DFT study on the sensitivity of open edge graphene toward CO₂ gas

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A R T I C L E I N F O

Article history:
Received 13 May 2016
Received in revised form 20 June 2016
Accepted 21 June 2016
Available online 22 June 2016

Keywords:
Graphene
Computational study
Sensor
Electronic properties

A B S T R A C T

We investigated the sensitivity and reactivity of open edge zigzag and armchair graphene slabs toward CO₂ gas, using density functional theory calculations. Different levels of theory (B3LYP, oB97xD, and Minnesota 06 functionals) and basis sets were employed. The results reproduce and explain the electrical behavior which has been observed experimentally from the graphene upon the exposure to the CO₂ gas. We found that, unlike the pristine graphene, the open edge graphene layers may be promising chemical sensor for the CO₂ detection in agreement with the experimental results. Zigzag edges are more sensitive and reactive than the armchair types.

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1. Introduction

Carbon dioxide (CO₂) is a colorless, odorless and nonflammable gas which is used in large scales every years in the industry for carbonated beverage, and for production of carboxylic acids carboxates, urea, and carbon monoxide [1]. It is also a product of fossil fuel burning, ammonia production, grain fermentation, cellular respiration, and petroleum operations [2,3]. Developing a CO₂ chemical sensor with high sensitivity and fast response is of a great interest, and is necessary for the atmospheric control, medical applications, monitoring global warming and indoor climate, etc. [4–8]. The CO₂ detection is a challenging problem for researchers because of its inherent stability [9]. It is a non-polar molecule with zero electric dipole moment which makes it stable with small reactivity. However, researchers work to develop a selective, highly sensitive, portable, cost effective, and low power consuming CO₂ sensor with short recovery times and fast response [10,11].

Some of commonly employed materials for gas detection are polymers and metal oxides [12–18]. Recently, by advent of nanomaterials with hollow structures and particularly high surface/volume ratio the sensor industry has been revolted [19–24]. Application of different nanostructured materials such as nanosheets, nanotubes, nanocones, nanoclusters, etc. as gas sensors has been widely investigated [25–31]. In particular, graphene which is a sheet of carbon with sp² hybridization has unique thermal, electrical, mechanical, optical, and chemical properties which make it promising candidate for chemical sensor industry [32–35]. At room temperature, graphene has very large electron mobility, and therefore, its electronic sensitivity is very high. However, it has been shown that the pristine graphene is not proper for detection of some gases, and numerous studies have focused on the sensitivity improvement by structural engineering such as chemical functionalization, doping impurity atoms, decoration by transition metals, generating defects, etc [36–41]

Recently an experiment has shown that the CO₂ gas can be efficiently detected by the graphene which is manipulated via mechanical cleavage [42]. This gas sensor has been fabricated by mechanical cleavage and unlike other solid-state gas sensors, this sensor can be operated under ambient conditions and at room temperature [42]. After the infusion of CO₂ gas, the electrical conductance of the graphene increases sharply at the beginning, then gradually levels off until it reaches a steady-state value. It has been revealed that this type of graphene has short recovery time, fast response time, high sensitivity, and low power consumption. In this work, following the experimental work [42], we will cut the edges of graphene and investigate the reactivity and sensitivity of these open sites toward CO₂ gas based on the density functional theory (DFT) calculations. Our main purpose is to find and explain the origin of the electronic behavior of graphene which has been observed in the experimental work in the presence of CO₂ gas. We hope to find a relation between the calculated electronic properties and the experimentally observed electrical conductance change upon the CO₂ adsorption. DFT methods have been previously works predicting increased reactivity of similar graphene-like cluster
systems such as coronene, benzene and circumcoronene [43,44].

