Comparison of adsorbing NO\textsubscript{2} in boron and phosphorus doped graphene/ZnO heterojunction

Yanxin Jin, Jijun Ding\textsuperscript{1} and Haixia Chen

College of Science, Xi’an Shiyou University, Xi’an, Shaanxi 710065, China

\textsuperscript{1}Email: dingjj303@163.com

Abstract. As a new two-dimensional material, the adsorption properties of the graphene-like ZnO monolayer (ZnO-ML) have been investigated in our previous work. In this paper, the heterojunction are constructed using ZnO-ML and doped graphene. The electronic and adsorption properties of the boron doped graphene/ZnO (B-G/ZnO) and phosphorus doped graphene/ZnO (P-G/ZnO) heterojunction are investigated based on density functional theory (DFT). Firstly, the B-G/ZnO and P-G/ZnO heterojunction are constructed and their structures are optimized. Then, according to the comparison of adsorption energy and adsorption height, the most stable adsorption configurations are obtained. They are the T and T\textsubscript{0} site corresponding to the B-G/ZnO and P-G/ZnO heterojunction, respectively. Finally, in order to further explore the adsorption mechanism between the heterojunction and NO\textsubscript{2} molecule, the band structure, density of states (DOS) and the partial density of states (PDOS) in B-G/ZnO and P-G/ZnO heterojunction are compared. These results can provide more theoretical support for the adsorption properties of heterojunction based on the ZnO-ML.

1. Introduction
With the development of the industry, more and more toxic and harmful gases are discharged into the atmosphere. Especially, the human health and environment are damaged by nitrogen oxide (NO\textsubscript{2}) and carbon oxide (CO) [1]. Thus, it is necessary to investigate practical gas sensors to adsorb toxic gases. Graphene, due to its unique structure, can be used as a candidate material for gas sensors. It is successfully exfoliated from graphite in 2004 by Novoselov and Geim [2]. Graphene is a typical two-dimensional structure with the thickness of a carbon atom. In addition, it has good adsorption behaviors for gas molecule owing to a large specific surface area (2600 m\textsuperscript{2}/g) [3].

However, the pristine graphene has zero band gap. In order to overcome this problem, researchers devoted to open and control its band gap using heteroatom doping. The boron (B) and nitrogen (N) have similar radius as well as carbon atoms. Either B or N doping could change the band structure of graphene, which improves its electronic properties and adsorption ability for some gas molecules [4]. Thus, the B and N are usually selected as the doping atoms in graphene. Qin and Zhang [5] investigated that N doping graphene can enhance adsorption capacity for NO\textsubscript{2}.

Interestingly, based on the density functional theory (DFT), monolayer zinc oxide (ZnO-ML) has more excellent adsorption properties than that of bulk ZnO. Besides, ZnO-ML has honeycomb structure like graphene. It is found that the ZnO-ML has excellent adsorption performance in our previous work [6]. Fu et al. [7] reported that graphene oxide and ZnO nanocomposites serving as a sensor exhibits a good repeatability and high sensitivity to ammonia. Chen et al. [8] found that NO\textsubscript{2} adsorbed on ZnO-ML with oxygen vacancy defects show strong adsorption energy.
Due to both graphene and ZnO-ML doped with heteroatoms having excellent adsorption characters, the heterojunction composed of them may have more interesting properties in adsorption. In this work, Firstly, the boron (B) and phosphorus (P) atoms are used to substitute carbon atoms in graphene, respectively. Then, the heterojunction are constructed using ZnO-ML and B/P doped graphene. The optimized structures of NO$_2$ adsorbed on the heterojunction are investigated by DFT, and the most stable geometry configurations are obtained. Finally, the adsorption energy, adsorption height, band structure, density of states (DOS) and partial density of states (PDOS) based on the most stable configuration are calculated. Results show that the NO$_2$ molecule adsorbed on both the G-terminal of B-G/ZnO heterojunction and ZnO-terminal of P-G/ZnO heterojunction have the largest adsorption energy than other cases.

2. Calculation method

All structural optimization calculations are carried out using DFT based on the Dmol$^3$ module [9], and the electron exchange-correlation is processed by the generalized gradient approximation (GGA) of Perdew-Burke Ernzerhof (PBE) [10]. It is supposed that the DFT semi-core pseudopotential (DSPP) and adopting double numerical plus polarization (DNP) basis set are propitious to study gas-molecule-adsorption systems. In order to correct van der Waals forces, the Grimme scheme is used [11]. And the vacuum layer is set as 20 Å to make the interaction between the periodic images reach the minimum. To ensure sufficient accuracy, the convergence tolerance of energy, max displacement and force are less than 1.0×10$^{-5}$ Ha, 0.005 Å and 0.002 Ha/Å, respectively. For structure optimization, the global orbital cutoff is chosen as 4.4 Å in these computations, and the smearing energy is used to 0.005 Ha. The Brillouin zone is sampled with a 5×5×1 k-point grid with Gaussian smearing width of 0.2 eV. The initial model of graphene and ZnO-ML are derived from Materials Studio 8.0 package. The ZnO-ML is cleaved from (001) direction of bulk wurtzite. Then, the graphene layer (4×4×1 supercell) is introduced to match the 3×3×1 supercell of ZnO-ML. The lattice mismatch is 0.94%, which is similar with other literatures [12]. For heterojunction, the atoms are fully relaxed, the adsorption energy ($E_{\text{ad}}$) which is used to determine the stability of the adsorption model is calculated by using the following equation:

$$E_{\text{ad}} = E_t - (E_h + E_g)$$

Where, $E_t$ is the total energy of adsorbing the gas molecules by the heterojunction, $E_h$ and $E_g$ are the total energies of the single heterojunction and the NO$_2$ gas molecule, respectively. In the heterojunction, the dependence of $E_{\text{ad}}$ on charge state for each adsorption site is calculated to determine the most stable sites for adsorbing. The heterojunction have two adsorption terminals including graphene and ZnO. The graphene terminal have three typical adsorption sites, such as top (T), bridge (B) and hollow (H) sites, respectively. However, there are four adsorption sites in the ZnO terminal, and the T site is divided into the top of Zn (T$_{\text{Zn}}$) and O (T$_{\text{O}}$) atom, respectively.

