

Research Article

Highly Sensitive CO Gas Sensor from Defective Graphene: Role of van der Waals Interactions

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Layered materials, such as graphene, have attracted increasing interests since they can be extensively used in gas sensors, spintronic devices, and transparent electrodes. Although larger size of graphene sheets has been fabricated, in reality, the existence of the defects in layered materials is almost inevitable during the manufacturing process. Here, we performed the state-of-the-art density-functional theory calculations to study the interactions between CO molecule and the pristine and defective graphene layers, with the aim of designing a CO gas sensor with higher sensitivity. The van der Waals interactions predominate the binding between the CO gas and the sensor, and also significantly enhance the stability of the system. The defective graphene strongly interacts with CO, and thus enhances the sensitivity of the graphene and further tunes the electronic and magnetic properties of the entire system. Our computed results clearly demonstrate that the defective graphene could be a good sensor for gas molecules.

1. Introduction

Carbon-based materials, such as nanotubes and graphene, are widely accepted as a good sensor to monitor small gas molecules, such as CO, NO, NO₂, and NH₃ molecules [1–9]. In particular, the detection of the CO molecule to prevent poisoning is of vital importance, due to the fact that CO is colorless, tasteless, and odorless, but toxic and flammable. Carbon nanotubes were often used as building blocks in gas sensors, which is capable of effectively monitoring extremely low concentrations of gases [10–13]. Since fabrication in 2004 by Novoselov et al. [14], graphene, the two-dimensional material, has attracted increasing interests as a gas sensor, thanks to its huge specific surface area, good electrical conductivity, stable chemical performance, high Young's modulus, and excellent optical performance [3, 8, 15–17]. In particular, Zhang et al. [16] theoretically studied small gas molecules (CO, NO, NO₂, NH₃) adsorption on four graphene layers (pristine, B and N-doped, and defective graphene) using the local-density approximation (LDA) method and exploited their potential applications as gas sensors. Although efforts are being undertaken to enhance the performance of gas

sensor, many challenges remain in the field, such as the low binding energy, low sensitivity, and bad selectivity.

A prerequisite to design an effective sensor is the understanding of the interactions between the gas molecules and the substrate. However, from the point of view of modelling, the accurate description of their interactions remains a big challenge, due to the well-known fact that the gas/substrate binding arises from the dedicated balance between various types of bonding: covalent bonding, van der Waals (vdW) interactions, hydrogen bonding, charge transfer, and Pauli repulsion [15, 18–20]. Thanks to the recent development of vdW-inclusive methods in the framework of density-functional theory (DFT) [21, 22], the role of vdW force between small molecules in the gas phase has been reasonably described and is well understood. Notably, the vdW energy is of extreme importance in two-dimensional materials but is often ignored in previous DFT calculations when studying the gas sensors.

In this contribution, we performed various types of vdW-inclusive DFT calculations to study the interactions between CO molecule and graphene layers. Although larger size of graphene sheets has been fabricated, in reality, the existence

TABLE I: Adsorption energy (E_{ad} in eV) and equilibrium molecule-substrate distance (d in Å) of the CO adsorbed on different sites.

| Systems | Structures | LDA | | PBE | | PBE + vdW (TS) | |
|-------------------|------------|-----------------|-------------------|-----------------|-------------------|-----------------|-------------------|
| | | E_{ad} | d | E_{ad} | d | E_{ad} | d |
| CO on G | a | -0.10 | 3.01 | 0.03 | 3.14 | -0.05 | 2.84 |
| | b | -0.04 | 2.72 ^a | 0.04 | 2.97 ^a | -0.03 | 2.68 ^a |
| | c | -0.08 | 2.82 | 0.02 | 3.22 | -0.03 | 2.77 |
| | d | -0.03 | 2.71 ^a | 0.05 | 2.85 ^a | -0.04 | 2.71 ^a |
| | e | -0.08 | 2.61 | 0.06 | 2.85 | -0.03 | 2.76 |
| | f | -0.06 | 2.63 ^a | 0.07 | 2.72 ^a | 0.03 | 2.47 ^a |
| | g | -0.11 | 2.86 | 0.04 | 3.10 | -0.10 | 2.79 |
| | h | -0.12 | 2.69 | 0.04 | 2.97 | -0.11 | 2.88 |
| | i | -0.12 | 2.83 | 0.03 | 3.09 | -0.09 | 2.85 |
| | j | -0.12 | 2.82 | 0.03 | 3.14 | -0.10 | 2.91 |
| CO on defective G | k | -0.36 | 2.90 | -0.25 | 3.09 | -0.32 | 2.63 |
| | l | -2.75 | 1.32 ^b | -2.05 | 1.33 ^b | -2.15 | 1.33 ^b |

a refers to the distance between the O atom in CO and the C atom in graphene.
b refers to the shortest bond length.