2. Computational details

A graphene slab consisting of 116 carbon atoms was selected which its ends were saturated with 28 H atoms to reduce the boundary effects. The structural optimization, energy calculations, natural bond (NBO) and frontier molecular orbitals analyses were done at B3LYP level of theory, employing 6-31G* basis set as executed in the GAMESS suite of program [45]. The B3LYP has been revealed to be a consistent and commonly used level of theory in the study of different nanostructures [46–53]. As there is no universal exchange-correlation-density functional for all property calculations, and functionals may give different results. Therefore, the effect of density functional was investigated. To this aim, four Minnesota functionals of Truhlar group [54–56] including M06-L, M06, M06-2X, and M06-HF with 0, 27, 54, and 100% Hartree Fock (HF) exchange, respectively, were tested. To modeling the effect of graphene cleavage on the adsorption of CO2 and the electronic sensitivity of graphene, we removed some H atoms from the zigzag and armchair edges and studied the CO2 adsorption behavior in these sites.

2.1. The HOMO-LUMO gap is defined as

\[ E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \]  

where \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) are the HOMO and LUMO energies. The electronic sensitivity of the graphene is calculated by the ratio between the numerical difference of the initial HOMO-LUMO gap measured in the clean cage (\( E_g^1 \): reference value) and the HOMO-LUMO gap calculated in the presence of CO (\( E_g^2 \)), with respect to the reference value, \( s = [(E_g^2 - E_g^1)/E_g^1]*100 \). The adsorption energy is defined in the usual way as:

\[ E_{\text{ad}} = E(\text{CO}_2/\text{graphene}) - E(\text{graphene}) - E(\text{CO}_2) \]  

where \( E(\text{CO}_2/\text{graphene}) \) corresponds to the energy of the graphene (pristine of manipulated) in which the CO2 was adsorbed on the surface, \( E(\text{graphene}) \) is the energy of the isolated graphene, \( E(\text{CO}_2) \) is the energy of an isolated CO2 molecule.

3. Results and discussion

3.1. The CO2 adsorption on the pristine graphene

The optimized graphene and its complex with CO2 molecule are shown in Fig. 1. The calculated adsorption energy based on the B3LYP/6-31G* method is about −1.1 kcal/mol which is in good agreement with the results of Lee et al. [57]. We also repeated the calculations with \( \omega \)B97X-D functional. The adsorption energy is about −4.1 kcal/mol at \( \omega \)B97X-D level of theory with the same basis set. The more negative adsorption energy at the dispersion corrected \( \omega \)B97X-D level shows that the main nature of this interaction is weak dispersion which B3LYP cannot predict it well. As a comparison, it has been shown that nonpolar H2 molecule is adsorbed on a coronene surface with an adsorption energy of −5.0 kcal/mol (−1.2 kcal/mol) at dispersion corrected B3LYP level of theory [58]. Wannado et al. have demonstrated that the adsorption energy of CO molecule on the pristine graphene is about −1.28 kcal/mol at B3LYP level of theory. They showed that doping the graphene with transition metal atoms significantly increases the reactivity and sensitivity [59].

The NBO charge transfer is about 0.002 e from the graphene to the CO2. Also, the results of Table 1 show that the electronic properties HOMO, LUMO, and HOMO-LUMO are not sensitive toward CO2 adsorption. For example, the HOMO-LUMO gap is changed slightly by about less than 1% after the CO2 adsorption at all density functionals. It can be concluded that the presence of CO2 cannot be detected by the pristine graphene due to the weak interaction and small charge transfer which is in good agreement with experimental results. The molecular electrostatic potential surface (MEP) plot for the CO2/graphene in Fig. 1 indicates a clear discontinuity along CO2-graphene surface. This discontinuous zone is associated with less directional bonds that are usually weak consistent with less negative adsorption energy. Also, it can be seen that the CO2 molecule has no effect on the electrostatic potential of the adsorbing site which is in agreement with the small NBO charge-transfer.

