Theoretical study on absorption of formaldehyde in graphene

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Abstract: Density functional theory (DFT) based ab-initio calculations were used to study formaldehyde (CH_2O) adsorptive behavior on graphene sheet. The results indicate that formaldehyde molecule is weakly bound to graphene with small adsorption values (approximately −0.064 eV), but the interaction between CH_2O and graphene sheets can be greatly strengthened by means of doped atoms, which can provide a basis for the development of CH_2O storage materials.

Key words: density functional theory; absorption; formaldehyde (CH_2O) molecule; grapheme

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Formaldehyde (CH_2O) is well known as the most common environmental and industrial pollutant because of its colourless and extremely flammable toxic gas at a high concentration[1-3]. In view of its hazardous nature, CH_2O removal technologies including lots of physical and chemical methods have been developed. Recently, ultra-high ability of graphene (two-dimensional carbon atoms sheet of sp^2 hybrid orbital) with high specific surface area (2 630 m^2/g) to capture molecules has been demonstrated[4]. It has been proven to be a good potential as a superior adsorbent for many other molecules such as H_2, CH_4, CO_2, N_2, NH_3, NO_2, H_2S, SO_2, etc.[5] while the interfacial reaction between graphene sheet or its derivatives and CH_2O molecule has been studied through many calculations that have proved strong possibility of graphene[6-8]. Al-doped graphene was found to be an effective functional material for detecting CH_2O molecule[6]. ZHANG et al.[7] found that doped Ti atom could greatly improve the interaction of CH_2O with graphene. Furthermore, it was found that graphene defected by the transition metal atoms doped Stone-Wales exhibited larger binding energy and shorter bond length with adsorption of CH_2O molecule[8]. But clearly, several challenges and doubtful points in practice still exist, such as how to control the desirable doped sites, binding sites and functionalities effectively. The difference of the interactions between graphene sheets and CH_2O molecule should be systematically studied.

In this study, the interfacial interaction between CH_2O molecule and graphene was explored by density functional theory (DFT) calculations. The adsorption energy, total electron density and electron density difference were calculated in detail to evaluate the effect of the modified groups.

1 Computation details

CH_2O adsorption simulations were calculated with an efficient ab-initio computer code and the DFT program DMol3 in Materials Studio was used to investigate the interactions between the CH_2O molecule and pure or modified graphene. A 4×4 graphene super cell is modelled with a large distance of 30 Å between adjacent graphene sheets and a single CH_2O molecule

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adsorbed on it. A double-numerical plus polarization (DNP) basis set was employed to produce highly accurate results while keeping the cost of computational fairly low[9-10]. The generalized gradient approximation (GGA) was used for exchange correlation functional, as described by PW91[11]. Monkhorst-Pack schemes with 5×5×1 *k*-point mesh were used in special points sampling in the Brillouinzone[12]. A Fermi smearing of 0.005 Ha (1 Ha=27.211 4 eV) and a global orbital cutoff of 5 Å were employed. The convergence inenergy, force and displacement were set at 1.0×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å, respectively. The binding energy (E_{ads}) was defined according to the following equation

$$E_{ads} = E_{graphene+molecule} - (E_{graphene} + E_{molecule}), \quad (1)$$

where $E_{graphene+molecule}$, $E_{molecule}$ and $E_{graphene}$ represent the total energy of the system, the energy of CH_2O molecule, and the energy of pure or modified graphene sheet, respectively. A negative E_{ads} value corresponds to stable adsorption. The more negative the E_{ads} value, the more stable the adsorbed structures.

2 Results and discussion

2.1 Structural properties

We optimized a structural model of 4×4 graphene sheet, and the calculated C-C bond length is found as 1.423 Å which is close to the previous results[13]. A vacuum with a slab approximately 10 Å was added onto the graphene sheet so that the adsorbent molecule would only interact with one side of the graphene sheet. The optimized graphene sheet is shown in Fig. 1.

