Adsorption of gas molecules on graphene nanoribbons and its implication for nano-scale molecule sensor

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Abstract

We have studied the adsorption of gas molecules (CO, NO, NO2, O2, N2, CO2, and NH3) on graphene nanoribbons (GNRs) using first principles methods. The adsorption geometries, adsorption energies, charge transfer, and electronic band structures are obtained. We find that the electronic and transport properties of the GNR with armchair-shaped edges are sensitive to the adsorption of NH3 and the system exhibits n-type semiconducting behavior after NH3 adsorption. Other gas molecules have little effect on modifying the conductance of GNRs. Quantum transport calculations further indicate that NH3 molecules can be detected out of these gas molecules by GNR based sensor.

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I. INTRODUCTION

Sensing gas molecules is critical to environmental monitoring, control of chemical processes, space missions, and agricultural and medical applications\[1\]. Solid-state gas sensors are renowned for their high sensitivity which have made them ubiquitous in the world\[2,3\]. In the past few years, a new generation of gas sensors have been demonstrated using carbon nanotubes (CNTs) and semiconductor nanowires\[4,5,6,7,8,9,10,11\]. It was reported that semiconducting CNTs could be used to detect small concentration of NH\(_3\), NO\(_2\), and O\(_2\) with high sensitivity by measuring changes of the CNTs conductance upon exposure to the gases at room temperature\[4,5,6,7,11\].

Graphene, a single atomic layer of graphite, has been successfully produced in experiments\[12,13\], which have resulted in intensive investigations on graphene-based structures because of fundamental physics interests and promising applications\[14\] (e.g., gas sensor\[15\]). Importantly, graphene can be patterned via standard lithographic techniques into quasi-one-dimension materials\[13,16,17\], graphene nanoribbons (GNRs), which have many properties similar to CNTs, such as energy gap dependence of widths and crystallographic orientation\[18,19\]. Different from CNTs, however, GNRs present long and reactive edges which make GNRs not only notably more accessible to doping\[18,20,21\] and chemical modification\[22,23,24,25\], but also more susceptible to structural defects and impurities\[21\].

Theoretical studies of gas molecular adsorption on the graphene surface have been reported recently\[26,27\], which showed that NO\(_2\), H\(_2\)O, NH\(_3\), CO and NO molecules are physically adsorbed on the pristine graphene: NH\(_3\) and CO molecules will act as donors while H\(_2\)O and NO\(_2\) will act as acceptors, which are consistent with previous experiment\[15\]. Compared with graphene, GNRs are advantageous in small volume and free reactive edges. In experiments, the edges of GNRs are not well controlled\[16,17\] and it is hard to obtain fully saturated edges without any dangling bond (DB) defects. It is well known that DB defects around the vacancy sites or at the tips play a very important role in CNTs gas sensors because they are very chemically reactive\[28,29,30\]. Similar to CNTs, when there are DB defects at GNRs edges, covalent attachment of chemical groups and molecules also significantly influences their electronic properties\[22,24,25\]. Therefore, it is very interesting and important to study the feasibility of using GNRs as gas sensors.

In this article, using density functional theory (DFT) calculations, we study the adsorp-
tion of gas molecules (CO, NO, NO₂, O₂, N₂, CO₂ and NH₃) around the sites of DB defects on armchair GNRs (AGNRs, having armchair-shaped edges) and explore the feasibility of using AGNRs as gas sensors. Following conventional notation [31], a GNR is specified by the numbers (n) of dimer lines and zigzag chains along the ribbon forming the width, for the AGNR and zigzag GNRs (ZGNRs, having zigzag-shaped edges), respectively. For example, the structure in Fig. 1a is referred as a 10-AGNR (i.e., n = 10). Previous works show that all AGNRs are semiconductor while ZGNRs are metallic [18, 31]. We focus on semiconducting AGNRs instead of metallic ZGNRs, since it is expected that gas molecule adsorption will have a much smaller effect on modifying the electronic properties of (metallic) ZGNRs. It is found that although all gas molecules can influence the electronic structure of AGNRs, only NH₃ molecule adsorption can modify the conductance of AGNRs remarkably by acting as donors while other gas molecules have little effect on conductance. This property can be utilized to detect NH₃ out of other common gases, which is requisite and significant in industrial, medical, and living environments [32].

II. CALCULATION METHOD AND MODEL

Our electronic structure calculations were performed using the DFT in the spin-polarized generalized gradient approximation (GGA) with PW91 functional for the exchange and correlation effects of the electrons, as implemented in Vienna Ab initio Simulation Package (VASP) [33]. The electron-ion interaction was described by the ultrasoft pseudopotentials and the energy cutoff was set to be 400 eV. Structural optimization was carried out on all systems until the residual forces on all ions were converged to 0.01 eV/Å. The quantum transport calculations were performed using the ATK 2.3 package [34], which implements DFT-based real-space, nonequilibrium Green’s function formalism. The mesh cutoff is chosen as 150 Ry to achieve the balance between calculation efficiency and accuracy.