3.2. The CO2 adsorption on the edges of pristine graphene

3.2.1. Armchair edges

For considering the reactivity and sensitivity of the armchair edges of graphene toward the CO2 gas, we removed the hydrogen atoms (six H atoms) from one armchair edge of the graphene and optimized the geometry (Fig. 2). There exist two possible spin states for this structure including singlet and septet. In the singlet state, it has been assumed that all electrons are paired but in the septet one, six electrons are unpaired on six carbon atoms whose hydrogen atoms are removed. Our calculations indicate that the singlet state is more stable than the septet one by about 69.4 kcal/mol. It seems that two electrons on each of C–C bond tend to be paired. Calculations show that after the hydrogen removing, the C–C bonds are shortened from 1.39 to 1.25 Å, confirming the electron pairing.

For CO2 adsorption on the armchair edge, we explored several initial adsorption configurations, and found four local minima as shown in Fig. 3. In the configuration A, a CO2 molecule attaches from its carbon atom to a carbon atom of the edge, with adsorption energy about 19.7 kcal/mol (Table 2). The formed C–C bond is calculated to be about 1.48 Å and an NBO charge of 0.156 e transfers from the graphene to the CO2 molecule. We checked the spin state for this configuration and found that the triplet state with two unpaired electrons is more stable than the singlet one about 31.4 kcal/mol. Our spin density calculations (Fig. 4) indicates that these electrons more localized on the adsorbing C carbon and its neighboring carbon atom. This reveals that the CO2 adsorption disturbs the C–C bond and weakens it, separating two paired electrons. Bond length calculations shows that after the CO2 adsorption the C–C bond is enlarged by about 0.11 Å (Fig. 3).

In the configuration B, the CO2 molecule attacks to a carbon atom of the edge from one O head and forms an O–C bond with length of 1.39 Å, with adsorption energy about 36.6 kcal/mol (Table 2). An NBO charge of 0.109 e transfers from the graphene to the CO2 molecule. Similar to the configuration A, the triplet state is more stable than the singlet one by about 29.1 kcal/mol. Also, the C–C bond which adsorbs the CO2 molecule is weakened and its length is increased from 1.25 to 1.35 Å. In the configuration C, the CO2 attaches from its oxygen atoms to two carbon atoms of the edge, forming a heptagonal ether ring, with adsorption energy of 31.0 kcal/mol. Our calculations show that the stable spin state for this configuration is quintet. This indicates that the adsorption process weakens the adsorbing C–C bonds generating four unpaired electrons. The spin density plot in Fig. 4 indicates that these four electrons is distributed on the newly formed heptagonal ring and two adjacent carbon atoms.

In the configuration D, a CO2 molecule attaches from its carbon
and an oxygen atom to the armchair edge of graphene, forming a lactone group as shown in Fig. 3. The adsorption energy for this process is about $-8.5$ kcal/mol, and a charge of 0.201 e transfers from graphene to CO$_2$ molecule. The formed C-C and O-C bonds are calculated to be about 1.46, and 1.37 Å, respectively. Like the configuration C, the spin state for this configuration is triplet state with two unpaired electrons. From the adsorption energy analysis (Table 2), it can be concluded that only lactone formation is energetically favorable in accordance with previous reports [60] and the others are rejected because of positive adsorption energies.

### 3.2.2. Zigzag edges

Similar to the case of armchair edge, we removed the hydrogen atoms (six H atoms) from one zigzag edge of graphene and optimized the geometry (Fig. 2). Unlike the armchair edge, our calculations shows that six electrons on the edge carbon are unpaired and the spin state is septet. Singlet state is less stable that the septet one by about 91.2 kcal/mol. For the CO$_2$ adsorption on the zigzag

<table>
<thead>
<tr>
<th>Functional</th>
<th>System</th>
<th>$E_{ad}$ (kcal/mol)</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>Graphene</td>
<td>-3.83</td>
<td>-3.38</td>
<td>0.45</td>
<td>-</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Complex</td>
<td>-4.63</td>
<td>-2.83</td>
<td>1.80</td>
<td>-</td>
<td>0.48</td>
</tr>
<tr>
<td>ωB97xD</td>
<td>Graphene</td>
<td>-4.64</td>
<td>1.81</td>
<td>-0.48</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2. Optimized structure of open ended zigzag and armchair graphenes. Distances in Å.
It seems that since all the electrons are paired on the armchair edge, this isomer is more stable and, thus, less reactive than zigzag edge which has radical character with unpaired electrons. Our calculations confirm that the singlet armchair construction is more stable than the septet zigzag one by about 66.1 kcal/mol.