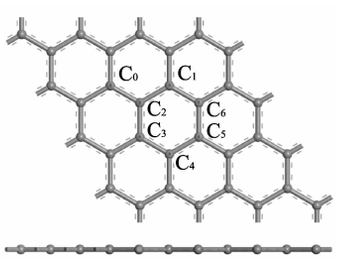


Fig. 1 Model of graphene

A CH_2O molecule was added onto the graphene sheet to investigate the influence of interactions between the graphene sheet and the CH_2O molecule. The structural properties of the group modified graphene were carefully studied.

2.2 Energetic properties

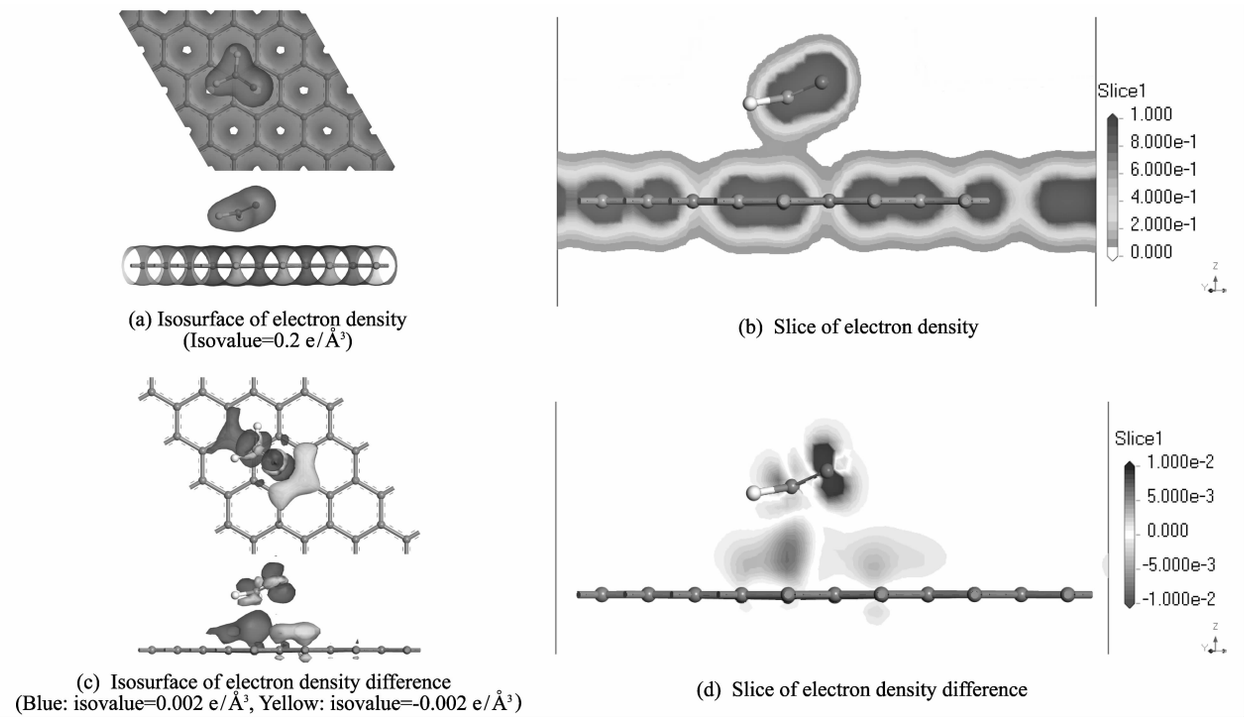
In order to obtain the most stable adsorption configuration, the gas molecule is initially placed at different positions above the graphene or modified graphene with various orientations. After relaxation, the optimized configurations obtained from the different initial states are compared to search for the most favorable one.

