Interactions of Ethanethiol with Defective Graphene: First-Principle Calculations

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Abstract—A first-principle study based on density functional theory was conducted to investigate the interaction of ethanethiol molecule with both defected and defect-free graphene. The calculated results reveal that the ethanethiol molecules can be bound to the surface of defected graphene more tightly in comparison with the defect-free graphene. The configurations and density of states of the combined systems show that the interaction between the ethanethiol molecule and defected graphene is quite different from the defect-free graphene, which is consistent with the Mulliken analyses. It is expected that the simulation results presented in this work would be valuable to the applications of various graphene-based nanometer devices.

Keywords—Ethanethiol molecule; Graphene; Stone-Wales defect; Vacancy; Density functional theory

I. INTRODUCTION

Graphene, a single atomic layer of graphite, has been proved to be successfully prepared in experiments and ready for a great deal of nano-production applications [1-2]. Researches on graphene are being pursued to explore unusual and even unexpected properties, ranging from spintronic devices [3], composites [4, 5] and gas sensors [6-8]. A number of recent researches on carbon nanotubes (CNTs) are focused on the interactions between CNTs and organic compounds such as alkyamines [9-12] and organosulfur compounds [13, 14], in order to find hybrid materials that may possess idealized electrical and mechanical properties eventually. The modification of GaN surfaces by the attachment of organic molecules would greatly widen its applications in the field of biosensors and electronic devices [15-18]. It should be noted that Ethanethiol (C2H5SH) is one of typical sulfur organic compounds (SOC). The functionalization of traditional semiconductors and zeolites surfaces with C2H5SH molecules has been calculated by using density functional theory (DFT) methods [19, 20]. The nature of the interactions between organic molecules and nanostructures is of growing scientific interest. To the best of our knowledge, the graphene can be considered to possess most of the extraordinary properties of the CNTs, however, theoretical study and associated numerical simulation have not been found to investigate the direct noncovalent bonding of C2H5SH to the graphene.

Most of previous studies of carbon nanostructures [21-23] have shown that various defects are common phenomena in carbon-based nanomaterials, and defect-based carbon structures have been focused to graphene. Those research results suggested that the active adsorption sites in graphene might be defects. To date, the interactions between C2H5SH molecule and defected graphene have not been reported yet. Therefore, understanding the properties of C2H5SH molecule adsorption on the defected or defect-free graphene becomes essential for the future applications.

The present paper is mainly concerned with theoretical study and associated molecular simulation of the interactions of C2H5SH molecule with defected and defect-free graphene by using first principle calculations. The effects of Stone-Wales (SW) defect (a 90° rotation of a carbon dimmer) and vacancy defect (removal of one C atom in graphene) on the electronic characteristics of adsorption system were investigated. The charge transfer occurs when C2H5SH molecule interacts with graphene and exhibits obvious effect on the density of states (DOS) of the adsorption system. The present work may pave the way for understanding the interaction mechanisms between C2H5SH and graphene.

II. COMPUTATIONAL DETAILS

The computational simulation was performed by the use of SIESTA code [24, 25] which is based on the framework of density functional theory (DFT), with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof [26]. It should be noted that the distance between adsorbate and the graphene surface is somewhat overestimated and consequently the binding energy will be underestimated in GGA. The core electrons are represented by norm-conserving pseudopotentials in its fully nonlocal (Kleinman-Bylander) form. All the calculations were conducted with a double-$\xi$ plus polarization (DZP) basis set. A $4\times4\times1$
Monkhorst-Pack grid for k-point sampling of the Brillouin

zone was established, and the atomic positions were relaxed until all the forces are lower than 0.01 eV/Å. The mesh-cutoff was set to be 150 Ry.

The supercells of graphene with SW defect (SW-g) and vacancy defect (V-g) consist of 80 and 79 C atoms, respectively. A periodic boundary condition is applied to the supercell. The vacuum space is 18 Å in the vertical direction, which is sufficient to eliminate the interaction effect existed between adjacent graphene sheets in the supercell. In order to make the computational results comparable, identical conditions are employed for the isolated C$_2$H$_5$SH molecule, the graphene and the combined systems as well. To verify the validity of the method, the density of states of V-g is shown in Fig. 1, which is consistent with the value cited in the literature [27]. It can be seen that the acceptor-like states near the Fermi level was observed.

