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Adsorption of acetyl halide molecules on the surface of pristine and Al-doped graphene: Ab initio study

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ABSTRACT

We have scrutinized the adsorption energy, electronic structure, natural bond analysis (NBO), density of state (DOS) and global indices for adsorption of acetyl chloride (AC) and acetyl fluoride (AF) on the surface of pristine graphene as well as Al-doped graphene. The adsorption energies have been calculated for the most stable configurations of the molecules on the surface of pristine and Al-doped graphene. According to the calculated parameters, there is very weak physical adsorption of AC and AF on pristine graphene while strong adsorption takes place in the case of Al-doped graphene. The charge transfer from adsorbed molecules to Al-doped graphene surface was confirmed by the natural bond orbital as well as the Mulliken population analysis while there is no charge transfer with pristine graphene. Additionally, the density of states results reveal that orbital hybridization takes place between above-mentioned molecules and Al-doped graphene sheet, whereas there is no hybridization between the molecules and the pristine graphene. Our calculated adsorption energies for the most stable position configurations of AC and AF on Al-doped graphene were $-68.8\,\mathrm{kJ\,mol^{-1}}$ ($-52.6\,\mathrm{kJ\,mol^{-1}}$ BSSE corrected energy) and $-78.4\,\mathrm{kJ\,mol^{-1}}$ ($-64.3\,\mathrm{kJ\,mol^{-1}}$ BSSE corrected energy) which are correspond to chemisorptions process respectively. These results point to the appropriateness of Al-doped graphene as a powerful adsorbent for practical applications.

1. Introduction

Acetyl chloride (CH_3COCl) and acetyl fluoride (CH_3COF) are two acid chlorides derived from acetic acid. They are colorless, corrosive, volatile liquid which are one of the most important reagents for synthesis of esters and amides of acetic acid and also frequently used in the derivatization of amines and alcohols [1]. Because of their high volatility at ambient temperature, their adsorption is vital to prevent the wasting and also to recovering them.

After the Overture of carbon nanotubes (CNT) [2], much consideration has been paid to this kind of materials owing to their outlandish structure as well as properties [3] in the broad range of purposes including sensors [4], the storage of different gases [5], catalysis applications [6], and field emission [7].

A completely available surface is created by arranging thin lattice of carbon atoms in a honeycomb pattern which causes the exposing of a large part of carbon atoms by molecules. It is established that the improvement in the charge concentration of graphene after adsorption of different molecules could be used to produce high sensitive electrically based sensors. The changing in the resistivity because of molecules adsorbed on graphene relates to sensing properties which can be considered as donors or acceptors. Moreover, because of existing special binding site in graphene, it would be possible the understanding of the configuration of molecules near the surface [8]. Also the straightforward production of graphene sheets and its potential for miniaturization are the other positive characters of graphene toward sensing application.

Numerous theoretical researches based on DFT calculations have been done to show the interaction energies of single molecules and small molecular with a graphene sheet [9–11].

Whilst graphene has 2D structure, the adsorption of molecules with pristine graphene is weakly through physisorption. So, it will not be reasonable to use pristine graphene for adsorption process of specific molecules. To conquer the insensitivity of these molecules on pristine graphene, doped graphenes owing to the creation of 3D structure, have been considered for detections. It is established that higher sensitivity of graphene toward different molecules could be achieved by doping metals [12–16].

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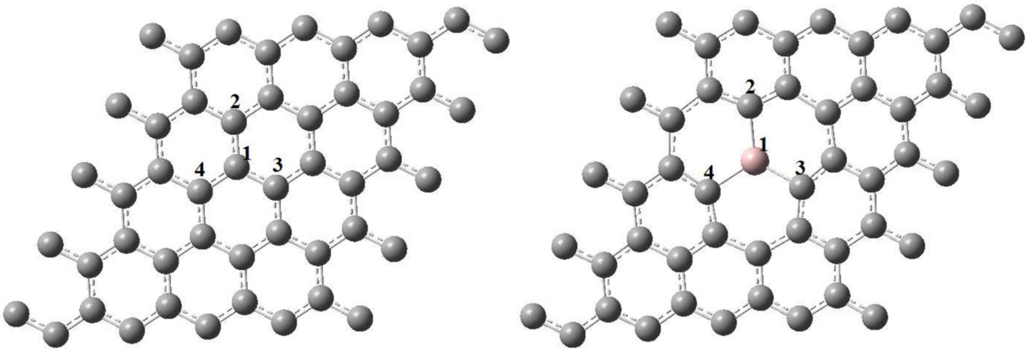

Fig. 1. Relaxed geometries of isolated PG (left) and AlG (right).

Theoretic studies show that the replacement of atom by doping could modify the band structure of graphene [17–19] so the applications of graphene could be mainly enhanced.

