Short Communication

Ab initio Study of the Effect of H_2O Molecules Adsorption on the Semiconducting Graphene Nanoribbon

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The H_2O molecules adsorption effects over electronic transport properties of Armchair Graphene Nanoribbons (A-GNR) was theoretically studied using Non Equilibrium Green Function (NEGF) formalism along with Ab initio calculation. Three different orientations and adsorption sites are considered to calculate the adsorption energies. The calculated adsorption energies for those orientations also suggest that adsorption in metallic A-GNR has much smaller effect on its transport properties.

Keywords: NEGF, Ab initio, Adsorption energy, Transport properties.

1. INTRODUCTION

In recent years, gaseous molecule adsorption in nano-patterned material has been grabbed the attention of researchers and scientists [1-3]. Since gas and vapor adsorption on these systems could change their electronic properties, therefore, these properties can be used to measure the sensing performance of the systems. Previously, researchers concentrated to their work on the interaction of small gas molecules on graphene, such as CO, NO_2 and NH_3 with the pristine graphene in theory [4, 13, 14] and CO_2 sensing using graphene sheet in experiment [5]. Interestingly, graphene is an interesting candidate for using as gas and vapor sensor due to its two dimensional character (thus maximizing the interaction of adsorbates on the graphene layer), low Jhonson noise which suggests that adsorption can leads notable relative changes in carrier concentration and few crystal defects [6]. As a result, the interaction between small molecules and graphene can be highly enhanced by introducing adsorption into 2D nanosheets of graphene. Ab initio method of a H_2O molecule with GNR is important for finding the interaction energy in order to meet some technological application such as the design and implementation of humidity sensor. In this paper, it has been shown that water (H_2O) molecules adsorbed on GNR cause defects in it which facilitate to electron-tunneling of the band gap and cause widening of graphene band gap to 0.206 eV [1].

However, the changes in resistance are directly influenced by the amount of H_2O adsorbed on the graphene [3]. We have considered the orientations and adsorption sites of H_2O molecule on both semiconducting and metallic GNR to investigate the adsorption energies. Moreover, the strength of the molecular adsorbing is discussed in light of the highest occupied and lowest unoccupied molecular orbital commonly named as HOMO and LUMO respectively. Electronic and transporting properties of these systems such as Device Density of States (DDOS), Electrostatic Difference Potential (EDP), Conductivity (*G*) and

Current-Voltage (*I-V*) characteristics are greatly influenced by the adsorption of H_2O. We have considered three cases such as semiconducting A-GNR ($N = 10$), metallic A-GNR ($N = 11$) and cascade A-GNR to realize the effect of H_2O adsorption on A-GNR to get an overview about comparison of their sensing performance. This paper discusses the optimum area for adsorbing highest number of H_2O molecules to get maximum current. Adsorbing excessive number of water molecule in correspondence to its optimum value leads the decrement of sensing properties. To overcome this problem, a new device model has been proposed.

2. CALCULATION METHOD AND MODEL

The electronic band structure of graphene was calculated very early on [7]. The valence electrons of carbon atoms in graphene are sp^2 hybridized with the remaining p_z carbon orbitals forming an extended π-electron system that is responsible for the low energy transport and optical properties of graphene. The bonding π-states form the valence band and the antibonding π^*-states form the conduction band. These two bands touch at six points, the so called Dirac or neutrality points show zero bandgap semimetal characteristics whereas nano-patterning of graphene sheet can open up a bandgap upto ~ 1.4 eV [8], depending on the chirality of nanoribbon it can be Armchair or Zigzag. Armchair GNR (A-GNR) and Zigzag GNR (Z-GNR) shows semiconducting or semimetallic behaviour depending on the number of carbon atoms, N along the width of the nanoribbon [9, 15].