III. RESULTS AND DISCUSSION

The data of binding energy (E$_b$) were first calculated for all combined systems. The well-known expression for the $E_b$ of adsorbed system is defined as:

$$E_b = E_{\text{total}} - E_{\text{graphene}} - E_{\text{molecule}}$$

Where $E_{\text{total}}$, $E_{\text{graphene}}$ and $E_{\text{molecule}}$ denote the total energies of the relaxed graphene adsorbed system, isolated graphene and a C$_2$H$_5$SH molecule, correspondingly.

Figure 3. The density of states (DOS) for: (a) an isolated C$_2$H$_5$SH molecule, an isolated P-g, and the configuration A; (b) an isolated C$_2$H$_5$SH molecule, an isolated SW-g, and the configuration B; and (c) an isolated C$_2$H$_5$SH molecule, an isolated V-g, and the configuration C.

The adsorption of C$_2$H$_5$SH on the defected and defect-free graphene was investigated individually for the purpose of comparison. In order to search for the most stable adsorption configuration of C$_2$H$_5$SH on SW-g surface, three possible adsorption sites, including the center of a heptagon, hexagon and pentagon, were selected and assuming a
molecule approaching the graphene via its thiol (-SH) active site.

After a thorough structural optimization of the considered systems, the stable configurations are achieved and shown in Fig. 2 (Red-colored portion indicates the adsorption sites in the graphene). For the sake of understanding the influence of the introduced defects on the C$_2$H$_5$SH adsorption onto the graphene, the adsorption of C$_2$H$_5$SH on a perfect graphene (P-g) has also been investigated. The changes in geometry for the stable configurations were first investigated. Fig. 2a shows the interaction between P-g and C$_2$H$_5$SH at one site, which is labeled as configuration A. For the case of SW-g, it is found that the adsorption of C$_2$H$_5$SH molecule on the pentagon is the most stable state of adsorption (Fig. 2b), and it is labeled as configuration B. Fig. 2c refers to the V-g interacting with C$_2$H$_5$SH molecule, which is labeled as configuration C. For the case of configuration A, adsorption of C$_2$H$_5$SH does not result in any significant structural distortion in the graphene, and all C atoms within the graphene are nearly 0.07 Å below the original plane. It is different from configuration A, the calculated results show that the configurations B and C are changed significantly along the axis perpendicular to graphene surface. In the configuration B, there is one SW defect in graphene, which leads to two pairs of five-membered and seven-membered rings. A part of SW defect deviate from its original plane in the downward direction which makes the part far away from the SW defect protrude out of the plane in the opposite direction. This phenomenon is due to a strong repulsion between the S atom of C$_2$H$_5$SH molecule and the π electron clouds of graphene, and the strong repulsion is possibly caused by the existence of SW defect. When this repulsion is finally compensated by van der Waals forces, those atoms reach their equilibrium positions. A similar situation was found in configuration C, the part of C atoms near the vacancy is shifted out of the original plane owing to the interaction between the S atom of the C$_2$H$_5$SH molecule and the dangling bonds.

For a thorough understanding of the interaction between graphene and C$_2$H$_5$SH molecule, the calculated binding energies $E_b$ for all considered systems are summarized in Table 1. The results obtained indicate that the C$_2$H$_5$SH is easier to be adsorbed on the pentagon of the SW-g. Table 1 also presents the binding distance (D) of the C$_2$H$_5$SH above the adsorbed sheet, which is defined as the minimum distance between adsorbate and C atom of graphene. The calculated binding energy for the energetically favorable configuration and the binding distance are about -0.88 eV and 3.33 Å, respectively. The binding interactions for all considered systems can be described as physisorption owing to their smaller binding energy and larger equilibrium distance in comparison with typical chemisorption. It has been found that the present results are quite different from the previous research work [16], pointing out that C$_2$H$_5$SH prefer to be adsorbed on the defect-free CNTs over the hexagon of carbon atoms in comparison with the adsorption on the defective CNTs. This difference may be caused by the effect of the curvature of CNTs.