III. RESULTS AND DISCUSSION

DB defects would exist at both edges of GNRs due to the fact that the two edges of a GNR are equivalent in nature. So we will focus our study on double-edge-defect case (i.e., both edges have DB defects). What is more, we also perform test calculations for the single-
FIG. 1: (a) The optimized structure of 10-AGNR with edge dangling bond (DB) defects, where the arrow shows the periodic direction. The sites of DB defects are shown by yellow. C atoms and H atoms are denoted by large and small (white) spheres, respectively. (b) Density of states (DOS) of perfect 10-AGNR (top panel) and spin-polarized DOS of 10-AGNR with DB defects (middle and bottom panels). The Fermi level is set to zero (the top of valence band). The middle (blue) and bottom (red) panels in the figure correspond to minority spin and majority spin, respectively. The green area corresponds to local DOS of the two carbon atoms (yellow balls in (a)) with DB defects.

edge-defect case (DB defects only exist at one edge), and find little difference in essential results compared with the double-edge-defect case. The structure with one DB defect per edge per five unit cells in the ribbon axis direction is adopted in our calculations, as shown in Fig. 1a, corresponding to a DB defect concentration of 0.04 Å⁻¹. [Several different initial configurations with one DB defect per edge have been considered and we find that the one shown in Fig. 1a is most favorable (stable) in energy.] Due to the dangling $\sigma$-bonds at the edges, the ground state of this system is spin-polarized with the magnetic moment of 1 $\mu$B
FIG. 2: Optimized structure of 10-AGNRs with gas molecule adsorption: (a) CO, (b) NO, (c) NO₂, (d) O₂, (e) CO₂, and (f) NH₃. We only show the structure around the adsorbed molecule.

per DB, which is localized at the carbon atoms with DB defects. Spin-polarized density of states (DOS) of this system is shown in the middle and bottom panels of Fig. 1b. For better comparison, the DOS of perfect 10-AGNR with the same supercell is also presented (the top panel). It can be seen that the perfect 10-AGNR is paramagnetic semiconductor with a band gap of 1.2 eV, consistent with our previous study [18]. When there are DB defects at the ribbon edges, two new peaks appear in the DOS (indicated by the arrows in Fig. 1b). The local density of states (LDOS) analysis (the green area in Fig. 1b) shows that the two peaks are mainly contributed by the edge carbon atoms with DB defects. These two DB states are localized, respectively, within the valence band for minority spin and at the bottom of conduction band for majority spin, different from the usual DB states which are localized within band gap [35].

We start by investigating the adsorption geometries of seven gas molecules on 10-AGNR with DB defects (Fig. 1a). Only the gas molecules adsorption around the sites of DB defects is considered. Several different initial orientations of gas molecules on 10-AGNRs are adopted in searching the most stable configurations. Fig. 2 shows the top views of
TABLE I: Calculated adsorption energies ($E_{\text{ads}}$) and charge transfer ($CT$) from the gas molecules to the 10-AGNR.

| Molecules | CO  | NO  | NO$_2$ | O$_2$ | N$_2$ | CO$_2$ | NH$_3$ |
|-----------|-----|-----|--------|------|------|-------|-------|
| $E_{\text{ads}}$ (eV) | -1.34 | -2.29 | -2.70  | -1.88 | 0.24 | -0.31 | -0.18 |
| $CT$ (e)  | -0.30 | -0.55 | -0.53  | -0.78 | /    | -0.41 | 0.27 |

10-AGNR with adsorbed molecules. We find that different gas molecules prefer different geometries in the adsorption: (a) CO molecule lies in the AGNR plane with C-C distance of 1.35 Å and a C-C-O angle of 168.6°. The bond length of the adsorbed CO is 1.18 Å, a little longer than that of an isolated molecule (1.13 Å), indicating that adsorption process will weaken the original C-O bond of gas molecule. (b) NO molecule sits out of the AGNR plane with a C-N-O angle of 118.2°, and the C-N and N-O distances are 1.43 Å and 1.24 Å, respectively. Also, the bond length of the adsorbed NO is 0.07 Å longer than that of an isolated molecule. (c) The adsorbed NO$_2$ has C-N and N-O distances of 1.47 Å and 1.25 Å and a O-N-O angle of 127°, and the O-N-O plane is tilted 60° with respect to the ribbon plane. Our results are consistent with previous studies [24, 25]. (d) O$_2$ sits in the ribbon plane with C-O and O-O distances of 1.37 Å and 1.38 Å respectively and a C-O-O angle of 116.2°. The bond length of O$_2$ molecule increases by 0.15 Å after adsorption. (e) The geometry of CO$_2$ adsorbed on the ribbon edge is different from that of an isolated CO$_2$ molecule: it is not linear structure anymore but similar to the NO$_2$ configuration. This indicates that the bond of CO$_2$ transfers from $sp$ into $sp^2$ hybridization in order to lower the total energy. The C-C and C-O distances are 1.51 Å and 1.26 Å respectively, and the C-O-C angle is 127°. (f) The adsorbed NH$_3$ molecule sits 1.49 Å away from the edge carbon atom, the H-N distance is 1.03 Å and the dihedral angle is about 21° between the C-N bond and the AGNR plane. Besides the above gas molecules, we also study the N$_2$ molecule adsorption on the AGNR, and find that it is difficult for N$_2$ to adsorb on the ribbon due to its inert nature.

