Electronic and transport properties of chemically functionalised zig-zag graphene nanoribbons: First principle study

SATYENDRA SINGH CHAUHAN[1] [iD],*, PREMLATA NARWARIYA[2], A K SRIVASATAVA[2] and PANKAJ SRIVASTAVA[3]

[1]ITM Group of Institutions, NH-75, Opposite Sithouli Rly Station, Jhansi Road, Gwalior 474 001, India
[2]Jiwaji University, Sachin Tendulkar Road, Kailash Nagar, Mahalgaon 474 001, India
[3]ABV-Indian Institute of Information Technology and Management, Gwalior, Morena Link Road, Gwalior 474 015, India
*Corresponding author. E-mail: sschauhan_71@rediffmail.com

Abstract.   In this work, we have performed the chemical functionalisation of metallic graphene nanoribbons (GNRs) with different functional groups. The analysis of graphene in terms of relative stability and electronic properties has been done. The HOMO–LUMO gaps are quantitatively analysed to reveal the influence of different functional groups including hydroxyl, carboxyl and hydrogen sulphide groups. Interestingly, the influence of edge functionalisation on the HOMO–LUMO gap of zig-zag graphene nanoribbons (ZGNRs) presents significant change using density functional theory (DFT). Understanding the electronic properties in terms of density of states and band structure of functionalised graphene is of great relevance today. It is found that the geometrical structures and electronic properties of the GNRs could be significantly changed with the oxygen containing group. With the carboxyl-functionalised GNRs, the interaction leads to a decrement in the HOMO–LUMO gap of graphene. This fact makes GNR a possible candidate for nanoelectronic devices.

1. Introduction

2D graphene has distinctive properties in various fields [1–3]. Its remarkable properties such as massless Dirac fermion behaviour [4–6], half-integer quantum Hall effect [7] and high mobility make it a superior candidate for various applications in nanoelectronics and spintronics devices [8,9]. Graphene became an eminent topic of research in material science after the successful synthesis of graphene in a monolayer form, by Geim and Novoselov [10]. As a result, various exciting phenomena have been observed in graphene viz., ultrahigh electron mobility (up to 200 000 cm^2/(V-s)) [11], conductance quantisation in mesoscopic graphene [12] and the possibility of superconductivity [13]. These attractive properties are attributed to the unique 2D confinement that is provided to its charge carriers which behave as massless Dirac fermions [14]. The more fascinating thin strips of graphene, generally known as graphene nanoribbons (GNR), exhibit width- and edge-dependent electronic properties. However, various methods have been demonstrated to obtain GNR with controlled edges [15,16], which reveal that the electronic properties can be tuned. The well-known characteristics of nanoribbons, i.e. edge geometry and width, can be considered as key parameters that determine the electronic properties of the ribbons [17–19].

The modification of electronic properties of nanoribbons by chemical functionalisation is a prominent method to make them potential candidates for several applications [20–22]. The nanoribbons intrinsically have dangling bonds at the edges, whose linear combinations form eigenstates near the Fermi energy, and this is responsible for the ribbon properties. These dangling bonds also provide active sites for chemical bonding, making the ribbons suitable for chemical modification. As the distinctive properties of the nanoribbons are due to their edge states, edge modification can prominently affect and control the electronic properties of the ribbons [23,24]. On functionalisation of the edges with

various functional groups, we can obtain various electronic properties. It is a fact that the same ribbon can become semiconductors, with wide range of band gaps, metallic and half-metallic by proper chemical functionalisation. Practically, the edge dangling bonds of the graphene sheets and nanoribbons can be saturated by hydrogen with proper hydrogenation procedures. The first step to modify the nanoribbons is to saturate one of the edges by an element or functional group while the other edge is saturated by H. It has been studied that the edge functionalisation with different functional groups can significantly affect their electronic structure close to Fermi level. One edge of the zig-zag nanoribbon is decorated with two H atoms while the other has one H transforming the antiferromagnetic nanoribbon into ferromagnetic [25]. Single-edge functionalisation of zig-zag nanoribbons leads to semiconductor with varying energy band gap or in regions of semiconductor–metal transition [26]. The modification of one or both edges of zig-zag nanoribbons with functional groups such as –O, –F, –OH, –NH$_2$, –CH, –BH and –B has been investigated. Feng *et al* [27] studied graphene with oxygen-containing functional groups and revealed that surface functionalisation has more evident effects on optical properties. Gao and Guo [28] theoretically proposed that the edge contacts can offer excellent properties due to shorter binding distances and larger binding energies. Further, when the edge sites of graphene are terminated by fluorine [29,30] there will be drastic changes in the electronic structure leading to a distinct increase in hydrophobicity [31,32]. The electronic properties strongly depend on the edge termination of the superlattices and chemical modification; the superlattices with zig-zag edge are characterised by tiny energy gap while the ones with arm-chair edge have a wide gap [33]. The electronic and transport properties of Li-doped graphene nanoribbons using an *ab-initio* approach was also reported recently and it is found that substituting two Li atoms at the carbon edges is more predominant than the other doping configurations [34]. An effect of strain on the structural and electronic properties of transition metal-doped arsenene nanoribbons was also reported using an *ab-initio* approach and it is suggested that straining the nanoribbons also modulates the band gap [35]. In particular, edges oriented along the high-symmetry zig-zag direction or along any low-symmetry (chiral) direction give rise to unique localised edge states [36–38] that are predicted to result in magnetic ordering.