of the defects in layered materials is almost inevitable during the manufacturing process. As such it is of fundamental interests to study the interactions of gas molecules with the defective graphene sheets. Our calculations showed that by introducing defects, even a single point vacancy, in the graphene layers, the sensitivity of the gas sensor can be significantly enhanced. Moreover, the electric and magnetic properties of the system are strongly perturbed upon interaction with the molecules. We demonstrate that the defective graphene would be a highly sensitive sensor for monitoring the CO gas.

2. Methods

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [23]. The interaction between the valence electrons and ionic cores is described by the projector augmented wave (PAW) method [24]. The LDA, the Perdew-Burke-Ernzerhof (PBE) form of the generalized-gradient approximation (GGA) [25], and the PBE + vdW (or TS) [26] are employed to describe electron exchange and correlation. The plane wave energy cut-off is set to 350 eV and the Brillouin zone is sampled with $3 \times 3 \times 1$ k -point mesh. The surfaces are modeled by periodic (5×5) supercell, which is separated by 15 Å of vacuum. A threshold for the convergence criteria of 0.001 eV/Å is used for the final force. For the calculation of density of electronic states (DOS), the k -point is set to $19 \times 19 \times 1$.

The adsorption energy of CO on graphene can be written as

$$E_{\text{ads}} = E_{\text{CO/Graphene}} - E_{\text{Graphene}} - E_{\text{CO}}, \quad (1)$$

where $E_{\text{CO/Graphene}}$, E_{Graphene} , and E_{CO} are the total energies of the relaxed CO on graphene system, free-standing graphene, and the isolated CO molecule, respectively.

To find the most favorable adsorption configuration, a CO molecule is initially placed at different positions above the pristine graphene (G) and the defective graphene (DG) with perpendicular or parallel orientation. We also use other

five vdW-inclusive methods, including DFT-D2 [27], DFT-D3 [28], vdW-DF, optPBE-vdW, and optB88-vdW [29, 30], to revisit the favorable adsorption configurations relaxed from the PBE + vdW method, with the aim of deeply understanding the role of vdW interactions in these adsorption systems.

3. Results and Discussion

Figure 1 shows the optimized configurations after full relaxation. The C-C bond length in graphene from our LDA, PBE, and PBE + vdW calculations ranges from 1.41 to 1.43 Å, in excellent agreement with the experimental data (1.42 Å) [31]. Also, the calculated atomic distance between O and C in CO molecule agrees very well with those from experiments (1.13 to 1.14 Å versus 1.13 Å [32]). The computed adsorption energies (E_{ad}) and the equilibrium molecule-substrate distances (d) are listed in Table I. The most stable configurations of the CO molecule on pristine graphene and defective graphene are configurations (h) and (l), respectively. The adsorption energy of CO on G is found to be -0.12 eV, along with the CO-substrate distance of 2.69 Å from the LDA functional. We found that the E_{ad} of configurations (g) to (j) are almost identical, suggesting the flat potential-energy surface for CO at the pristine graphene. Notably, our computed adsorption energy at the favorable configuration (h) agrees with that in [16]. The LDA results are close to those from the PBE + vdW method with an E_{ad} of -0.11 eV. In contrast, the PBE adsorption energies are positive, and the adsorption distances are considerably larger than those from LDA and PBE + vdW. Therefore, one could conclude that the GGA-PBE method tends to underestimate the adsorption energy and overestimate the adsorption distance, confirming the essential role of vdW interactions in these systems.

