First-principles Studies of Formaldehyde Molecule Adsorption on Graphene Modified with Vacancy, -OH, -CHO and -COOH Group

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ABSTRACT

Density functional theory (DFT) based ab-initio calculations were used to study the adsorption of CH\_2O molecule on the intrinsic and vacancy, -OH, -CHO or -COOH group modified graphene. The result indicated that in the optimized structural models of modified graphene, the C-C bond length around the vacancy, -OH, -CHO or -COOH group were compressed or stretched; The CH\_2O molecule weakly binds to the intrinsic graphene with the binding energy -0.228eV. The binding energy between CH\_2O and -COOH or -OH group modified graphene were -0.538eV and -0.474eV, which indicates that -COOH and -OH group modified graphene is most suitable for CH\_2O adsorption; Moreover, the isosurface of the total electron density and the electron density difference between the modified graphene and CH\_2O molecule were calculated, which illustrated the electron changes and distributions.

INTRODUCTION

Graphene based materials are the most promising candidate of gas adsorption, storage, separation and sensing due to its hierarchical pore structures, tuneable high surface area, chemical doping and surface functionalization. Graphene\cite{1-4} and its derivatives\cite{5-12} had been shown as the adsorption or sensing material for small gases. CH\_2O is well known as the most common environmental and industrial pollutant because of its colorless and extremely flammable toxic gas at a high concentration. Therefore, monitoring and controlling CH\_2O in both industrial and residential environments are essential. A great amount of effort has been done to find a sensitive technique for CH\_2O detecting. For example, a lot of theoretical studies\cite{13-15} have been carried out for CH\_2O adsorption on transition metal doped graphene. Zhou et al.\cite{13} used DFT method to study the adsorption of CH\_2O on Cr, Mn, Co doped graphene sheet, and the corresponding adsorption energies are approximately -2.197eV, -2.558eV and -2.808eV respectively. Main group metal (mainly Al) doped graphene can greatly increase its adsorption capability of CH\_2O...
molecule on the sheet\cite{16-18}. Qin et al\cite{17} used DFT method to calculate the adsorption energy of CH\textsubscript{2}O on Al doped graphene sheet, which is approximately -1.934eV. The adsorption of CH\textsubscript{2}O molecule on Nonmetal doped graphene was investigated. Zhou et al.\cite{19} used DFT method to study the B, N, S doped vacancy defected graphene sheet and the adsorption energies of CH\textsubscript{2}O on the B, N, S doped vacancy defected graphene are approximately -0.543eV, -0.165eV and -1.542eV respectively. The results showed that the metal doped graphene is more effective than the nonmetal doped graphene in detecting and removing gas molecules, which exhibited the larger binding energy.

Intrinsic graphene has perfect honeycomb structure, and it is difficult to dope hetero atoms into graphene efficiently and cheaply, and difficult to control accurately the adsorption sites into graphene\cite{20}. Graphene oxide (GO) is an analog of graphene with many different functional groups which make the physical and chemical properties of GO largely difference from those of graphene. What's more, GO is inexpensive and easy to prepare, unlike doped graphene, while GO has a large specific surface area like graphene. But few papers have been studied on the interaction of CH\textsubscript{2}O with GO system. In this study, the CH\textsubscript{2}O adsorption on GO which modified with different groups were explored by density functional theory (DFT) calculations. Vacancy, -OH, -CHO and -COOH group modified graphene sheets were studied. The adsorption energy, total electron density and electron density difference were calculated in detail to evaluate the effect of the adsorption system.

