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Adsorption of formaldehyde molecule on the intrinsic and Al-doped graphene: A first principle study

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ABSTRACT

To search for a high sensitivity sensor for formaldehyde (H_2CO), we investigated the adsorption of H_2CO on the intrinsic and Al-doped graphene sheets using density functional theory (DFT) calculations. Compared with the intrinsic graphene, the Al-doped graphene system has high binding energy value and short connecting distance, which are caused by the chemisorption of H_2CO molecule. Furthermore, the density of states (DOS) results show that orbital hybridization could be seen between H_2CO and Al-doped graphene sheet, while there is no evidence for hybridization between the H_2CO molecule and the intrinsic graphene sheet. Therefore, Al-doped graphene is expected to be a novel chemical sensor for H_2CO gas. We hope our calculations are useful for the application of graphene in chemical sensor.

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1. Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice and is a basic building block for graphitic materials of all other dimensionalities [1]. Its intriguing electric and transport properties have attracted wide attention since its discovery in 2004 [2–6]. Very recently, the possibility to use graphene as a highly sensitive gas sensor was reported by Schedin et al. [7]. They found that graphene is an exceptionally low-noise material electronically, which makes it a promising candidate not only for chemical detectors but also for other applications where local probes sensitive to external charge, magnetic field or mechanical strain are required. The sensitivity of NH_3, CO, and H_2O up to 1 parts per billion (ppb) was demonstrated, and even the ultimate sensitivity of an individual molecule was suggested for NO_2. Meanwhile, theoretical studies were performed to fully exploit the possibilities of graphene sensors. For example, using first-principle calculations, Leenaerts et al. investigated the adsorption of NH_3, NO_2, NO, CO and H_2O on graphene sheet [8]. Ao et al. found that the Al-doped graphene has high sensitivity to the CO molecules [9].

H_2CO is highly toxic and volatile. It is also a carcinogen [10,11]. So it is very important to monitor and control its exposure in both industrial and residential environments. Great efforts have devoted to search rapid, simple, sensitive methods for detecting H_2CO, including spectrophotometry, polarography, gas chromatography, and fluorometry [12,13]. Recently, using DFT calculations, Wang et al. proposed that the boron doped single walled carbon nanotube and silicon doped boron nitride nanotube to be potential candidates for detecting H_2CO molecules [14,15]. In this article, we report that the sensitivity of graphene system to H_2CO could be enhanced to a higher level through aluminum doping based on DFT. We hope our result may provide new insight to the gas sensors for virtual applications.

2. Method

All DFT calculations are performed using DMol^3 code [16,17] to study the interactions between H_2CO and the graphene surface. Structure optimizations and corresponding total energy calculations of the most stable geometries are based on the generalized-gradient approximation (GGA) function with the Perdew–Burke–Ernzerhof (PBE) correction [18]. Compared to local density approximation (LDA), GGA will not lead to a strong bonding of molecules. So, if the calculated molecules adsorb on graphene surface, they will definitely bind in a real system [19,20]. The DFT semicore pseudopotentials (DSPP) core treatment [21] is implemented for relativistic effects, which replaces core electrons by a single effective potential. To ensure that the results of the calculations are comparable, identical conditions are employed for the isolated H_2CO molecule, the graphene sheet and also the adsorbed graphene system. The k-point is set to $6 \times 6 \times 1$ for all slabs, which brings out the convergence criterion of 10^{-5} a.u. on energy and electron density, and that of maximum force of 0.002 Ha/Å. Self-consistent field procedure is carried out with a convergence criterion of 10^{-6} a.u. on energy and electron density.

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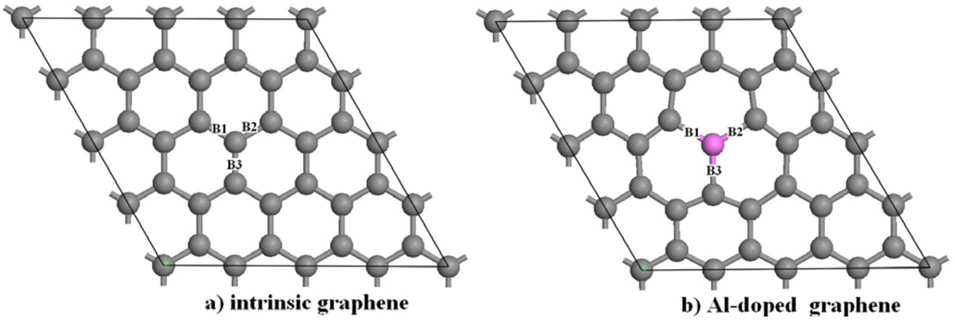