Moreover, the effects of hydroxyl, carboxyl and hydrogen sulphide groups with double edge functionalisation on graphene have not been studied yet. In this paper, we performed systematic investigation on the geometries, the electronic properties of ZGNRs on the basis of density functional theory (DFT) computations.
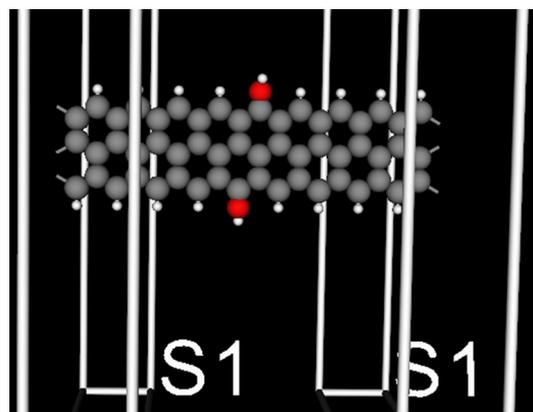

Figure 1. Schematic view of the functionalised two-probe 6ZGNR.

We reported the chemical functionalisation on GNRs with OH, COOH and H$_2$S groups.

2. Computational method

The simulation package employed for the computations is Atomistix Toolkit–Virtual NanoLab (ATK-VNL) based on the DFT calculations [39]. First-principle calculations within the spin-unpolarised density functional theory (DFT) were performed. The double zeta double polarised basis sets were employed for all the calculations. The exchange correlation term was calculated with local density approximation (LDA) as illustrated by Perdew and Zunger [40], because LDA gives a realistic description of the atomic structure. The carrier density mesh cut-off was set to 150 Rydberg (Ry) and the Brillouin zone was sampled as $1 \times 1 \times 100$ within the Monkhorst Pack scheme for the total energy and band-structure calculations. In this computation, ZGNR of ribbon width $N = 6$ with unit cells in a periodic box so as to make sure it is infinite in one dimension was considered. The width W of the nanoribbons is defined as the number of zig-zag chains for a zig-zag GNR. Chemical functionalisations with OH, COOH and H$_2$S groups on 6ZGNRS were studied. Figure 1 shows double edge functionalisation with OH group. Similar functionalisation is done with other groups also. To model the system, the system is divided into three parts: two electrodes and a scattering region. The electrodes are two semi-infinite metallic GNRs, and the scattering region is described by three unit cells of 6ZGNR plus two unit cells of the coupling region on each side.

Self-consistent calculations have been done by setting up suitable convergence criteria for the two-probe device configurations. In this simulation, spin-restricted calculations and minimal basis orbital functions to reduce

Table 1. Formation energy for all the considered edge configurations.

Functional groups	Formation energy (eV)
OH	0.17
H_2S	0.68
COOH	1.23

computational time were considered. Pulay iteration mixing algorithm with a tolerance of 10 Å and damping factor of 0.1 were used. The electronic structures (density of states and transmission coefficient) for the four structural configurations were calculated. The density of states (DOS) were investigated around the Fermi level for all four configurations.