**COMPUTATION DETAILS**

All calculations are performed by using an efficient ab-initio computer code: DMol\textsuperscript{3}, which was used to investigate the interactions between the CH\textsubscript{2}O molecule and intrinsic or modified graphene. A Triple Numerical plus polarization (TNP) basis set was employed to get highly accurate results. The generalized gradient approximation (GGA) was used for exchange correlation functional, as described by Perdewe-Burkee-Ernzerhof (PBE). Monkhorst-Pack schemes with 6x6x1 k-point mesh were used in special points sampling in the Brillouinzone. A Fermi smearing of 0.005Ha (1Ha=27.2114 eV) and a global orbital cutoff of 6.0Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: self consistent field tolerance, 1.0x10\textsuperscript{-6}Ha/atom; energy tolerance, 1.0x10\textsuperscript{-5}Ha/atom; maximum force tolerance, 0.002 Ha/Å; maximum displacement tolerance, 0.005Å\cite{21}. We have defined binding energy ($E_{ads}$) according to the following equation:

$$E_{ads}=E_{\text{graphene+CH2O}}-(E_{\text{graphene}}+E_{\text{CH2O}})$$

(1)

Where $E_{\text{graphene+CH2O}}$, $E_{\text{CH2O}}$ and $E_{\text{graphene}}$ represent the total energy of the system, the energy of the CH\textsubscript{2}O molecule, and the energy of the intrinsic 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.
RESULTS AND DISCUSSION

Structural properties: The system was modelled as 4×4 graphene super cell containing 32 atoms with a periodic boundary condition along the x-y plane. A vacuum with a slab approximately 60 Å was added onto the graphene sheet so that the adsorbent atom would only interact with one side of the graphene sheet. The optimized structural model of 4x4 intrinsic graphene was shown in Fig.1.a. Models of modified graphene sheet were built based on the model of intrinsic graphene. One C atom was modified with vacancy, -OH, -CHO and -COOH group. The optimized structure of the modified systems was obtained as shown in Fig.1.b~e. A CH₂O molecule was added onto the intrinsic or modified graphene sheet to investigate the influence of interactions between the graphene sheet and the CH₂O molecule. The structural properties of the group modified graphene were carefully studied.

When the C atom (C₀ in Fig.1.a) was replaced by a vacancy, the geometric structure of the defected graphene was dramatically changed. The C-C bonds around the defect in the modified structure were compressed or stretched which was changed from a perfect state 1.425Å to another length. When the C atom was modified by an -OH group (in Fig.1.e), the largest bond length of C-C around the defect increased to approximately 1.518Å, and the bond length of C-O (between graphene and -OH group) was approximately 1.446Å. However, when the C atom was modified by an -CHO group, the largest bond length of C-C around the defect increased to approximately 1.565Å which is approximately equal to the largest bond length (1.553Å) of -COOH group modified graphene sheet.

Energetic properties: In order to obtain the most stable adsorption configuration, the CH₂O molecule was initially placed at different position above the intrinsic 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.

|                  | G  | G-vacancy | G-CHO | G-COOH | G-OH |
|------------------|----|-----------|-------|--------|------|
| E_ads            | -0.228 | -0.3408 | -0.351 | -0.538 | -0.474 |
| Deviation        | 49.41% | 54.19% | 136.41% | 108.07% |
As shown in Table 1, the $E_{\text{ads}}$ between the intrinsic graphene sheet and the CH$_2$O molecule was about $-0.228\text{eV}$. The $E_{\text{ads}}$ between the vacancy and -CHO modified graphene sheet and the CH$_2$O molecule was approximately $-0.340\text{eV}$ and $-0.351\text{eV}$ respectively, the corresponding deviation was 49.41% and 54.19% respectively. The $E_{\text{ads}}$ between the -OH, -COOH group modified graphene sheet and the CH$_2$O molecule was approximately $-0.474\text{eV}$ and $-0.538\text{eV}$ respectively, the corresponding deviation was 136.41% and 108.07% respectively. It can be conclusion that the $E_{\text{ads}}$ between the intrinsic graphene sheet and the CH$_2$O molecule was increased a lot when the intrinsic graphene was modified by the vacancy, -CHO, -OH and -COOH group.

Previous studies\cite{13-19} have been done to research the doped graphene with CH$_2$O adsorption. The results indicated that CH$_2$O molecule strongly binds to the atom doped graphene. But, these doped graphene were prepared difficu ltly, and the graphite oxide (GO) was prepared easily. Hence, the graphene which was modified by the -OH and -COOH group would be the most promising candidates of the CH$_2$O molecule adsorption.