For the defective graphene, the configuration (l) in Figure 1 is found to be the most stable, where the CO tilts to the defective graphene and carbon atom pointing towards the vacancy. When using LDA, the adsorption energy of CO on DG significantly increases to -2.75 eV, with a CO-substrate distance of 1.32 Å. The E_{ad} computed from PBE and

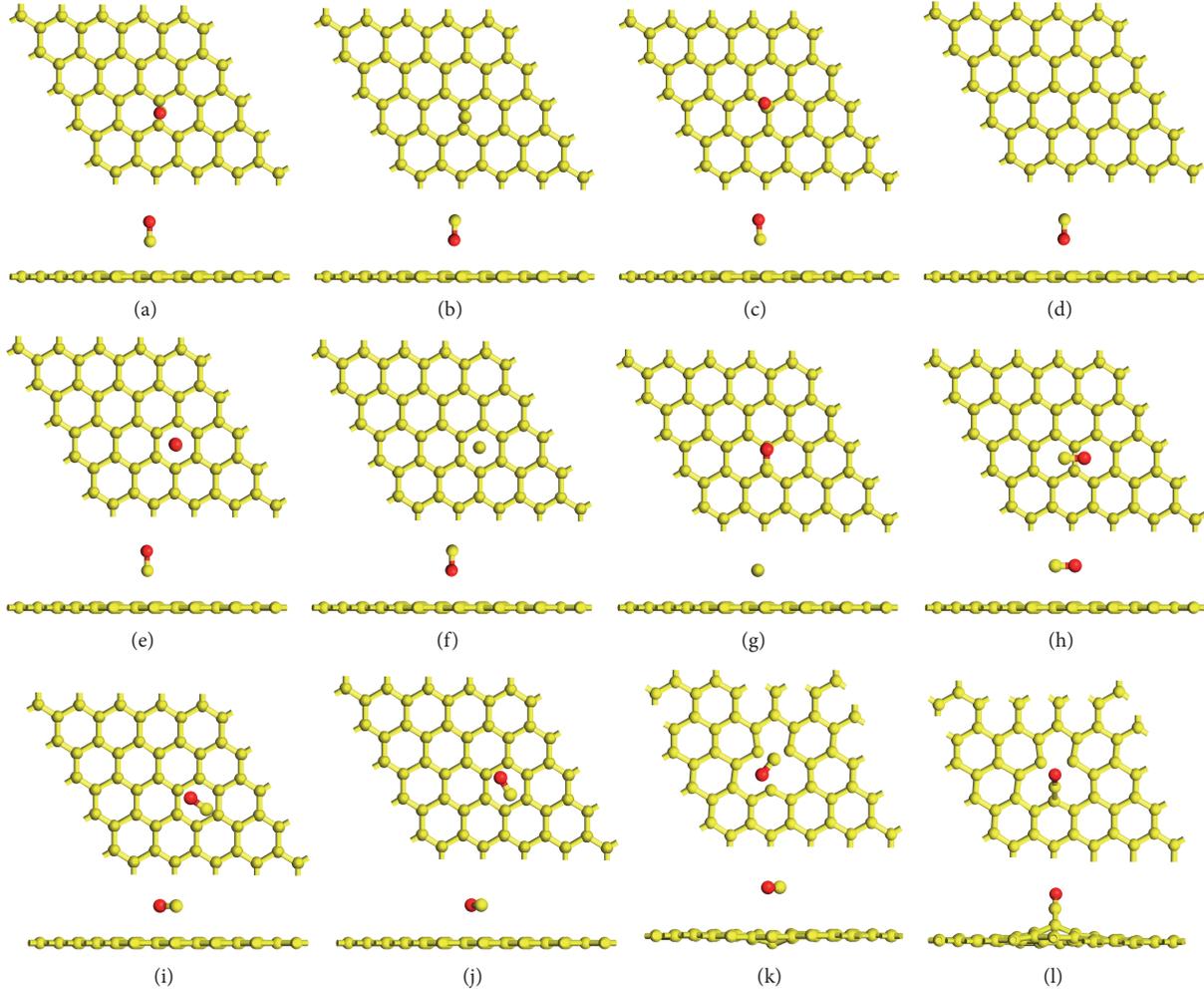


FIGURE 1: Top and side views of the adsorption structures for CO on graphene and defective graphene. (a) to (j) are for graphene and (k) to (l) are for defective graphene.

PBE + vdW are -2.05 and -2.15 eV, respectively, and the d value dramatically decreases to 1.33 Å. The distance is close to the bond length of a C=C double bond (1.34 Å), indicating the formation of the covalent bonds upon CO adsorption. As such, the CO molecule is chemisorbed at the defective graphene, with a significantly larger adsorption energy than for the pristine graphene sheet.