From calculation results, the E_{ads} between the pure graphene sheet and the CH_2O molecule is about −0.064 eV. According to other researches, atoms doped graphene is also a promising CH_2O adsorbed material. The researchers have studied the CH_2O adsorbed onto the B, N and S doped combining with vacancy graphene sheet. Their results show that B and S doped vacancy graphene sheets exhibit a good ability for CH_2O adsorption and the binding energies are about 0.543 eV and 1.542 eV, respectively[14]. It indicates that the adsorption ability of nonmetal doped graphene can also be fine. XIAN et al.[15] found that Al doped graphene exhibits a better CH_2O adsorption ability compared with that of the intrinsic graphene (approximately 1.725 eV). ZHOU et al.[8] used DFT method to study Cr, Mn, Co doped graphene sheet and adsorption energy of CH_2O (about 1.887 eV, 2.257 eV and 2.461 eV, respectively) which are greater than that of nonmetal atoms doped graphene sheet. As introduced by WANG et al.[4] (A review about the graphene-based materials), graphene based materials would be the most promising candidates of gas adsorption for its lower weight, lower price and safety in everyday use. They also mentioned that metal doped graphene sheet would change the adsorption behavior of CH_2O from physisorption to coulmb or kubas interactions. According to our and other's theoretical studies[6-8,14-15], both atoms doped and groups modified graphene could be the excellent CH_2O adsorption materials. The interactions between CH_2O and graphene sheets could be greatly strengthened.

2.3 Electronic properties

The electron density and electron density difference before and after CH_2O molecule adsorption were studied to illustrate the electron transfer during the adsorption of CH_2O molecule. As shown in Figs. 2(a) and (b), the isosurface of the total electron density indicate that the graphene sheet and the CH_2O molecule have the small isosurface area with an isovalue about 0.1e/Å^3. Thus, the CH_2O molecule has a weak interaction with the pure graphene sheet. These results are in accordance with the E_{ads} values. The graphene sheet has the small capability to capture CH_2O molecules.

Although overlapping of electrons was found between the CH_2O molecule and the doped graphene sheet, detailed electron transfer could not be observed. The electron density difference could be used to illustrate the gain and loss of electrons during the interaction. As shown in Fig. 2(c), the C atoms of graphene below the O atom demonstrat electron loss. The lost electrons formed intense interactions between the modifie C atoms of graphene and the CH_2O molecule.



(a) Isosurface of electron density (Isovalue=0.2 e/Å^3)

(b) Slice of electron density

(c) Isosurface of electron density difference (Blue: isovalue=0.002 e/Å^3, Yellow: isovalue=-0.002 e/Å^3)

(d) Slice of electron density difference

Fig. 2 Picture of CH_2O adsorption in graphene

The loss and gain of electrons could also be verified by Mulliken charge calculations before and after CH_2O molecule adsorption. As listed in Table 1, the effects of changes in the local charge value have been explored. The results can be very good agreement with previous data in Fig. 2(c).

Table 1 Charge of atoms in pure and modified graphene before and after DFT calculations

Atoms	C_0	C_1	C_2	C_3	C_4	C_5	C_6	O	C	H_1	H_2
Before ads	0.000	0.000	0.000	0.000	0.000	0.000	0.000	−0.370	0.039	0.165	0.165
After ads	−0.013	−0.008	−0.040	0.011	0.008	0.012	−0.008	−0.313	−0.007	0.144	0.142

3 Conclusion

The adsorption ability of an isolated CH_2O molecule on graphene sheets was theoretically investigated. The results indicate that the interactions between CH_2O and the graphene sheets can be greatly strengthened by doped atoms. The adsorption energy of one CH_2O molecule can not be improved with the heteroatoms density increasing, which indicats that group modified graphene sheets are the promising candidates of CH_2O adsorption materials. The re-

sults of our work may provide a basis for the adsorption or separation of CH_2O molecules using graphene based materials.

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石墨烯吸附甲醛分子理论研究

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摘　要： 基于密度泛函理论的第一性原理计算研究石墨烯与甲醛分子的吸附现象。结果表明，甲醛单分子与石墨烯的结合能约为－0.064 eV，结合强度较小；可通过掺杂原子提高石墨烯与甲醛分子的结合强度，这为甲醛分子的储存材料研究提供了参考。

关键词： 密度泛函；吸附；甲醛分子；石墨烯

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