![Figure 2. The isosurface (Isovalue: +0.2e/Å$^3$) of electron density of CH$_2$O adsorption on (a) intrinsic, (b) vacancy (c) -CHO,(d) –COOH, and (e) -OH doped graphene.](image)

**Electronic properties:** The changes of the electron density and the electron density difference were studied to illustrate the electron transfer during the CH$_2$O molecule was adsorb by the graphene which was modified by the vacancy, -CHO, -OH and -COOH group.

From the front and top view of Fig.2.a, b and c, the isosurface of the total electron density between the intrinsic, vacancy and -CHO modified graphene sheet and the CH$_2$O molecule was few. From the front view and top view of Fig.2.d and e, the isosurface of the total electron density between the -COOH or -OH modified graphene sheet and the CH$_2$O molecule was large. And the isosurface of the total electron density between the -COOH modified graphene sheet and the CH$_2$O molecule has the largest isosurface area, followed by the isosurface area between the -OH, -CHO or vacancy modified graphene sheets and the CH$_2$O molecule. These results are in accordance with the $E_{\text{ads}}$ values in table 1. The -COOH modified graphene sheet had the strongest capability to capture CH$_2$O molecules.

![Figure 3. Isosurface of electron density difference of CH$_2$O adsorption on (a) intrinsic , (b) vacancy, (c) -CHO, (d) –COOH, and (e) -OH modified graphene (Isovalue: yellow: -0.02e/Å$^3$, blue: +0.02e/Å$^3$).](image)

Although the overlapping of electrons was found between the CH$_2$O molecule and the -COOH modified graphene, detailed electron transfer could not be observed.
The electron density difference between the CH$_2$O molecule and the intrinsic or modified graphene could be used to illustrate the gain and loss of electrons. Fig.3 showed the isosurface of electron density difference of CH$_2$O adsorption on intrinsic and modified graphene. Taking -COOH group modified graphene as an example for analysis (see Fig.3.d), the electron density of C atom in -COOH modified graphene and CH$_2$O molecule decrease. The lost electrons formed intense interactions between the modified C atom and the CH$_2$O molecule. And the electron accumulation area was the largest between the -COOH group modified graphene and the CH$_2$O molecule. The electron accumulation area was the smallest between the intrinsic graphene and the CH$_2$O molecule (Fig.3.a).

CONCLUSIONS

The adsorption abilities of CH$_2$O molecule on vacancy, -OH, -CHO and -COOH group modified graphene sheets were investigated by DFT methods. The result indicated that around the defect in the optimized structural models of vacancy, -OH, -CHO or -COOH group modified graphene, the C-C bond length were compressed or stretched, which was changed from a perfect state 1.425Å to another length. The largest C-C bond lengths around the defect in the optimized structural models of modified graphene were 1.450Å, 1.518Å, 1.565Å or 1.553Å respectively. The $E_{\text{ads}}$ between the vacancy, -CHO, -OH, -COOH group modified graphene and the CH$_2$O molecule was approximately -0.340eV, -0.351eV, -0.474eV and -0.538eV respectively, the corresponding deviation was 49.41%, 54.19%, 136.41% and 108.07%, respectively. It indicated that -COOH and -OH group modified graphene sheets have a stronger ability to catch the CH$_2$O molecule, while the intrinsic graphene had the smallest capability to capture CH$_2$O molecules. This difference can be used to control the adsorption and desorption ability of graphene. The changes of the electron density and the electron density difference were calculated and obtained that the isosurface of the total electron density between the -COOH modified graphene sheet and the CH$_2$O molecule has the largest isosurface area, followed by the isosurface area between the -OH, -CHO or vacancy modified graphene sheets and the CH$_2$O molecule. These results are in accordance with the $E_{\text{ads}}$ values. The results of our works may provide a basis for the adsorption or separation of CH$_2$O molecules using graphene based materials.

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