Table 2 shows the comparison of calculated adsorption energy and equilibrium molecule-substrate distance at the most stable sites h and l of G and DG, respectively, between six vdW functionals. For configuration h, the E_{ad} from DFT-D2 (-0.09 eV) and DFT-D3 (-0.10 eV) are lower than that of PBE + vdW (-0.11 eV), and the vdW-DF (-0.14 eV) and optPBE-vdW (-0.16 eV) are higher. The best agreement can be found in the optB88-vdW functional, with an $E_{\text{ad}} = -0.11$ eV. A relatively wide range of E_{ad} (-0.09 to -0.16 eV) can be seen for the vdW-DF-type functionals, while the distance is from 2.77 to 3.02 Å. For configuration l, the E_{ad} values of DFT-D2 (-2.25 eV) and DFT-D3 (-2.17 eV) are higher than that of PBE + vdW (-2.15 eV), the vdW-DF (-1.80 eV), optB88-vdW (-2.04 eV), and optPBE-vdW (-2.01 eV) which

TABLE 2: Comparison of the calculated adsorption energy (E_{ad} in eV) and equilibrium molecule-substrate distance (d in Å) at sites h and l of graphene and defective graphene, respectively, between different vdW functionals.

| Methods | h | | l | |
|------------|-----------------|--------|-----------------|--------|
| | E_{ad} | d | E_{ad} | d |
| PBE + vdW | -0.11 | 2.88 | -2.15 | 1.33 |
| DFT-D2 | -0.09 | 2.87 | -2.25 | 1.33 |
| DFT-D3 | -0.10 | 2.92 | -2.17 | 1.33 |
| vdW-DF | -0.14 | 3.02 | -1.80 | 1.33 |
| optB88-vdW | -0.11 | 2.77 | -2.04 | 1.33 |
| optPBE-vdW | -0.16 | 2.93 | -2.01 | 1.33 |

are lower. Further analysis of the data in Table 2 shows that different vdW-inclusive methods give a relatively wide range in adsorption energies for the chemisorbed system. More specifically, the PBE + vdW and DFT-D3 give almost identical binding energies, which are about 100 meV larger than those from the DFT-D2 method. This is presumably because the