The calculated adsorption energies of the gas molecules with the 10-AGNRs are shown in Table 1. Herein, The adsorption energy is defined as: $E_{\text{ads}} = \{E_{\text{tot}}(\text{ribbon} + m\text{Molecule}) - E_{\text{tot}}(\text{ribbon}) - nE_{\text{tot}}(\text{Molecule})\}/m$, where $E_{\text{tot}}(\text{ribbon} + m\text{Molecule})$, $E_{\text{tot}}(\text{ribbon})$, and $E_{\text{tot}}(\text{Molecule})$ are the total energies of the AGNR with molecule adsorption, the isolated
FIG. 3: Band structure and density of states (DOS) of 10-AGNRs with gas molecule adsorption: (a) CO, (b) NO, (c) NO₂, (d) O₂, (e) CO₂, and (f) NH₃. The LDOS of gas molecules is also plotted (red filled area under DOS curve). The Fermi level is set to zero.

AGNR (with DB defects) and the molecules, respectively. And \( m \) is the number of molecules adsorption on the AGNR. The results reveal that all these adsorption configurations are energetically favorable except that the N₂ adsorption process is endothermic reaction (note: the negative adsorption energy corresponds to the exothermic reaction). The adsorption energies of CO, NO, NO₂, and O₂ are all larger than 1 eV, corresponding to strong chemisorption. The adsorption energies for the NH₃ and CO₂ on AGNRs are -0.18 eV and -0.31 eV respectively, indicating that the adsorption are between weak chemisorption and strong physisorption. The above results illuminate that gas molecule adsorption at AGNR edges is quite different
from the weak physisorption of gas molecules on the graphene surface[15, 27]. Furthermore, the Bader analysis[36] of the charge distribution is used to understand the nature of the interaction between the gas molecules and the AGNRs, and to evaluate the induced effects on the molecules. The trend of calculated charge transfer (Table 1) can be understood on the basis of relative electron-withdrawing or -donating capability of the adsorbed molecular groups. From Table 1 (note: the positive value means a charge transfer from the adsorbed molecule to the AGNR), we can see that CO, NO, NO₂, O₂, and CO₂ have electron-withdrawing capability, while NH₃ is electron-donating functional molecule. It is well known that NO₂ and O₂ are relatively strong electron-withdrawing molecules while NH₃ is relatively strong electron-donating molecule in other carbon-based materials[4, 5, 15, 27, 29]. Comparing with gas adsorption on the graphene (GNR) surface[27], the values of the charge transfer are much larger. This is consistent with our conclusion that the interaction between the gas molecules and the GNR edges is much stronger than that of surface.