Similar to the configurations B, C, and D of the armchair constructions (Fig. 3), we have predicted the corresponding Q, R, S configurations (Fig. 5), for the zigzag one, respectively. However, all the adsorption energies for zigzag cases are more negative than the corresponding armchair ones. In the both cases, the lactone forming is the most favorable process. The positive adsorption energy of the configuration Q indicates that the adsorption of CO2 from an oxygen head is energetically unfavorable. Calculations show that all of the complexes for zigzag structure are septet and the adsorption process does not help to electron pairing.

### 3.3. Electronic properties and sensing characteristic

One method to explore the sensitivity of an adsorbent toward a chemical is calculating the electrical change after the adsorption process [61–63]. In the computational studies, the electrical conductance has been frequently simulated by the change of HOMO-LUMO gap of semiconductor based on the following equation [64]:

\[
\sigma = A \ T^{3/2} \ \exp(-E_g/2kT)
\]

Fig. 3. Different configurations of CO2 adsorption at the armchair open end of graphene. Distances in Å.

Fig. 4. Spin density plots for CO2/armchair graphene complexes (see Fig. 3).

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{\text{ad}}) (kcal/mol)</th>
<th>(E_{\text{HOMO}}) (eV)</th>
<th>(E_{\text{LUMO}}) (eV)</th>
<th>(E_g) (eV)</th>
<th>(\Delta E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armchair</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>19.7</td>
<td>-3.97</td>
<td>-3.46</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>36.6</td>
<td>-3.99</td>
<td>-3.62</td>
<td>0.37</td>
<td>-13.9</td>
</tr>
<tr>
<td>C</td>
<td>31.0</td>
<td>-4.20</td>
<td>-3.77</td>
<td>0.43</td>
<td>-7.9</td>
</tr>
<tr>
<td>D</td>
<td>-8.5</td>
<td>-4.34</td>
<td>-3.59</td>
<td>0.76</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Table 2

Adsortion energy (\(E_{\text{ad}}\), kcal/mol) for different states of CO2 adsorption at the open armchair edge of graphene (Fig. 3). Energy of HOMO, and LUMO, and HOMO-LUMO energy gap (\(E_g\)) in eV. The \(\Delta E_g\) indicates the change of \(E_g\) after the adsorption process. The result obtained using B3LYP/6-31G*.
Experimental results and conclusions that of an experimental work [42]. Experimentally, Yoon et al. [42] have shown that the mechanically cleaved graphene sheets show significant conductance increase when they were exposed to CO2 gas. Also, they demonstrated that the response time of the graphene is less than 10 s, showing that the device has fast response to CO2 gas. Moreover, they demonstrated that the response time of the graphene is less than 10 s, showing that the device has fast response to CO2 gas. They concluded that these types of graphene may be promising candidates for CO2 gas sensing.

As shown in Table 4, for the configuration S, the adsorption energy is slightly increased (became more negative) by increasing the %HF exchange percentage of density functional. The HOMO, LUMO, and HOMO-LUMO gap of the graphene and its complex with CO2 significantly depend on the kind of density functional. The M06-L as a generalized gradient approximation (GGA) functional (with zero percentage of HF exchange) gives lower LUMO and higher HOMO compared to the hybrid M06, M06-2X, and M06-HF. Therefore, it gives a small HOMO-LUMO gap which is in accordance with the fact that GGA functionals underestimate the gap [65]. By adding and increasing the %HF exchange, the HOMO and LUMO are stabilized and destabilized, respectively, thereby enlarging the HOMO-LUMO gap. Although the absolute values of HOMO, LUMO, and HOMO-LUMO gap are much higher for the hybrid M06, M06-2X, and M06-HF.