Fig. 1. Optimized configurations of intrinsic graphene and Al-doped graphene, the bonds around the center C(Al) atom are labeled as B1, B2 and B3, gray and pink spheres are denoted as C and Al, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

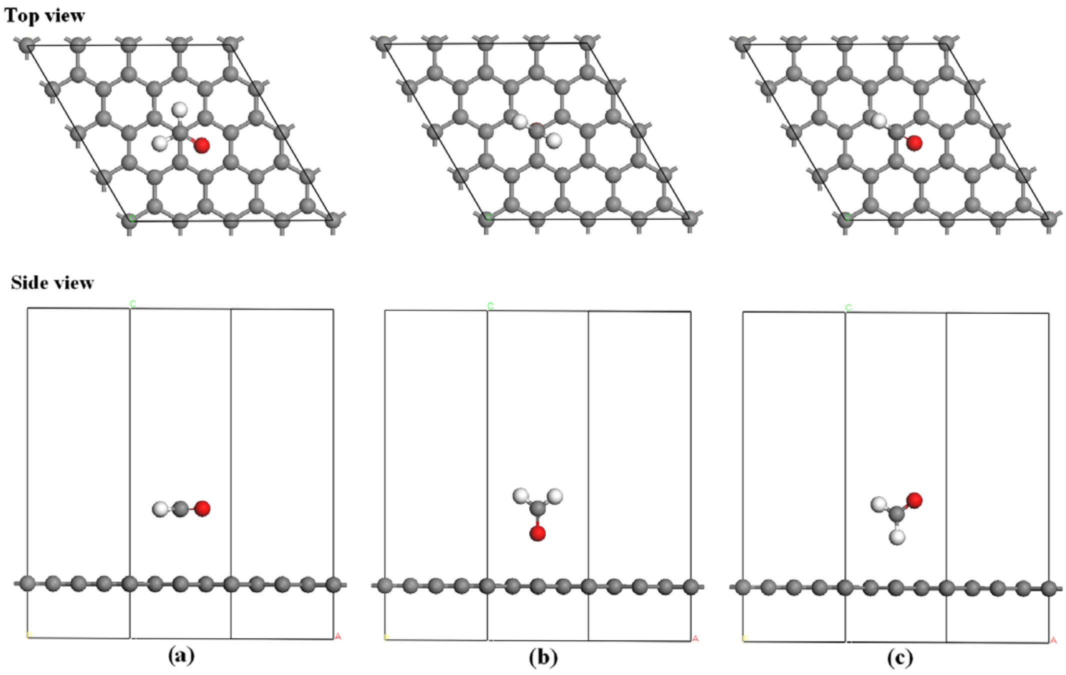

Fig. 2. Initial structures of a H_2CO molecule adsorbed on the intrinsic and Al-doped graphene (top and below panels show the top and side view, respectively): the adsorbed systems are labeled by (a), (b) and (c) with the O, C and H atoms of a H_2CO molecule close to the surface, respectively. Gray, pink, red and white spheres are denoted as C, Al, O and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) In Fig. 3, spheres have the same meaning as that in this figure.

In the present calculations, the periodic boundary condition is taken with the supercells. A vacuum width of 16 Å above is constructed, which ensures that the *z*-axis of the periodic supercell (perpendicular to the graphene layer) is large enough so that there is no interaction between graphene sheets of adjacent supercells. Optimized structural model of the 4×4 intrinsic graphene is shown in Fig. 1a. This ensured a lateral distance between H_2CO molecules of at least 8 Å to eliminate interaction between H_2CO molecules in neighboring supercells. Replacing the center carbon atom by an Al atom, the Al-doped system configuration can be obtained. Its optimized structure is shown in Fig. 1b. In this case, the concentration of the doped in graphene is 3.125% atomic ration. The bonds around the center C (Al) atom are labeled as B1, B2 and B3, which elongate from l_{c-c} = 1.420 Å to l_{Al-c} = 1.633 Å after the Al atom doping. This is in quite good agreement with Ao's results [9].

Table 1
The binding energy (E_b) and the distance of H_2CO above the graphene surface (d).

