND defects are examined in Fig. 2. In Fig. 2(a) the spin resolved band structures of 10-ZGNR is shown. The spin-up and spin-down bands are fully degenerate, the net magnetic moment of the AFM phase is zero and a 0.35 eV energy gap is observed. After the introduction of a 3NV defect, the energy bands near the Fermi level become asymmetric for different spin channels: in the spin-up channel, the Fermi level is shifted into the conduction band and metallicity is thus obtained, while the spin-down channel is semiconducting. Therefore, the 10-ZGNR containing a 3NV defect is half-metallic. Similarly, the 10-ZGNR containing a 4ND defect is also half metallic, with a metallic spin-down channel and semiconducting for the spin-up channel. The results demonstrate that the introduction of pyridine and porphyrin defects in GNRs can lead to the breaking of spin degeneracy, suggesting a feasible way of building spin devices based on GNRs.

The formation of pyridine-like nitrogen defects is very crucial for enhancing the metal binding to the defects. The strong interactions between the N and the ZGNR with defects can be explained through partial densities of states (PDOS), that is, N adsorption on the 3NV-ZGNR as shown in Figs. 3(a) and 3(b) for the 10-ZGNR. It is found that the p electrons of C and N atoms mainly contribute to the electronic states near Fermi level. In other words, strong interaction exists between the p orbitals of N and atoms due to their hybridization with each

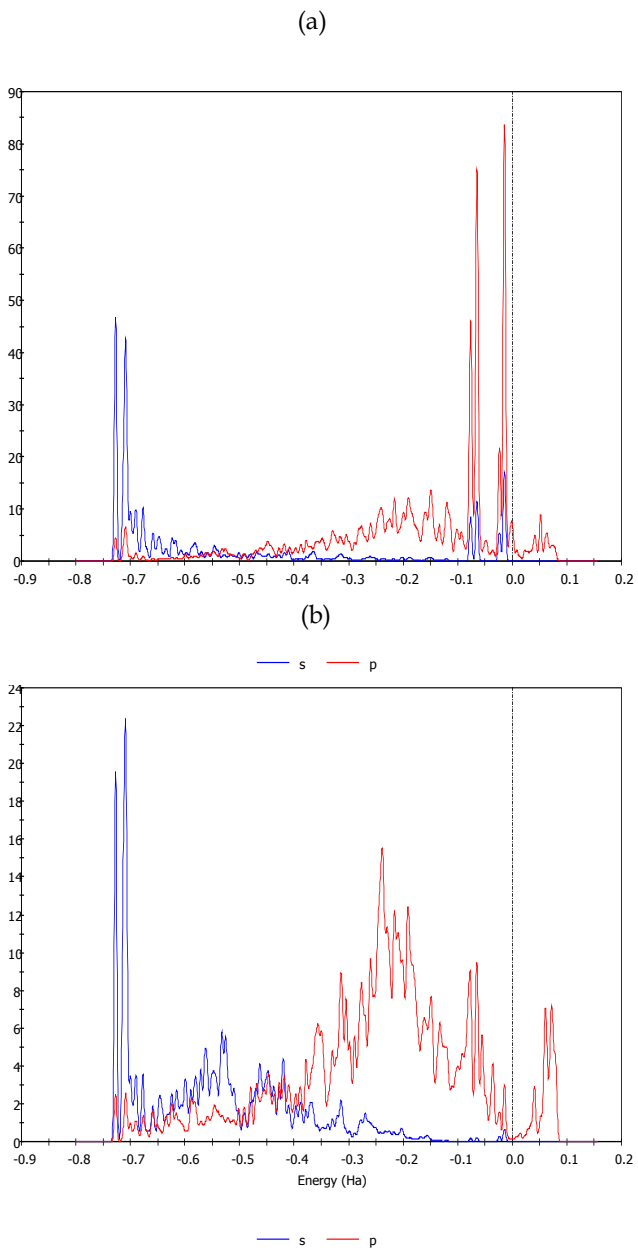

Fig.3. The PDOS of (a) N and (b) C in the adsorption system for the 10-ZGNR. The blue and red plots denote s and p orbitals, respectively.

each other. The ZGNR with 3NV defects uses two valence electrons to form a lone pair. The reactivity of the 3NV-ZGNR is greatly enhanced compared with the case of the pure ZGNR due to the non-bonding lone pair.

4 Conclusions

The electronic properties of zigzag graphene nanoribbons with pyridine and porpyrine defects were studied using spin-unrestricted density functional theory. The formation of configuration with pyridine and porphyrin defects close to the edge is energetically favored and thermodynamically stable. The calculated band structures and density of states denote

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that the impurities can impose a significant effect on the electronic properties of 10-ZGNR. Pyridine and porphyrin defects in ZGNR caused a semiconductor to half metallic transitions. Finally, the computations point out a feasible way for achieving spintronic devices based on ZGNRs in the very near future. .

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