As a dopant, Aluminum atom has been used toward doping process of graphene for diverse principles [20–29]. Characteristically, doping of Al into graphene transforms the electron density allotment in around of the doped atom. For this, C-atoms nearing the doped Al catch electrons because of their lofty electron attraction, while on the doped Al, reduce in electron density is created. The charge relocation makes the doped Al to act as an active site for gas molecules. Peres et al. [30–32] showed that this charge rearrangement can be established with advanced field theoretical methods.

We use a computational technique using DFT to simulate the adsorption of AC and AF molecules on the surface of pristine graphene as well as Al-doped graphene and examine their impacts on the electronic properties of the these surfaces.

To the best of our knowledge, there are no simultaneous theoretical studies toward adsorption of AC and AF molecules on the surface of pristine or modified graphene. We aim to quantum chemically investigation of AC and AF molecules adsorption on the surface of pristine graphene (PG) and Al-doped graphene (AlG) so we examined the geometrical structure, adsorption energy, natural bond orbital analysis, density of states, and Global indices of PG and AlG before and after interaction with AC and AF molecules.

2. Computational methods

In this study, all the structure optimizations, the NBO analysis, the DOS, and calculations of energies were carried out by using Gaussian 03 program package [33] with density functional theory (DFT) at the level of B3LYP/6–31G(d,p). We chose DFT method for our calculations because of its simple use and extension to large systems [34]. All of our calculations are based on the relaxed structures of any system. Before adsorption, all geometrical structures were fully optimized and all the atoms including PG, ALG, AC and AF were relaxed when AC and AF adsorbed on the surface of PG and AlG. A space width of 16 Å above is created, which makes sure that the z-axis of the periodic supercell is large sufficient so that there is no interaction between graphene sheets of bordering super-cells. Relaxed structural model of the 4×4 PG as well as AlG is given in Fig. 1.

The adsorption energies E_{ads} between the analytes and PG as well as AlG are defined as Eqs. (1) and (2) respectively:

$$E_{ads}(PG) = E_{\text{analyte}-\text{PG}} - (E_{\text{PG}} + E_{\text{analyte}}) \tag{1}$$

$$E_{ads(\text{AlG})} = E_{\text{analyte}-\text{AlG}} - (E_{\text{AlG}} + E_{\text{analyte}}) \tag{2}$$

where the $E_{\text{analyte}-\text{PG}}$ and $E_{\text{analyte}-\text{AlG}}$ correspond to the adsorbed systems of pristine graphene and Al-doped graphene, E_{PG} and E_{AlG} correspond to isolated pristine graphene and Al-doped graphene, and then E_{analyte} corresponds to isolated AC and AF respectively.

Following geometry optimizations, the electronic energies calculated for the most appropriate configuration during adsorption on the surface of AlG were corrected for basis set superposition error (BSSE) as shown in Eq. (3).

$$\Delta E_{ads,\text{CP}} = E_{ads} - E_{\text{BSSE}} \tag{3}$$

where $\Delta E_{ads,\text{CP}}$ is corrected counterpoise energy, E_{BSSE} is the energy of basis set superposition error. It should be mentioned that all the mentioned energies of the equations related to equivalently relaxed minimum energy structures. Also the adsorption energies are defined here as the negative i.e. the most stable structure relates to the largest negative value of ΔE_{ads}. Electronic properties (natural bond orbital (NBO) and Mulliken charge analysis), density of states (DOS), the energy of lowest unoccupied molecular orbital (LUMO), the energy of highest occupied molecular orbital (HOMO), and band gap (E_g) were calculated at the above mentioned level of theory. The charge transferring between AC, AF and the surface of both PG and AlG were calculated from the varying of the charge concentration on the mentioned molecules after interaction. This calculation has been done by NBO analysis and the results were compared to Mullikan charge analysis. Chemical potential (μ) is defined based the subsequent equation [35]:

$$\mu = \frac{-(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \tag{4}$$

where E_{HOMO} is the energy of highest occupied molecular orbital and E_{LUMO} is the energy of lowest unoccupied molecular orbital. In addition, hardness (ŋ) can be calculated using the Koopmans' theorem [35] as: $ŋ = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$. Softness (S) [35] and electrophilicity (ω) [35] are described as the subsequent equations, respectively.

$$S = \frac{1}{2\eta} \tag{5}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{6}$$

3. Results and discussion

3.1. Doping behavior of Al

The structure of graphene changes significantly upon doping graphene with Al atom. Fig. 1 represents the geometric structure of isolated PG and AlG after relaxation. As shown in Table 1, the bond length was changed from 1.43 Å for C—C at PG to 1.85 Å for Al—C at AlG. This is accomplishing with the distortion of hexagonal structure of graphene. In order to examine the changing in the electronic structure of graphene caused by Al doping, the charge distribution