

Computational Study on the Electronic Properties of Functionalized Graphene Nanoribbon

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Abstract

Graphene, the starting material for all the carbon nanostructures, has attracted the attention of all the researchers worldwide due to its remarkable electronic and transport properties like quantum Hall effect at room temperature, an ambipolar electric field effect along with ballistic conduction of charge carriers, tunable band gap and high elasticity. Graphene is a flat monolayer 2D system of carbon atoms organized into a honeycomb lattice with sp² hybridization. Graphene is a zero band gap material which is the defining concept for semiconductor materials and essential for controlling the conductivity by electronic means. However bilayer graphene shows band gap of 0.25 eV when a vertical electric field is applied. A large number of methods have been employed to calculate graphene's properties; one of them is theoretical study using density functional theory (DFT) method. Here in this article we are calculating band structure, density of states and transmission spectrum using density functional theory calculations by varying the length and the width of graphene nanoribbon (GNR). Functionalization studies of GNR have also been conducted using ATK-DFT.

Keywords;- graphene, density functional theory, band structure, functionalization

1. Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. The current interest in graphene can be attributed to three main reasons. First, its electron transport is described by the Dirac equation and this allows access to quantum electrodynamics in a simple condensed matter experiment [1–5]. Second, the scalability of graphene devices to nano dimensions [6–10] makes it a promising candidate for applications, because of its ballistic transport at room temperature combined with chemical and mechanical stability. Remarkable properties extend to bilayer and few-layers graphene [4–6, 8, 11]. Third, various forms of graphite, nanotubes, buck balls, and others can all be viewed as derivatives of graphene and, not surprisingly, this basic material has been intensively investigated theoretically for the past 60 years [12]. These properties have result in the application of graphene in different areas like field effect transistor, spin electronics, biosensors, lasers, photo detectors, as MRI contrast agent etc [13-17]. The electronic structure of these graphene nanoribbons (GNR) depends on the width and chirality [18-21]. Functionalization offers the opportunity to change the electronic properties of graphene nanoribbons (GNR). One of the easiest approaches to functionalize GNR is carboxylation and amidation. Carboxylation of graphene and carbon nanotubes is usually carried out via interaction

with oxidizing inorganic acids [22- 23]. Acid treatment creates dangling bonds on the surface of carbon materials that can be progressively oxidized to hydroxyl (-OH), carbonyl (dCO), and carboxyl (-COOH) functional groups [24- 25].

Unique properties arising from its honeycomb-lattice structure allow us to observe strange relativistic effects at speeds much slower than the speed of light. In addition, ability to manipulate the motion of the electrons in graphene paves the way to virtually lossless and ultrafast transistors with atomic dimensions [26].

In this paper, we apply ab initio density functional computational methods to study the mechanism of effect of chemical functionalization of graphene nanoribbons by CONH2 group. The goal of our study is to analyze the electronic properties of carboxylated graphene nanoribbons, determine the band structure, density of states (DOS), transmission spectrum of CONH2 group on GNR.

2. Computational Method

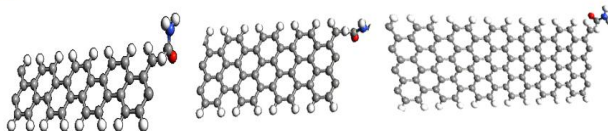
Our calculations are based on density functional theory combined with double zeta polarized states. The Atomistix ToolKit - Density Functional Theory (ATK-DFT) program can model the electronic properties of closed and open quantum systems with Density Functional Theory models using numerical basis sets. For open systems, the density matrix is calculated using non-equilibrium Green's functions, while for closed or periodic systems it is calculated by diagonalizing the Kohn-Sham Hamiltonian.

The Density Matrix defines the electron density, and the electron density sets up an effective potential, i.e. the Hartree and exchange-correlation potential. From the effective potential, we can obtain the Kohn-Sham Hamiltonian. In DFT, the electronic structure of the system is described in terms of the one-electron Kohn- Sham Hamiltonian

$$H_{iel} = \frac{-\hbar^2}{2mv^2} + V^{eff}[n](r)$$

In this equation the first term describes the kinetic energy of the electron. The second term describes an effective potential energy of the electron moving in the mean field from the other electrons, where the other electrons are described in terms of the total electron density.

a)



b)

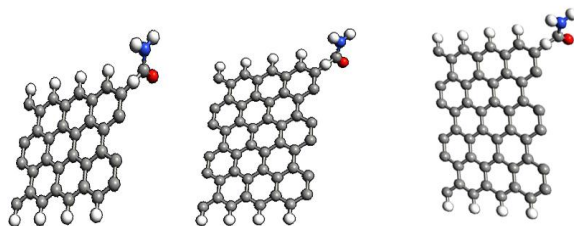


Figure 1. (a) AGNR functionalized with amide group (b) ZGNR functionalized with amide group. The white, gray, red balls denote hydrogen, carbon and oxygen atoms respectively

The mesh cutoff is set to be 150 Ry, and the convergence of total energies is set to be 10⁻⁵ Ry. The exchange and correlation potentials are also approximated by local density approximation (LDA) functional. The width of the ribbon is varied from N=2 to N=4 (as shown in Figure 1) so as to notice the effect on band structure as the band gap is inversely proportional to the width of the ribbon.