3. Result and discussions

The functionalisation on the edges of ZGNRs was performed to investigate whether the functional groups prefer to be functionalised to either edge of ZGNRs. Three different functional groups, hydroxyl $(-OH)$, carboxyl $(-COOH)$ and hydrogen sulphide $(-H_2S)$ groups, were studied. In general, geometry optimisation shows that the edge functionalisation significantly alter the GNR structure. For this, the following optimised geometries were found: H_2S sits 1.396 Å away from the edge carbon, the H–S distance is 1.031 Å and the H–S–H plane is tilted $\sim 20°$ with respect to the plane of the ribbon. The OH remains on the graphene plane with C–O and O–H distances of 1.377 and 0.967 Å, respectively and a C–O–H angle of $\sim 108°$. The plane defined by O–C–O of the COOH has an angle of $\sim 52°$ with respect to the plane of the ribbon and the C–C, C–O_1, C–O_2 and O_2–H distances are 1.427, 1.219, 1.355 and 0.975 Å, respectively.

To investigate the interaction between the functional groups attached on the edges of ZGNRs, supercell calculations on the energy for the configuration of three functional groups as the distance between the functional groups changes from 4 to 13 Å were done. To compare stability, the simple expression to define the edge formation energy (E_F) [41] for each configuration is defined as

$$E_F = \frac{E_{total}^{GNR} - N_C\mu_C - N_H\mu_H}{N_C^{edge}},$$

where N_C is the total number of carbon atoms in the ribbon, N_C^{edge} is the number of carbon atoms at the two edges of the ribbon, N_H is the total number of passive hydrogen atoms added at both edges, E_{total}^{GNR} is the total

energy of the ribbon containing $N_C + N_H$ atoms, μ_C is the chemical potential of carbon and μ_H is the chemical potential of hydrogen. Carbon atoms are assumed to come from a reservoir of graphene and so

$$\mu_C = \frac{E_{total}^{graphene}}{N}$$

for a graphene unit cell of N carbon atoms. Small variations in the edge formation energy with different functional groups are observed. The edge formation energies for the three structures are listed in table 1. It can be seen that ZGNR has the largest negative formation energy for COOH group, indicating that this edge is thermodynamically more stable and can spontaneously form. The small energies suggest that they are probably stable at room temperature. Moreover, it indicates that the functionalisation is chemical in nature.