In general humidity sensing through GNR is a process of vapour (H_2O) adsorption in graphene surface where the oxygen ion in H_2O. In this paper we investigate the change in electronic transport in GNR due to H_2O adsorption. The electronic transport calculations were performed by implementing non-equilibrium Green's function (NEGF) formalism [10, 11, 15]. Ballistic current through GNR sheet considering self-consistent field imposed by

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H_2O molecules is calculated using Launder's equation.

$$I = \frac{2q^2}{h} \int_{-\infty}^{\infty} dE \, T(E) \, (f_L^+ - f_R^+),$$

where, q = charge of electron and h = Plank's constant. f_L^+ is the Fermi function of left electrode and f_R^+ is the Fermi function for right electrode.

$$f_{L,R}^+ = \frac{1}{1 + e^{(E - E_F^{L,R})/K_B T}},$$

where, K_B = Boltzmann's constant. $E_F^{L,R}$ is the electrochemical potential at left or right contact and $T(E)$ is the transmission spectrum.

$$T(E) = Tr[\Gamma^L G^R \Gamma^R G^A]$$
$$G^R(E) = [G^A(E)]^\dagger = [(E + i\delta_+)S - H - \Sigma^L(E) - \Sigma^R(E)]^{-1}$$

Here, $G^R(E)$ is Retarded Green's function where S and H are overlap integral matrix and device Hamiltonian matrix respectively. Self-energy terms are represented by $\Sigma^L(E)$ and $\Sigma^R(E)$ respectively for left electrode and right electrode. Here $'Tr'$ represents Trace of a matrix and $\Gamma^L = i[\Sigma_L - \Sigma_L^\dagger]$ and $\Gamma^R = i[\Sigma_R - \Sigma_R^\dagger]$. δ_+ is an infinitesimally positive number. Matrix S and H provides the atomistic description of GNR which is dependent on tight-binding P_Z orbital hopping parameter, previously calculated by Reich et al. [12]. In our simulation we have calculated Device Density of States (DDOS), conductance (G) and Electrostatic difference potential (EDP) using following equations.

$$DDOS(E) = \frac{1}{2\pi} Tr[G^R(\Gamma^L + \Gamma^R)G^A]$$
$$G(E) = \frac{2q^2}{h} Tr[\Gamma^L G^R \Gamma^R G^A]$$
$$EDP\left(\frac{r}{max(r)}\right) = \frac{U(r) - max(U(r))}{max(U(r)}$$

where, $U(r)$ is the electrostatic potential calculated from Poisson's equation using finite difference algorithm and r represents two dimensional space coordinates(x, y, z). In our work the effect of vapour adsorption is modelled by change in tight binding hopping parameter and local effective potential using ab-initio study. The adsorption energies is calculated as

$$E_{ads} = \{E_{GNR+mH2O} - (E_{GNR} + m \, E_{H2O})\}/m,$$

where, $E_{GNR+H2O}$ is the total energy of GNR with an adsorbed H_2O molecule, E_{GNR} and E_{H2O} are the total energies of pristine GNR (semiconducting or metallic) and isolated H_2O molecule respectively and m is the number of adsorbed H_2O molecule.

3. RESULT AND DISCUSSION

For the adsorption of H_2O molecule on semiconducting or metallic GNR, we have considered three adsorption sites, namely on top of a carbon atom (T), the centre part of carbon hexagon (C) and the middle point of C-C bond (B). For all of three configurations, we have analysed different orientations of H_2O molecule and calculated adsorption energies (Table 1). The centre part of carbon hexagon of semiconducting GNR as an adsorption site is shown the most interaction with H_2O molecule in order to get the highest binding energy. In this

paper, two charge transfer mechanism is being considered. Firstly, if the HOMO is above the Fermi level of pristine GNR (the dirac point), there is a charge transfer to GNR from adsorbate and if the LUMO is below the Fermi level, charge transfer will take place to adsorbate from GNR. Secondly, the charge transfer between adsorbate and GNR can be partially determined by the mixing of the HOMO and LUMO of adsorbates with GNR, which is known as hybridization. Three orientations have been considered of H_2O molecule with respect to GNR surface: starting from the O atom, the O-H bonds pointing up (u), down (d) and parallel to GNR surface.