	Intrinsic graphene		Al-doped graphene	
	E_b (eV)	d (Å)	E_b (eV)	d (Å)
C close	−0.083	3.127	−3.703	1.877
O close	−0.032	3.327	−3.721	1.876
H close	−0.053	2.866	−2.525	2.319

3. Results and discussion

To evaluate the interaction between a H_2CO molecule and adsorption sheet surface, we first calculated the binding energy (E_b) of adsorbed systems, which is defined as

$$E_b = E_{\text{total}} - (E_{\text{sheet}} + E_{H_2CO})$$

where the E_{total}, E_{sheet} and E_{H_2CO} denote the total energy of intrinsic or Al-doped graphene adsorbed system, isolated graphene or Al-doped graphene and a H_2CO molecule, respectively. A negative E_b corresponds to a stable adsorption structure.

We first search the stable adsorption geometry of H_2CO on intrinsic and Al-doped graphene. Various possible adsorbing

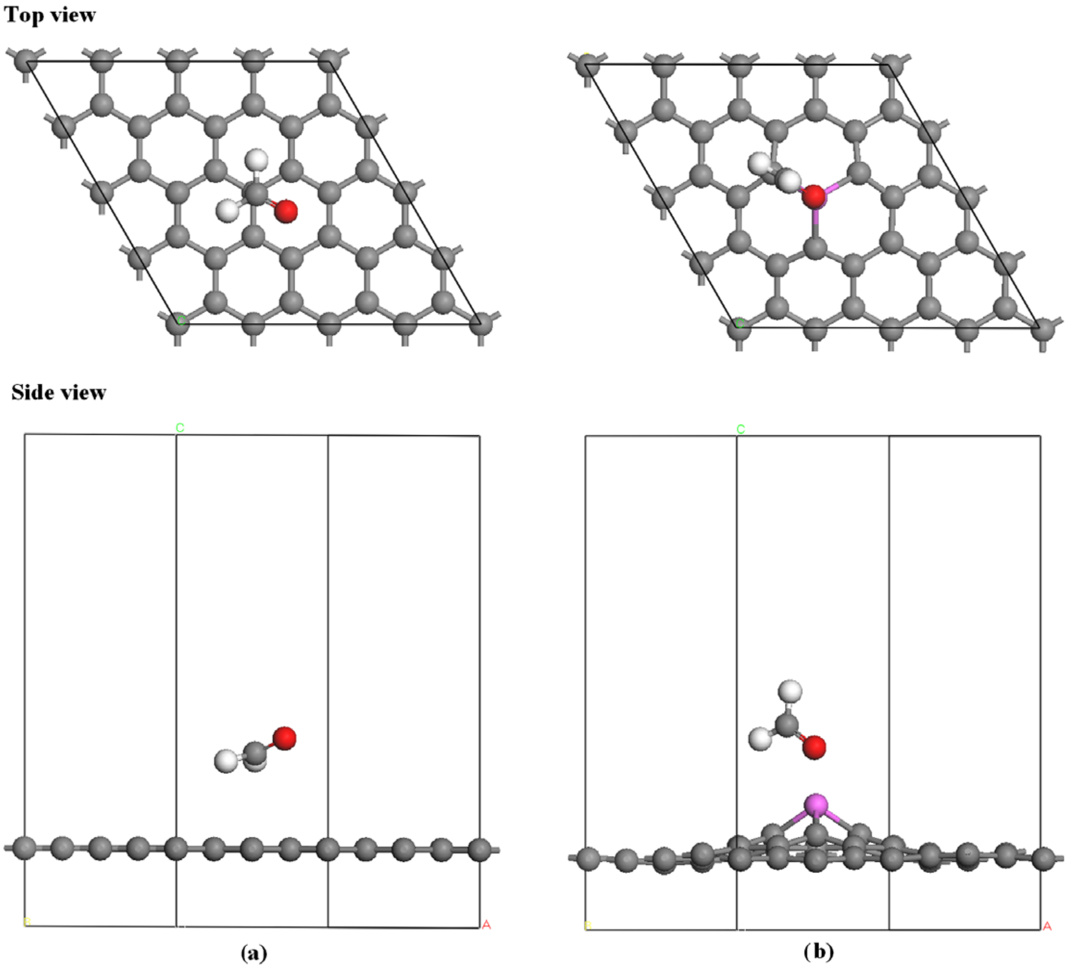

Fig. 3. Optimized most stable configurations of (a) intrinsic graphene and (b) Al-doped graphene.