Table 3 displays that enlarging the basis set slightly affects the HOMO, LUMO levels, HOMO-LUMO gap, and adsorption energies. Also it has no significant effect on the HOMO-LUMO gap change upon the adsorption process.

Table 3

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{ad}}$ (kcal/mol)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zigzag</td>
<td>89.5</td>
<td>-4.48</td>
<td>-3.44</td>
<td>1.04</td>
<td>-36.3</td>
</tr>
<tr>
<td>P</td>
<td>14.6</td>
<td>-4.62</td>
<td>-3.33</td>
<td>1.29</td>
<td>-20.7</td>
</tr>
<tr>
<td>Q</td>
<td>33.2</td>
<td>-4.54</td>
<td>-2.95</td>
<td>1.59</td>
<td>-2.3</td>
</tr>
<tr>
<td>R</td>
<td>-89.5</td>
<td>-4.48</td>
<td>-3.44</td>
<td>1.04</td>
<td>-36.3</td>
</tr>
</tbody>
</table>

Fig. 5. Different configurations of CO2 adsorption at the zigzag open end of graphene. Distances in Å.

Table 4

| Method       | System            | $E_{\text{ad}}$ (kcal/mol) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_g$ (eV) | $\Delta E_g$ (eV) |
|--------------|-------------------|-----------------|-----------------|---------|-----------------|-----------------|-----------------|---------|-----------------|---------|-----------------|---------|
| M06-1/6-3G+  | Graphene          | -4.11           | -3.42           | 0.69    | -48.6           |
| M06/6-3G+    | Complex           | 83.3            | 4.18            | -3.82   | 0.36            | -48.6           |
| M06/6-3G+    | Graphene          | -4.74           | 2.84            | 1.90    | -31.6           |
| M06-2X/6-3G+ | Complex           | -4.73           | 3.36            | 1.37    | -27.9           |
| M06-HF/6-3G+ | Graphene          | -9.28           | 5.32            | 3.05    | 2.27            | 18.4            |
| M06-HF/6-3G+ | Complex           | -9.89           | 6.47            | 4.98    | 4.49            | -13.4           |
| B3LYP/6-311 +G* | Graphene        | 86.2            | -4.73           | 3.73    | 1.01            | 31.6            |
| B3LYP/6-311++G** | Complex        | 84.8            | -4.79           | 3.79    | 1.00            | 31.7            |

where $k$ is the Boltzmann’s constant and $A$ (electrons/m$^3$ K$^{2/3}$) is a constant. Herein, we compare the results of this equation with those of an experimental work [42]. Experimentally, Yoon et al. [42] have shown that the mechanically cleaved graphene sheets show significant conductance increase when they were exposed to CO2 gas. Also, they demonstrated that the response time of the graphene is less than 10 s, showing that the device has fast response to CO2 gas. They concluded that these types of graphene may be promising sensor for CO2 gas can operate at room temperature and under ambient conditions.

Fig. 5. Different configurations of CO2 adsorption at the zigzag open end of graphene. Distances in Å.
4. Conclusions

In accordance with the experimental results, using DFT calculations, we demonstrated that open edge graphene slabs are more suitable chemical sensor than pristine ones for CO2 gas. We revealed that the theoretical predicted HOMO-LUMO gap decrease is a good index for the electrical conductance increase in the experiment. The zigzag edges are more reactive and sensitive toward CO2 because of its radical characteristic. The electronic properties including HOMO, LUMO, and HOMO-LUMO gap and the adsorption energies much more affected by kind of density functional compared to the basis set changing. The CO2 adsorption energy on the pristine graphene is about −1.1 kcal/mol but it increases to −89.5 kcal/mol for zigzag open edge graphene at B3LYP level of theory. Upon the adsorption of CO2, the HOMO-LUMO gap of zigzag open edge graphene decreases from 1.63 to 1.04 eV. This significantly increases the electrical conductivity which is in good agreement with the experimental results.

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