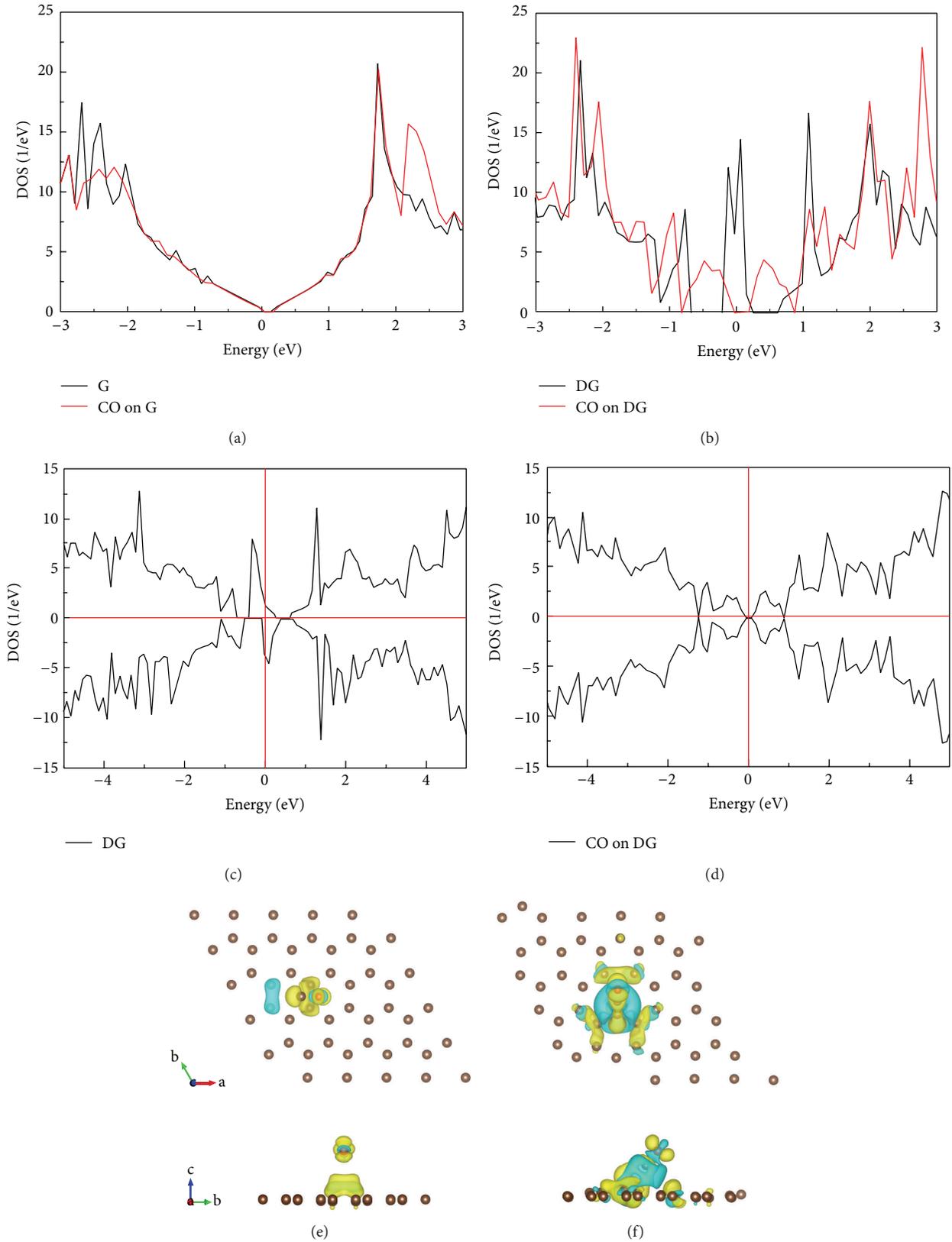


FIGURE 2: The DOS for (a) CO on pristine graphene and (b) CO on defective graphene. Spin-polarized density of states (DOS) for (c) defective graphene and (d) CO on defective graphene. The Fermi level of the system is set to zero. Calculated differential charge densities for (e) CO on pristine graphene and (f) CO on defective graphene. Blue color and yellow color show the areas with $\Delta\rho < 0$ and $\Delta\rho > 0$, respectively. Note that different isosurface levels were used in plots (e) and (f): $0.0002 \text{ e}/\text{\AA}^3$ for the former and $0.002 \text{ e}/\text{\AA}^3$ for the latter.