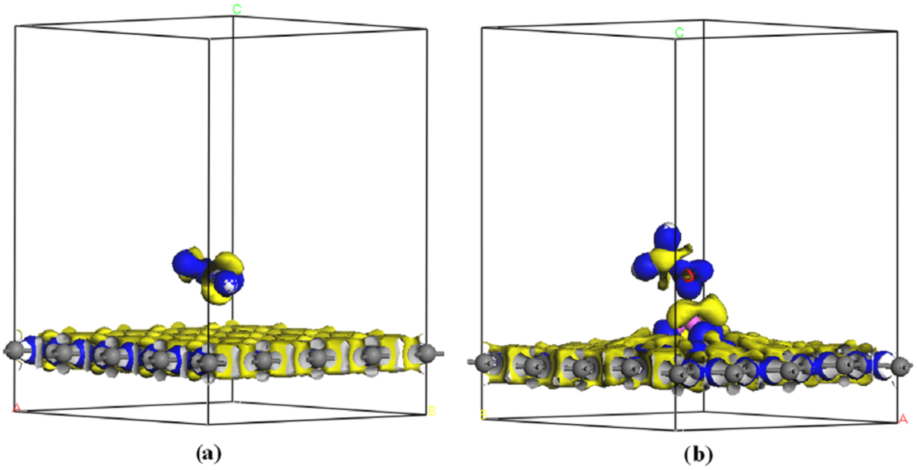

Fig. 4. The electronic density difference isosurfaces for (a) H_2CO-graphene system and (b) H_2CO-Al-doped adsorbed systems with energy preferred configuration (graphene systems). The blue region shows the electron accumulation, while the yellow region shows the electron loss. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

configurations are investigated. Our results show that the adsorption energy is primarily determined by the atom type which is closer to the adsorbed sheet. The variation of E_b results would be within a range of 0.005 eV to rotation around the axis perpendicular to the surface and through the carbon atom of H_2CO. Therefore, in this article three most stable representative adsorption configurations, in which the graphene is close to the carbon (Fig. 2a), oxygen (Fig. 2b) and hydrogen (Fig. 2c) atom of H_2CO, are selected to describe this problem. Initial configurations of adsorbed systems are shown in Fig. 2. The center atom in graphene surface is C atom

Table 2
The bond length (*l*) and the net electron transfer parameters (*q*) of the most stable intrinsic graphene and Al-doped graphene before and after adsorption of H_2CO molecule.

System	Configuration	Bond	Bond length *l* (Å)	q^a
H_2CO-intrinsic graphene	Without adsorbed	B1	1.420	–
		B2	1.420	
		B3	1.420	
	Adsorbed	B1	1.426	0.019
		B2	1.426	
		B3	1.426	
H_2CO-Al-doped graphene	Without adsorbed	B1	1.702	–
		B2	1.702	
		B3	1.702	
	Adsorbed	B1	1.887	0.085
		B2	1.887	
		B3	1.888	

[a] Electrons transferred from the graphene sheet to H_2CO molecule.

for intrinsic graphene or Al atom for Al-doped graphene. In Fig. 2a, H_2CO molecule is residing parallel to the surface, while others are residing perpendicular.

According to the calculated adsorption energies, the most stable configuration can be determined. As shown in Fig. 2 and Table 1, for the intrinsic graphene system, the calculated E_b values for (a), (b) and (c) are −0.083, −0.032 and −0.053 eV, respectively. Although configuration with C atom close to the intrinsic graphene (Fig. 3a) has the lowest E_b value −0.083 eV, the differences in adsorption energies of various sites are no more than 0.05 eV. Therefore, we predict that the mobility of H_2CO on graphene will be high at room temperature. Adsorption of H_2CO does not result in any significant structural distortion in the graphene, and the C–C bonds (B1, B2 and B3 in Fig. 1a) were slightly lengthened by 0.006 Å. Table 1 also presents the binding distance (*d*) of the H_2CO above the adsorbed sheet, which is defined as the length between the center C (Al) atom in adsorbed sheet and the atom of H_2CO molecule close to the center atom. For all adsorption sites in intrinsic adsorbed system, the H_2CO molecule is found floating