For a fully understanding of the change in the electronic structure produced by C$_2$H$_5$SH molecule adsorption, the electronic density of states (DOS) was calculated for the combined systems and compared with the corresponding DOS for the C$_2$H$_5$SH molecule and graphene individually. Fig. 3a shows the total electronic DOS for the configuration A, and it can be seen from the figure that the total DOS of the configuration A is nearly the sum of the DOS values of their individual parts. These results show that the interaction between the adsorbent and adsorbate is quite weak, and no apparent hybridization between the orbitals of the individual parts takes place, this phenomenon is in accordance with its binding energy. For the configuration B and C, the results obtained (Fig. 3b and c) indicate that the DOS below the Fermi level is affected by the adsorption of C$_2$H$_5$SH in the defective surface. It is worth noting that the DOS of the defected graphene where the C$_2$H$_5$SH is adsorbed shifts down slightly in comparison with a bare defected graphene (pointed by arrows in Fig. 3b and c). This shift may be explained by the reduction in effective Coulomb potential due to the charge transfer. On the other hand, the difference in Fermi levels of the graphene surface and the combined systems clearly shows a charge transfer between the adsorbent and adsorbate in the adsorption process. Hence, the Mulliken charge analyses have been conducted to evaluate the amount of electron transfers between the C$_2$H$_5$SH molecule and graphene. The charge transfer of five different adsorption configurations, which are from the graphene to the C$_2$H$_5$SH molecule, is also shown in Table 1. Charge analysis shows 0.076 eV has been transferred from SW-g to the C$_2$H$_5$SH molecule (configuration B), which is larger than that of configuration A. Mulliken analysis points out that there exists a stronger interaction in the configuration B in comparison with configuration A. Furthermore, the interaction can be explained by the breaking of delocalized π bonding of graphene. It is interesting to note that the charge transfer from V-g to the C$_2$H$_5$SH molecule (0.117 eV) is larger than that of configuration A too, which is consistent with their binding energy. The large quantity of charge transfer in configuration C can be explained by the presence of dangling bonds (C1, 82

<table>
<thead>
<tr>
<th>System C$_2$H$_5$SH/graphene</th>
<th>Defect-free</th>
<th>Stone-Wales defect</th>
<th>vacancy</th>
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</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>-0.2960</td>
<td>-0.8753</td>
<td>-0.8300</td>
</tr>
<tr>
<td>D (Å)</td>
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<td>3.33</td>
<td>3.193</td>
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<tr>
<td>$\Delta E$ (eV)</td>
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<td>-0.076</td>
<td>-0.075</td>
</tr>
<tr>
<td>$\Delta Q$ (eV)</td>
<td>-0.072</td>
<td>-0.072</td>
<td>-0.072</td>
</tr>
</tbody>
</table>

### Table 1. Binding Energy, Binding Distance and Charge Transfer of Five Different Combined Systems.
C2 and C3 shown in Fig. 2c) which act as acceptor-like states near the Fermi level. Furthermore, our results indicate that C2H5SH molecule prefers to interact with defective graphene rather than the defect-free graphene.

IV. CONCLUSION

The interaction effects between a C2H5SH molecule and graphene with and without introduced defect were investigated separately by using the density functional theory. The simulation results show that C2H5SH molecule is prejudiced to be adsorbed on the defected graphene in comparison with the adsorption on the defect-free graphene. The change of the geometry and density of states after the C2H5SH molecule adsorption was also investigated. Eventually, it is found that the DOS of configuration B (adsorption of C2H5SH molecule on the SW-g) and C (adsorption of C2H5SH molecule on the V-g) where the C2H5SH is adsorbed shift down slightly in comparison with a bare SW-g and V-g, respectively, and Besides, a larger charge transfer in configuration B and C in comparison to configuration A indicates that there exists a stronger interaction effect between the C2H5SH molecule and the defected graphene than that of defect-free graphene. Consequently, all the results prove that the more active adsorption sites in the graphene are produced by defects. It is expected that the theoretical and molecular simulation results presented in this work are valuable to the design and manufacture of graphene-based nanometer devices.

ACKNOWLEDGMENT

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REFERENCES


Figure 2. Stable configurations after relaxation. (a) C$_2$H$_5$SH/P-$\tau$, (b) C$_2$H$_5$SH/SW-$\tau$ and (c) C$_2$H$_5$SH/V-$\tau$ (left and right panels show the top and side view, respectively).