Density functional theory study of CH$_4$ and CO$_2$ adsorption by fluorinated graphene

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Phenomena related to global warming have been of particular interest among researchers, strongly encouraging them to identify various methods of adsorbing contributing gases, such as CH$_4$ and CO$_2$[1,2]. Many adsorbents have been widely proposed and studied to remove greenhouse gases from the atmosphere and protect the environment [3,4]. Carbon-based materials for adsorption are an intriguing subject owing to their very high specific surface area, low weight, and elasticity [5,6]. Among various carbonaceous materials, graphene has attracted much attention from researchers for these reasons; consequently, this material has been empirically and theoretically investigated for possible applications, such as gas sensors [7-10].

Yoon et al. [7] reported the fabrication of a graphene-based CO$_2$ sensing device that exhibited a fast response to CO$_2$ and high recyclability due to the weak interaction between CO$_2$ and graphene. Schrier [8] studied the adsorption of several gas molecules, including CO$_2$ and CH$_4$, on pristine graphene and fully fluorinated graphene at finite temperature. He reported that complete fluorination of graphene is not an effective method for nonpolar gas molecules, such as CH$_4$ and CO$_2$, because the fluorine atom has the lowest polarizability of all atoms, and its dispersion interaction is weak. In addition, for nonpolar molecules, dispersion interactions play the largest role in adsorption. Lee et al. [9] reported the effect of fluorination of a carbon-based substrate on CH$_4$/CO$_2$ separation. They reported that the CO$_2$ adsorption capacity increased up to 22.5% owing to fluorination with an F/C ratio (%) of 32%-43%.

Although experimental studies on the adsorption of gas molecules onto carbon-based substrates have provided much useful information, computational studies at the molecular level can provide detailed information to investigate the interaction between adsorbed gas molecules and substrates. In this study, density functional theory (DFT) calculations were performed to investigate CH$_4$ and CO$_2$ adsorption on pristine and fluorinated graphene. This research extends existing knowledge of fluorinated carbon-based materials and their adsorption efficiency from a theoretical viewpoint. The results of this investigation also shed light on further possibilities for computational research on fluorinated carbon-based materials.

The DFT calculations were conducted using the Biovia DFT package DMol3 [11], considering the generalized-gradient-approximation (GGA) as well as the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functionals with the double numerical polarized basis set. The GGA-PBE functional has been successfully used to describe the interaction between organic molecules and a carbon-based substrate [12-18] or an inorganic substrate [19-23]. We used a $5 \times 5 \times 1$ Monkhorst–Pack $k$-point mesh [24] with a 12.30 Å $\times$ 12.30 Å $\times$ 15.00 Å periodic boundary condition for the graphene substrate.

The adsorption energy ($E_{ads}$) was defined as

$$E_{ads} = E_{substrate+gas} - E_{substrate} - E_{gas},$$

where $E_{substrate+gas}$ represents the energy of the entire system, $E_{substrate}$ is the energy of the substrate system alone, and $E_{gas}$ is the energy of the isolated gas molecule. Lower adsorption energy values indicate greater stability according to the definition of the equation. Because
dispersion interactions play an important role in the interaction between gas molecules and substrates, it is crucial to incorporate accurate calculations of the dispersion forces. Therefore, we applied the dispersion-corrected DFT (DFT-D3) method for a better description [25].

Figs. 1 and 2 show the geometrically optimized structures with adsorption sites at the top, hollow, and bridge sites of pristine and fluorinated graphene to determine the most energetically stable configuration with CH\textsubscript{4} and CO\textsubscript{2} molecules, respectively. The top, hollow, and bridge sites are adsorption sites on the top of the carbon atom, in the hollow of the six-membered carbon ring, and on the bridge of the carbon–carbon bond, respectively. Table 1 summarizes the adsorption energies of all of the configurations with each gas molecule on the substrate.

The DFT calculation showed that the configuration (Fig. 1a) in which the carbon of methane with a hydrogen tripod was placed atop the carbon atom of the graphene substrate was the most stable site for CH\textsubscript{4} adsorption. The adsorption energy (\(E_{\text{ads}}\)) of CH\textsubscript{4} and CO\textsubscript{2} molecules on pristine and fluorinated graphene substrates is shown in Table 1.