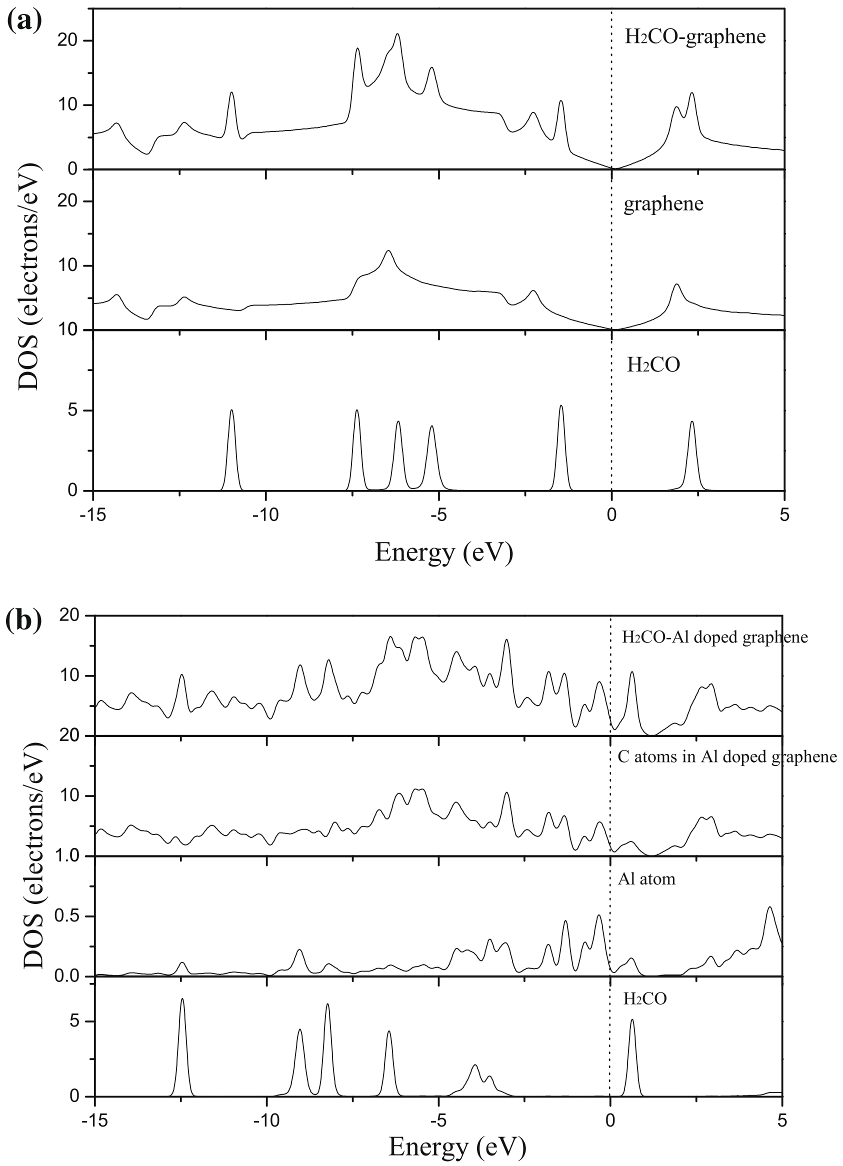

Fig. 5. The electronic density of state (DOS) for (a) H_2CO-graphene system and (b) H_2CO-Al-doped graphene system with preferred configuration. The dash line indicate the Fermi level.

above the graphene sheet at about 3 Å, and there is no evidence of formation of chemical bonds between the H_2CO molecule and the graphene. The small binding energy and large d values indicate that H_2CO undergoes physical adsorption on intrinsic graphene due to weak van der Waals interaction between them. While for the Al-doped adsorbed systems, dramatic structural changes could be seen after H_2CO adsorption. From Table 1, we found that after adsorption, the configuration obtained from the initial structure with O atom close to the doped surface (Fig. 3b) has the most stable relaxed structure. The Al–C bond lengths were elongated from 1.702 to 1.887, 1.887 and 1.888 Å for B1, B2 and B3 in Fig. 1b, respectively. This results in the Al atom protruding the graphene sheet. The corresponding E_b of H_2CO in the Al-doped graphene system is −3.721 eV, which is over 44 times larger than that of H_2CO in the intrinsic graphene system. Compared with the E_b of H_2CO in other systems, such as 0.881 eV in B-doped SWCNT systems and 1.824 eV in Si-doped BNNT systems [14,15], the Al-doped graphene is energetically favorable for H_2CO adsorption. Moreover, the distance between the H_2CO molecule and Al atom in the doped graphene is 1.876 Å, being much shorter than that in the intrinsic graphene system.