The calculated band structures and DOS of 10-AGNRs with molecule adsorption are shown in Fig. 3. Comparing with the DOS of AGNR (Fig. 1b), the total DOS of the system and LDOS of the molecules show that these molecules modulate the electronic property of AGNRs in different manners: i) CO and NO molecules adsorption introduces impurity states in the band gap and the Fermi levels of two systems cross these states, as shown in Figs. 3a and 3b. Therefore, gas adsorption will decrease the original band gap, and probably have some influence on the optical properties of AGNRs. For CO adsorption,
there are two half-occupied states in the band gap, but we do not expect these impurity states can enhance the conductance of the system because these states are very localized and deep in the original band gap. It would be very difficult for charge carriers to transit between the valence (or conduction) band and impurity states at finite temperature. ii) LDOS analysis (Fig. 3c) shows that NO\(_2\) adsorption will introduce fully-occupied states which are strongly hybridized with the original “bulk” states in the valence band and these states are nonlocalized. It suggests that the interaction between NO\(_2\) molecules and dangling bonds of the ribbon is very strong, consistent with the calculated adsorption energy. The Fermi level is pinned in the top of valence band, which is the same as the case of the ribbon without molecule adsorption, so the system is still semiconducting. iii) Figs. 3d and 3e show the cases of O\(_2\) and CO\(_2\) adsorptions, respectively. From LDOS analysis we can see that the states contributed by CO\(_2\) (or O\(_2\)) molecules are localized around the top of valence band and hybridize with the original valence band. Partial charge density analysis (Fig. 4a) shows that the states near the Fermi level are quite localized and mainly contributed by CO\(_2\) molecule and the carbon atoms of ribbon around the CO\(_2\) molecule. This suggests that the conductance of this system can not be enhanced notably. When the molecular doping concentration is low enough, these impurity states will become more localized on the gas molecules. But due to these half-occupied impurity states being near the top of valence band, the electrons of the valence band can transit into these states and the system will exhibit \(p\)-type semiconducting behavior at finite temperature. iv) NH\(_3\) molecule adsorption induces unoccupied local states in the conduction band, and more importantly, the Fermi level is shifted into original conduction bands, resulting in \(n\)-type semiconducting behavior (Fig. 3f). Furthermore, partial charge density analysis (see Fig. 4b) shows that the states near the Fermi level are mainly contributed by the carbon atoms of the ribbon rather than NH\(_3\) molecules. The above results indicate a transition from semiconducting to conducting behavior after NH\(_3\) molecule adsorption. The stabilization of the Fermi level in the conduction band by the impurity resonant levels was also reported in semiconductors doped by Cr and Tl\(^{37, 38}\).

Among all gas molecules considered, obviously NH\(_3\) molecule adsorption can greatly enhance the conductance of AGNRs, where the system will exhibit metallic behavior after NH\(_3\) adsorption. CO\(_2\) and O\(_2\), on the other hand, may enhance the conductance of GNRs to some extent at finite temperature since the CO\(_2\) and O\(_2\) adsorption will turn AGNRs
FIG. 5: The $I$-$V_{\text{bias}}$ curves for the GNR sensor before and after the adsorption of NH$_3$ and CO$_2$. The inset shows the schematics of such a GNR sensor, consisting of one 10-AGNR (detection region) and two metallic 7-ZGNRs leads. The gas molecules can be adsorbed around the DB defects of the GNR sensor.

to $p$-type semiconductor. Based on the analysis, we can expect that AGNRs may act as effective sensor to detect NH$_3$ out of other gas molecules discussed above by measuring the change of conductance after the gas adsorption. What is more interesting, the adsorption energy of NH$_3$ molecule is only -0.18 eV (Table I), so NH$_3$ molecules can be desorbed at higher temperature. This implies that GNR sensors could be recycled more than once.

A design of a GNR-based junction (GNR sensor) to detect NH$_3$ is given in the inset of Fig. 5 as an example. It contains a 8.60 nm long 10-AGNR with one DB defect per edge as the detection region and two semi-infinite metallic 7-ZGNRs as the leads. Gas molecules can be adsorbed on the DB defect sites, and the conductance is measured by applying a bias voltage through the junction. The DB defect concentration in this model is about 0.011/Å per edge, which is practical in experiments. We calculate a series of current versus bias voltage ($I$-$V_{\text{bias}}$) curves for such GNR junction with different gas molecule adsorption on the edges. For the sake of clarity, we only show $I - V_{\text{bias}}$ curves for the AGNRs before and after NH$_3$ and CO$_2$ adsorption due to the fact that the currents induced by other gas molecules adsorption are almost zero (much smaller than the currents induced by CO$_2$ or NH$_3$ adsorption). As shown in Fig. 5, without gas molecule adsorption, the channel (GNR sensor) exhibits a semiconducting behavior, and the current is always zero even under a bias of 0.5 V. After NH$_3$ adsorption, however, the current increases notably and $I$-$V_{\text{bias}}$ curve is
nearly linear, corresponding to a metallic behavior of ohmic contact. CO$_2$ adsorption can also increase the current, but its value is much smaller than that induced by NH$_3$ adsorption. This phenomenon indicates that NH$_3$ can be detected out of other gases by applying a bias voltage upon the GNR junction, which is consistent with our analysis based on electronic properties.

IV. SUMMARY

In summary, we have performed first-principles calculation to study the adsorption geometries and electronic structure of graphene nanoribbons with gas molecule adsorption. We find that NH$_3$ molecule adsorption can significantly influence the electronic and transport properties of AGNRs, while other gas molecules have little effect. Based on this characteristic, we demonstrate that an AGNR can be used to detect NH$_3$ molecules out of many familiar gas molecules. Furthermore, our work also suggests an effective way to fabricate $n$-type ($p$-type) transistors by NH$_3$ (CO$_2$ or O$_2$) adsorption on graphene nanoribbons.

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