In order to understand the chemical stability of the doped graphene, it was analysed for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO–LUMO gap provides some insight on the chemical stability. The variation of HOMO and LUMO energy gap of the pure and functionalised ZGNRs is shown in figure 2, which shows significant changes. A general characterisation of the electron structure was done by analysing the regularities recorded in the HOMO, LUMO energies and HOMO–LUMO gap (E_G), along different configurations. E_G for the OH- and H_2S-terminated systems generally increase with 6ZGNR. In contrast, the energy gap in COOH-terminated case is lower than that of pristine ZGNR. This suggests that the COOH-terminated system is more stable with the *ab-initio* optimised geometries, indicating that the effect of geometry distortion in edge-functionalised graphene is the dominating factor for tuning the HOMO–LUMO gap of graphene. As can be seen, particularly, the COOH group behaves significantly different from the other two functional groups in edge-functionalised GNR. The HOMO–LUMO gap levels can be continuously tuned with different oxygen containing groups as a consequence of orbital interactions. In general, electron-donating groups such as $-OH$, $-H_2S$ increase the HOMO energy, while electron-withdrawing groups such as $-COOH$ lower the LUMO energy, resulting in a decreased HOMO–LUMO gap [42]. Energy gap tunability is demonstrated in the energy diagram with the narrowing of the HOMO–LUMO gap. The calculated E_G for the pristine 6ZGNR and functionalised GNR with $-OH$, $-COOH$ and $-H_2S$ are 0.69, 0.85, 0.48 and 0.75 eV, respectively. Therefore, the effect of functional groups located on the edge plane in ZGNR is crucial.
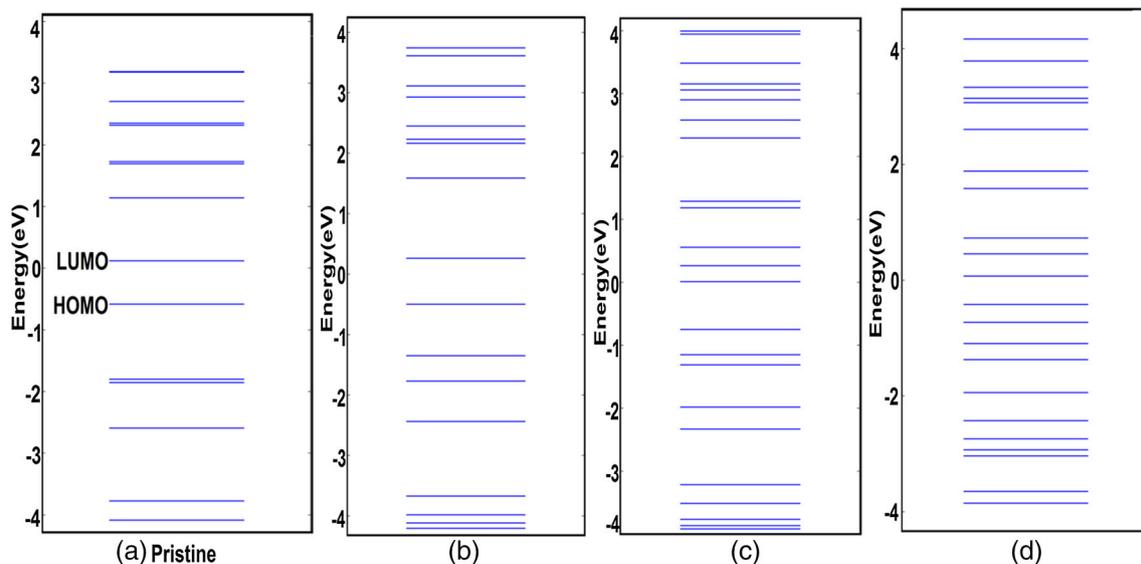
Figure 2. Energy diagram of (**a**) Pristine 6ZGNR, (**b**) OH-terminated 6ZGNR, (**c**) H$_2$S-terminated 6ZGNR and (**d**) COOH–terminated 6ZGNR.
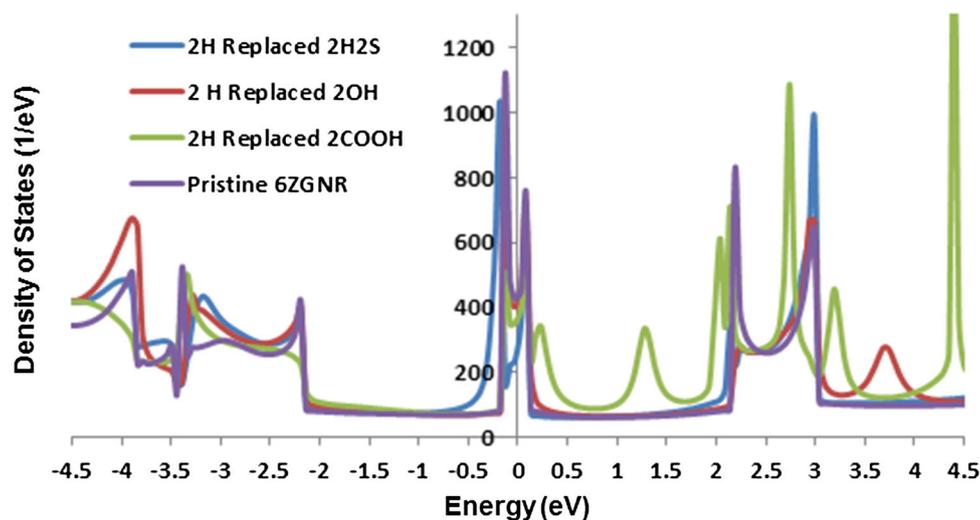

Figure 3. Density of states of pristine and functionalised 6ZGNR.

The electronic structures for the functionalised ZGNRs are studied to examine the influence of functionalisation on the electronic structures. In order to elucidate the electronic properties of the 6ZGNR, the electronic density of states (DOSs) were calculated. Figure 3 shows the total DOS curves obtained from our LDA calculations. These curves demonstrate that the presence of graphene edge states results in a relatively large contribution to the DOS near the Fermi energy in a nanoscale system. Thus, these edge states play important roles in the electronic properties of nanosized graphitic systems. A high DOS at a specific energy level means that many states are available for occupation. A DOS of zero means that no states can be occupied at that

energy level. The DOS for the ZGNR with two edges functionalised with COOH shows high peak at 4.4 with the energy value of 1547.8 eV at the vicinity of Fermi level. Interestingly, some peaks of the DOS around the Fermi energy were observed there. DOSs were calculated for pristine ZGNR, OH, COOH and H$_2$S after edge-functionalisation where each electronic state was represented in terms of Gaussian function (G) where

$$G = \frac{1}{\sqrt{2\pi}\alpha}e^{\frac{\varepsilon-\varepsilon_i}{2\alpha^2}}$$