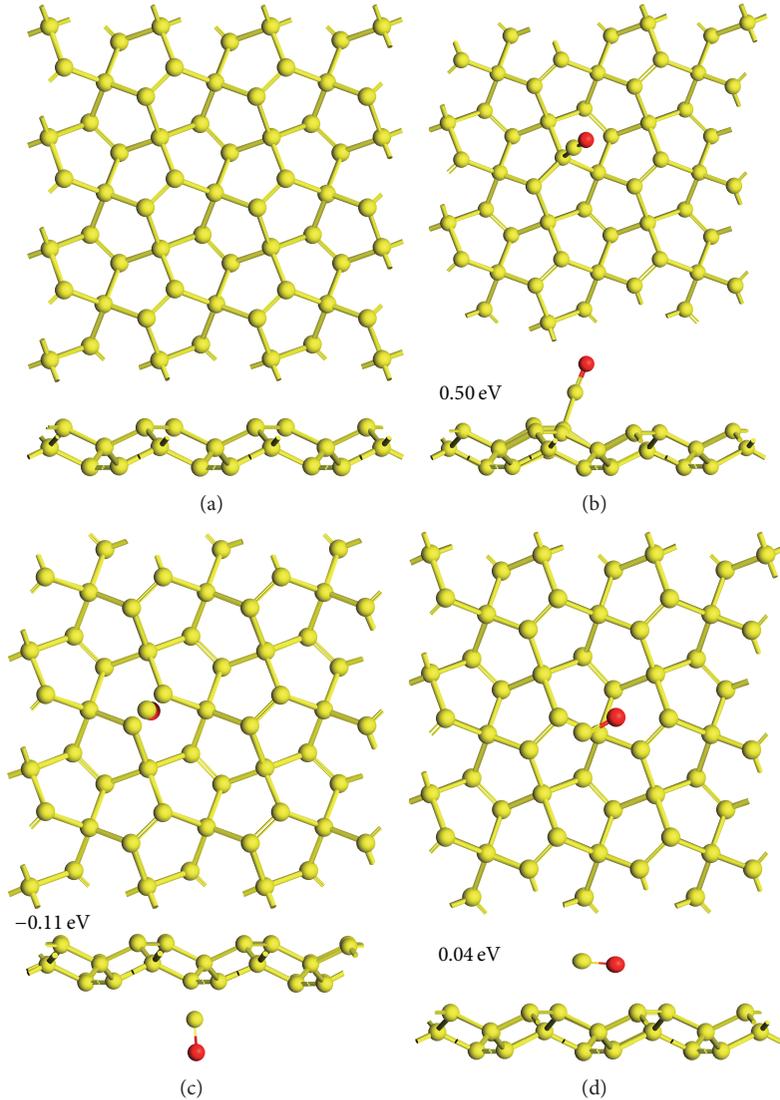


FIGURE 3: Top and side views of (a) the penta-graphene sheet, (b) to (d) CO adsorbed on the penta-graphene sheet at different sites. The adsorption energies are also shown in the figure.

former methods utilized the environmental dependent vdW parameters in DFT calculations. The vdW-DF functional gives the highest binding energy due to the well-known overly repulsive exchange part (revPBE) used in this approach [18]. Although the E_{ad} ranges from -1.80 to -2.25 eV, their related distances for all functionals are the same (1.33 Å). This indicates that the adsorption distance is determined by the covalent bonding, rather than the vdW interactions, for the chemisorbed systems.

To better understand the change in the electronic structure caused by CO adsorption, we computed the electronic density of states (DOS) for CO on G and further compared it with that of CO on DG. As shown in Figure 2(a), almost no electron orbital overlaps between CO molecule and the graphene in the CO on G system due to the physisorptive nature of bonding in this case. On the contrary, the DOS plots of CO and the defective graphene in the CO on DG system are significantly hybridized (Figure 2(b)), clearly implying

the strong chemisorption between the CO molecule and the defective graphene. It is inferred that the adsorption of CO on DG brings apparent perturbation to electronic properties of the defective graphene. Also, the spin-polarized DOS analysis shows that the DG is magnetic (1.68 μ_B) whilst the magnetism vanishes upon the CO adsorption (see Figures 2(c) and 2(d)).

To obtain the charge redistribution after the adsorption process, we further computed the differential charge densities (DCD), which is defined as

$$\Delta\rho = \rho_{\text{CO/Graphene}} - \rho_{\text{Graphene}} - \rho_{\text{CO}}, \quad (2)$$

where $\rho_{\text{CO/Graphene}}$ represents the total electronic density for the CO/graphene system and ρ_{Graphene} and ρ_{CO} are the densities for the isolated graphene (or defective graphene) and CO molecule, respectively. In Figures 2(e) and 2(f), we present the results of $\Delta\rho$ at the CO-G and CO-DG interfaces.

Very weak charge transfer can be observed from graphene (blue color, $\Delta\rho < 0$) to the CO molecule (yellow color, $\Delta\rho > 0$) in Figure 2(e). For CO-DG in Figure 2(f), a significant charge transfer is observable from CO to defective graphene.

Finally, we made a comparison of graphene with the newly proposed penta-graphene [33] to confirm the better performance for the defective graphene as a CO gas sensor. As shown in Figure 3(a), the penta-graphene possesses 54 C atoms, and the optimized lattice constants are 10.69 Å from PBE + vdW method. The total thickness of the relaxed structure is 1.26 Å and the buckling is 0.63 Å. There are two kinds of C atoms, the sp^3 - and the sp^2 -hybridized C atoms named C1 and C2, respectively. The C1–C2 is 1.53 Å and C2–C2 is 1.33 Å, while the bond angle of C2–C1–C2 is 131.1°. Three different configurations are shown in Figures 3(b) to 3(d). The most favorable configuration is site c with an E_{ad} of -0.11 eV and a distance of 2.19 Å. The remaining two configurations are both unstable due to the positive E_{ad} . Then we calculated the formation energy of the graphene (-9.28 eV) and penta-graphene (-8.39 eV) per atom, respectively. We found the formation energy of graphene is lower than that of penta-graphene.

4. Conclusions

In summary, the interactions between CO molecule and the pristine and defective graphene layers using different vdW-inclusive functionals were investigated. CO is physisorbed on the perfect graphene sheets, along with low adsorption energy and almost no charge transfer. In contrast, the defective graphene is reactive to bond with CO molecule, and their interactions tune the electronic and magnetic properties of the adsorption system. Our calculations demonstrate the potential application of defective graphene as a highly sensitive CO gas sensor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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