![Fig. 1. Optimized geometry of CH\textsubscript{4} molecule on pristine and fluorinated graphene substrates: (a, b) hydrogen tripod of CH\textsubscript{4} directed to the substrate adsorbed onto top and hollow sites of pristine graphene, respectively; (c, d) hydrogen tripod of CH\textsubscript{4} directed away from the substrate adsorbed onto top and hollow sites of pristine graphene, respectively; (e, f) hydrogen tripod of CH\textsubscript{4} directed to the substrate adsorbed onto top and hollow sites of fluorinated graphene, respectively; (g, h) hydrogen tripod of CH\textsubscript{4} directed away from the substrate adsorbed onto top and hollow sites of fluorinated graphene, respectively. Gray, white, and purple denote carbon, hydrogen, and fluorine, respectively.](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>Pristine graphene</th>
<th>Fluorinated graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Top (Fig. 1a and e)</td>
<td>–151</td>
<td>–185</td>
</tr>
<tr>
<td>C-Hollow (Fig. 1b and f)</td>
<td>–140</td>
<td>–163</td>
</tr>
<tr>
<td>H-Top (Fig. 1c and g)</td>
<td>–84</td>
<td>–114</td>
</tr>
<tr>
<td>H-Hollow (Fig. 1d and h)</td>
<td>–84</td>
<td>–112</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2O-Bridge (Fig. 2a and e)</td>
<td>–136</td>
<td>–176</td>
</tr>
<tr>
<td>C-Bridge (Fig. 2b and f)</td>
<td>–188</td>
<td>–224</td>
</tr>
<tr>
<td>2O-CTop (Fig. 2c and g)</td>
<td>–144</td>
<td>–192</td>
</tr>
<tr>
<td>Perpendicular (Fig. 2d and h)</td>
<td>–101</td>
<td>–163</td>
</tr>
</tbody>
</table>
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The adsorption energy was measured to be −188 meV. Other configurations showed weaker adsorption energies of −136, −144, and −101 meV, respectively, in comparison to the configuration mentioned above. As seen in Table 1, CO₂ is more strongly adsorbed on graphene than CH₄. Because CO₂ has a higher quadrupole moment [(−14.27 ± 0.61) × 10⁻⁴⁰ Cm²] [26] than CH₄, whose quadrupole moment is zero, it is reasonable to conclude that graphene shows a preference for CO₂ over CH₄ in terms of adsorption. This trend agrees with the result reported by Wood et al. [27].

For CO₂ adsorption, the most stable configuration (Fig. 2b) has the carbon placed in the middle of a covalent bond between two carbon atoms of the substrate, with the two oxygen atoms placed atop the adjacent hollow hexagonal sites. The adsorption energy was measured to be −151 meV. The adsorption energy was −140 meV when the carbon of methane was placed at the hollow site of the graphene substrate (Fig. 1b). The configurations (Fig. 1c and d) in which the methane molecule with the hydrogen tripod was directed away from the substrate showed weaker adsorption energies (−84 meV) than those with the hydrogen tripod directed toward the substrate. To investigate the effect of fluorination with a single gas molecule, we added a fluorine atom on a carbon of the graphene substrate to partially fluorinate the substrate. The same configurations of the gas molecule were used to calculate the adsorption energy on the fluorinated graphene, as shown in Fig. 1e-h. The results indicate that the adsorption energies of the CH₄ molecule were increased by 17%–35% (−112 to −185 meV) compared to those on the pristine graphene substrate.

For CO₂ adsorption, the most stable configuration (Fig. 2b) has the carbon placed in the middle of a covalent bond between two carbon atoms of the substrate, with the two oxygen atoms placed atop the adjacent hollow hexagonal sites. The adsorption energy was measured to be −188 meV. Other configurations (Fig. 2a, c, and d) for the interaction between CO₂ and pristine graphene showed weaker adsorption energies of −136, −144, and −101 meV, respectively, in comparison to the configuration mentioned above (Fig. 2b). The adsorption energy in the perpendicular orientation (Fig. 2d) was almost half that of the most stable orientation. As seen in Table 1, CO₂ is more strongly adsorbed on graphene than CH₄. Because CO₂ has a higher quadrupole moment [(−14.27 ± 0.61) × 10⁻⁴⁰ Cm²] [26] than CH₄, whose quadrupole moment is zero, it is reasonable to conclude that graphene shows a preference for CO₂ over CH₄ in terms of adsorption. This trend agrees with the result reported by Wood et al. [27].

The same gas molecule configurations were used to calculate the adsorption energy of a CO₂ molecule on the fluorinated graphene substrate, as shown in Fig. 2e-h. The results show that adsorption of CO₂ on the fluorinated graphene improved by 19%–62% (−163 to −224 meV) compared to that on the prista-
When we look at the effect of fluorination of graphene, because of the quadrupole moment in CO$_2$, the negatively charged fluorine atom on graphene [28] interacted more strongly with CO$_2$, which led to the better adsorption compared to the CH$_4$ molecule. We also calculated the electrostatic potential maps of the most stable configurations of the adsorbed CH$_4$ and CO$_2$ molecules on the pristine and fluorinated graphene substrates (Figs. 1b and f, 2b and f), as shown in Fig. 3. The bluish region of the map indicates a possible reactive region with respect to nucleophilic attack. The electrostatic potential maps suggest that fluorinated graphene has a larger reactive region with the gas molecule than pristine graphene. Therefore, this result demonstrates that partially fluorinated graphene helps enhance CH$_4$ and CO$_2$ adsorption.

In summary, we performed DFT calculations on the interaction between CH$_4$ and CO$_2$ gas molecules and graphene substrates. We found that CH$_4$ was most strongly adsorbed on pristine graphene when the methane hydrogen tripod was directed to the carbon atom on the substrate, and CO$_2$ was most strongly adsorbed on pristine graphene when the carbon dioxide oxygens were placed on adjacent hollow hexagonal sites on the substrate. The CO$_2$ molecule was more strongly adsorbed on the graphene substrate than the CH$_4$ molecule. Finally, fluorination of graphene helps enhance CH$_4$ and CO$_2$ adsorption.

**Conflict of Interest**

No potential conflict of interest relevant to this article was reported.

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**References**


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