Table 1 – The adsorption energy is determined by the orientation of adsorbate (u = pointing up, d = pointing down and n = pointing parallel) and adsorption sites (C = center of carbon hexagonal, T = top of carbon atom and B = the center point of C-C bond)

Posi-si-tion	Orien-tation	Adsorption Energy, E_a(eV)	Distance, d(Å)	Charge Transfer, $\Delta Q(e)$
C	u	22.98	4.35	0.025
C	d	23.55	4.85	$-$ 0.013
C	n	25.31	4.13	0.018
T	u	21.82	4.32	0.025
T	d	20.26	4.70	$-$ 0.012
T	n	24.01	4.15	0.019
B	u	20.91	4.30	0.025
B	d	23.30	4.70	$-$ 0.012
B	n	24.01	4.15	0.017

However, all properties are seems to be invariant with respect to the rotation of the axis perpendicular to surface and the oxygen atom, therefore we have considered only the centre of carbon hexagonal (C) as adsorption sites. It is found in semiconducting GNR that when O atom points to the GNR surface, there is significant charge transfer to the GNR which is shown in Fig. 1 (a) and Fig. 1 (b) but, if the H atom points to the GNR surface, there is little charge transfer to H_2O molecule.

(a)

(b)
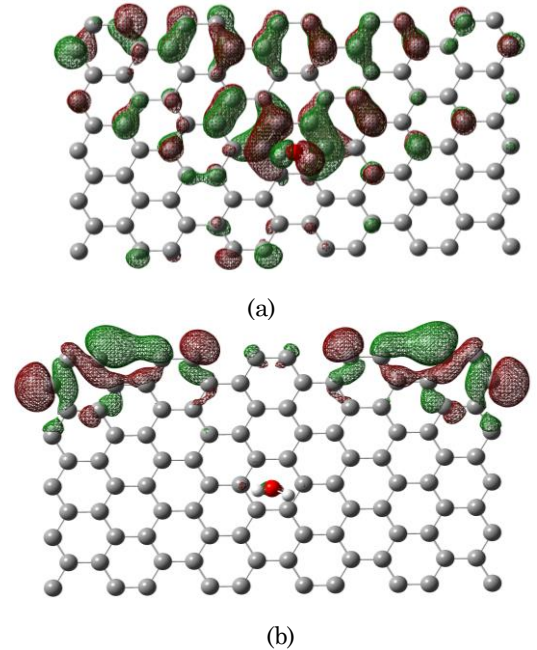
Fig. 1 – (a) Highest Occupied Molecular Orbital (HOMO) (b) Lowest Unoccupied Molecular Orbital (LUMO) of semiconducting GNR (orientation = d, adsorption site = C)

It is to be noted that the formation of HOMO and LUMO of H_2O molecules and their orientations play an important role in charge transfer mechanism. It is found that HOMO is located mostly on the O atom where LUMO is mostly located on the H atom. A small mixing of orbital between adsorbates and GNR above Fermi level is found in pointing up and pointing parallel direction, which causes a charge transfer to GNR from adsorbates. However, there is also a stronger mixing with the orbital below the dirac point as they are close to energy level but this does not induce any charge transfer because all the orbitals are filled. In pointing down direction, a strong interaction is taken place between the surface of GNR and the LUMO of adsorbates below the dirac point

as a result some charge is transferred to H_2O molecule from GNR due to the mixing of orbitals. However, there is a strong interaction in orbital above the dirac point, but this does not induce any charge transfer as all the orbitals are empty above Fermi level. Again, in pointing parallel direction, there is a strong interaction in HOMO but at the same time, there will almost same interaction in LUMO. There will be a charge transfer from the H_2O molecule to GNR, but, because of the interaction with the LUMO, it will be smaller. However, we focus only semiconducting A-GNR as we have found that in case of metallic GNR, the adsorption effect have a smaller impact over modifying the electronic properties.

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