3. Results and Discussion

The width of the AGNR and the ZGNR are denoted by the number of armchair chain and zigzag chain respectively as shown in figure 1. We have functionalized side of GNR with one amide group to see its effect on the electronics properties of GNR. The width of GNR has been varied to compare the difference between the band structures for different geometries. We have shown three different structures of width 2, 3 and 4 each for armchair and zigzag configuration as shown in figure 1(a) and figure 1 (b). In DFT for each element a pre-build basis set is already defined. In this paper for calculations we have used double zeta polarized basis set for hydrogen, carbon and oxygen. The double zeta polarized set is defined as one which includes one confined orbital and one analytical split for each occupied valence orbital in the atom and one polarization orbital for the first unoccupied shell in the atom.

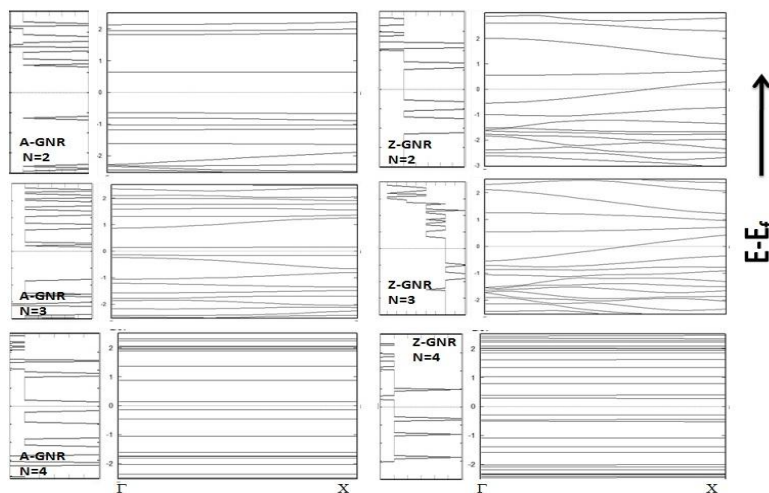


Figure 2. (a) transmission spectrum and the band structure of armchair GNR (b) transmission spectrum and band structure of zigzag GNR. The width of the ribbons in both the cases is varied from N=2 to N=4

In figure 2(a), the transmission spectrum and the band structure of armchair GNR has been shown. As for the 2-AGNR it can be clearly seen that there is wide band gap and there is more distribution of energy levels around the conduction band. For 3-AGNR, band gap decreases as compared to the 2-AGNR and also the distribution of energy levels slightly increase in the valance band. This can be related to the quantum confinement effect as GNRs are one dimensional material unlike graphene which is a

2D structure. Due to the quantum confinement effect the energy levels in GNR are confined.

The electron density of the GNR is defined by the occupied eigen states and is given as:

$$n(r) = \sum_{\alpha} |\psi_{\alpha}(r)|^2 f\left(\frac{\epsilon_{\alpha} - \epsilon_F}{kT}\right)$$

where $f(x) = 1/(1 + e^x)$ is the Fermi function, ϵ_F is the Fermi energy, and T the electron temperature.

Figure 2(b) represents the transmission spectrum and the band structure of ZGNR. ZGNRs are also functionalized with one amide group. The band structure shows almost same type of pattern in all the cases. The band gap decreases as the width of the ribbon increases in case of armchair GNR as they have semiconducting behavior. However, zigzag GNR doesn't show prominent band gap due to their metallic behavior.

We also observe a strong rise in the in the transmission values upon increasing the width of the ribbons representing the incremental transport channels that become available in broader GNRs. Thus functionalization of GNR with the amide group affects the electronic properties. The band structure and transmission spectrum shows noticeable change as the width of the ribbon is varied.

4. Conclusion

We have presented DFT studies for the band structures, energy gaps and transmission spectrum of armchair and zigzag GNRs. The calculations were based upon the exchange and correlation potential using the local density approximation method (LDA). The dependence of the gap size on the width of the zigzag GNR was much smaller than the armchair GNRs indicating that band gap engineering using GNRs could be more difficult.

We have found that the electronic properties of armchair GNRs are very sensitive to small changes in the ribbon width, as reflected by the emergence of three different case of armchair GNR. In future we plan to extend our analysis to GNRs having stones vales defect as defects provides preferential site for the attachment of functional groups

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