In the following, we will limit the following discussion to the most stable configurations of intrinsic and Al-doped graphene adsorbed systems. To investigate the changes of electronic structures in graphenes caused by the adsorption of H_2CO molecule, electron density difference $\Delta\rho$ is calculated, which illustrates how the charge density changes during this adsorption process. $\Delta\rho$ is defined as

$$\Delta\rho = \rho_{\text{total}} - (\rho_{\text{sheet}} + \rho_{\text{H}_2\text{CO}})$$

in which ρ_{total}, ρ_{sheet} and $\rho_{\text{H}_2\text{CO}}$ denote electron density of the intrinsic or Al-doped graphene adsorbed system, graphene or Al-doped graphene and a H_2CO molecule for the adsorbed system, respectively. The electronic densities difference of energy favorable intrinsic and Al-doped graphene with H_2CO adsorptions are shown in Fig. 4. In this plot a loss of electrons is indicated in yellow[1], while electron enrichment is indicated in blue. Fig. 4a shows that the bond in the intrinsic graphene and H_2CO are of covalent nature because the preferential electron accumulation sites are mainly located within the bond rather than heavily centered on a particular atom. No charge accumulation could be seen between intrinsic graphene and H_2CO. This indicated the interaction between the adsorbed molecule and the sheet is mainly electrostatic in nature. While the chemisorption of H_2CO on Al-doped graphene can be seen from Fig. 4b. In this case, Al atom loses electrons while O and C atom of the molecule gain electrons. Notably, some charges accumulate between O of H_2CO and Al atoms, which confirm the binding between H_2CO and Al-doped graphene induced by adsorption. The above results derived from Fig. 4 are supported by the data from Mulliken charge analysis [22], where O decrease from −0.304e to −0.442e and C decrease from 0.001e to −0.115e. As listed in Table 2, about 0.085 e is transferred from the Al-doped graphene to the H_2CO molecule, which is 4 times more than 0.019 e in the intrinsic graphene. This result again proves the doping of Al atom change the electronic transport properties of the graphene.

To better understand the electronic properties of these intrinsic and Al-doped graphene systems, we also calculated the electronic densities of states (DOS) for the pristine and Al-doped graphene as well as their energy preferable adsorbed systems. In this part, the Kohn–Sham DOS is computed using a $18 \times 18 \times 1$ Γ-centered Brillouin-zone sampling, and the energy eigenvalues are smeared with Gaussians of width of $\sigma = 0.1$ eV. The DOS plot for the H_2CO-graphene system is determined and shown in Fig. 5a. As comparisons, partial densities of state (PDOS) plots of H_2CO molecule and graphene sheet also depicted there. There is no evidence for hybridization between the H_2CO molecule and the intrinsic graphene sheet, the molecular orbitals of the adsorbates are recognizable as sharp peaks in the supercell DOS and the Dirac point of this adsorbed system is clearly visible. These results show that the graphene states are nearly unaltered by the adsorption of the H_2CO molecule. Therefore, intrinsic graphene cannot be a good sensor material to detect the presence of H_2CO molecules, similar to that of H_2CO adsorption on carbon nanotube [14]. Unlike the intrinsic adsorbed system, the adsorption of the H_2CO molecule alters the Al-doped graphene electronic structure. The partial PDOS results in Fig. 5b shows that the H_2CO molecule hybridizes with Al atom and carbon atoms of graphene sheet at −12.5, −9, −4 and 0.6 eV relative to E_f. We find that the H_2CO highest occupied molecular orbital (HOMO) is more than 2.5 eV below the Fermi level and therefore does not give rise to any doping. However, the lowest unoccupied molecular orbital (LUMO) is always quite near to the Fermi energy, i.e., at about 0.6 eV. This orbital (H_2CO–$2\pi^*$) can be populated by the sheet electrons as a result of thermal excitations. Therefore, both ionic bonds induced by the charge transfer and covalent bonds due to the overlap of orbitals contribute to the bonding of this adsorption process. The Al-doped graphene would be a promising sensor material to detect H_2CO molecules.

4. Conclusion

In summary, with DFT calculations, the adsorptions of H_2CO on the intrinsic and Al-doped graphene are studied. Compared with the intrinsic, H_2CO molecules are strongly adsorbed onto the Al-doped graphene with high binding energy value and short distance between the H_2CO molecules and the surface. The net electron transfer from the Al-doped graphene to H_2CO is 4 times more than that in the intrinsic graphene. Furthermore, the density of states (DOS) results show that orbital hybridization could be seen between H_2CO and Al-doped graphene sheet, while there is no evidence for hybridization between the H_2CO molecule and the intrinsic graphene sheet. Therefore, the Al-doped graphene is expected to be a novel sensor for the detection of H_2CO molecules.

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