with broadening $\alpha = 0.02$ eV. The Fermi energy is set at zero by defining $E_F = (E_{HOMO}+E_{LUMO})/2$. The effect of attaching COOH to the 6ZGNR is the appearance of
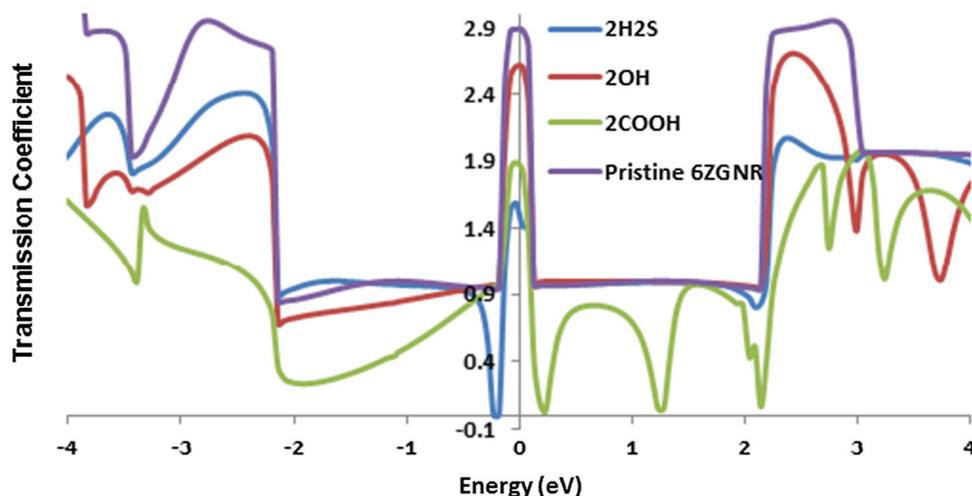
Figure 4. Transmission spectra of pristine and functionalised 6ZGNR.

new peaks in the spectrum. It also indicates the increased intensity. These results imply that the functionalisation affects the electronic properties.

Based on the optimised structures, we next investigated the electron transport properties of the 6ZGNR by constructing a two-probe system. The transmissions were given in the zig-zag direction. Periodic boundary conditions were imposed on the plane perpendicular to the transport direction. The computed zero-field transmission spectra are shown in figure 4, which apparently mimic the metallic behaviour of the nanoribbon. The transmission properties are a function of the band structure near the Fermi energy. The transmission spectra corresponding to the structures had zero transmission gap around E_F, correspondingly showing the metallic nature of the doped ZGNR. It can be seen that the transmission coefficient is an integer showing the occurrence of sharp peak at the very vicinity of the Fermi level. At zero bias, the magnitude of the transmission dips for the COOH functional group has more visible oscillations. Also, we observed that the transmission gap around the Fermi level is nearly flat, but there are peaks in the case of COOH indicating that new electronic states are introduced around the Fermi level. The introduction of electronic states around Fermi level suggests further reduction in energy gap. The peaks in transmission spectra contribute toward HOMO–LUMO formations and the transmission coefficient in the bias window decreases steadily with the edge functionalisation. The changes in the electronic structure indicate quantum transport property variation upon the edge attachment of carboxyl group. This property can be used for building neurosensors using ZGNRs. A noticeable suppression in transmission probability values is observed when COOH group is attached to the ZGNR. This result in an unbiased condition indicating that there may be an even

greater change in quantum conductance after the attachment of COOH group. As a result, it is important to note that HOMO–LUMO gaps have intimate relationships with electronic states. This indicates that the effect of geometry distortion in edge-functionalised graphene is a dominating factor for tuning the HOMO–LUMO gap.

4. Conclusion

In order to elucidate the underlying electronic properties of GNR, we studied edge functionalisation in graphene nanoribbons with three different functional groups. We systematically studied the electronic properties of graphene functionalised with OH, COOH, and H_2S. The edges have the ability to accumulate more charges and electron transports than the pristine GNR. The density of states of a given quantum system is important for understanding electrical conductivity and other electronic response functions. The HOMO–LUMO gaps are calculated with edge-functionalisation effect and it shows that oxygen-containing group on ZGNR has a profound effect on electronic properties.

It was found that the carboxyl group behaves significantly different from the other functional groups in electronic mechanism. Functionalisation strongly affects the electronic structure of ZGNRs. The HOMO–LUMO energy gap widens if the edge is functionalised with the hydroxyl group. The calculation also shows that the electrical conductivity of the system would be significantly improved by attaching COOH to the ZGNR.

Acknowledgements

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