3. Results and discussion

Different heterojunction models composed of ZnO-ML and doped graphene (B or P atoms) have been considered. The heterojunction are constructed after geometric optimization. Their formation energies are negative, which indicates that the models are stable and existing. In Figure 1 (a)-(d), there are two parts including upper and lower corresponding to the top and side views, respectively. Figure 1 (a)-(b) shows the optimized structures of B-G/ZnO and P-G/ZnO heterojunction. The initial distances between the layers are set as 3 Å in two kinds of heterojunction, after relaxation, they decrease to 2.86 Å and 2.06 Å respectively. It indicates that the P-G/ZnO has larger distortion than that of B-G/ZnO heterojunction, which is due to P having larger atom radius and stronger non-metallic properties than that of carbon atoms.

For each adsorbate, seven adsorption sites are considered, including three typical sites in the graphene terminal (T, B, and H) and four adsorption sites (T$_{\text{Zn}}$, T$_{\text{O}}$, B and H) in the ZnO terminal. In this work, NO$_2$ molecule is used as adsorption gas. According to equation (1), the adsorption energy
$E_{ad}$ in seven adsorption sites are calculated, as shown in Table 1. All the adsorption energy is negative, indicating that it is an exothermic process and the reaction is spontaneous. For both the B-G/ZnO and P-G/ZnO heterojunction, as long as the terminal is the same, the adsorption energy is almost same for all the adsorption sites. The difference in adsorption energy between ZnO and graphene terminal is only about 0.2 eV for the B-G/ZnO heterojunction. Also, its adsorption energy is smaller than that of P-G/ZnO.

Figure 1 (c)-(d) shows the most stable adsorption configurations of NO$_2$ adsorbed on the B-G/ZnO and P-G/ZnO heterojunction after full relaxation, respectively. The initial distances between NO$_2$ and interface is also 3 Å. For B-G/ZnO, the T site of the graphene terminal has the largest adsorption energy (-0.797 eV) and shorter distance ($d=1.76$ Å) between the NO$_2$ and heterojunction. In addition, the NO$_2$ parallel to or perpendicular to the heterojunction is defined according to the angular relationship between the two nitrogen atom lines and the plane of the heterojunction. As shown in Figure 1 (c), NO$_2$ molecule is parallel to the heterojunction. No matter which the initial adsorption site is, T is the stable site. The introduction of NO$_2$ causes graphene distortion, and the B atom has a little angle in graphene. In the Figure 1 (d), the internal structure of the P-G/ZnO heterojunction have been squeezed by NO$_2$ molecules, and T$_O$ is the most stable site with adsorption energy of -2.593 eV. The distance between the NO$_2$ and the ZnO interface is 1.72 Å, which is shorter than that of B-G/ZnO heterojunction due to P having stronger non-metallic properties than that of carbon atoms.

![Figure 1](image)

Figure 1. The most stable heterojunction configurations of (a) B-G/ZnO, (b) P-G/ZnO, (c) B-G/ZnO adsorbing NO$_2$ and (d) P-G/ZnO adsorbing NO$_2$.

Table 1. The adsorption energies of NO$_2$ adsorbed on different adsorption sites in heterojunction.

| Adsorption Layer | B-G/ZnO | P-G/ZnO |
|------------------|---------|---------|
| Sites            | $E_{ad}$ (eV) | Sites       | $E_{ad}$ (eV) |
| ZnO terminal     |         |         |
| T$_O$/T$_Zn$     | -0.577/-0.520 | T$_O$/T$_Zn$ | -2.593/-2.505 |
| B                | -0.549  | B        | -2.590 |
| H                | -0.554  | H        | -2.586 |
| T                | -0.797  | T        | -0.587 |
| graphene terminal|         |         |
| B                | -0.792  | B        | -0.594 |
| H                | -0.792  | H        | -0.587 |
For the P-G/ZnO heterojunction, the largest adsorption energies corresponding to T₀ site of ZnO and B site of graphene terminal are -2.593 eV and -0.594 eV, respectively. Especially, the ZnO terminal adsorption energies of P-G/ZnO are larger, which is almost 5 times than that of B-G/ZnO. However, two kinds of heterojunction are belong to physical absorption, which indicates that there is no chemical bond between NO₂ molecule and heterojunction. For the B-G/ZnO, the most stable sites are T₀ and H in the ZnO and graphene terminal, respectively. Also, the T₀ and B are the most stable sites in the P-G/ZnO. A larger absolute value of adsorption energy correspond to a more stable adsorption configuration.

To understand the interaction between the doped graphene and ZnO-ML, the band structures of the heterojunctions are investigated, as can be seen in Figure 2 (a)-(b). The Fermi level lies on the zero energy and indicated by the black dashed line. The band gap could be modulated by doping and constructing heterojunction. As shown in Figure 2 (a), the band gap of B-G/ZnO heterojunction is 0.146 eV, and the band structure is only a superposition of B-G and ZnO-ML, it still retains the performance of doped graphene. The band structure of P-G/ZnO heterojunction is different from that of B-G/ZnO. In Figure 2 (b), there is an obvious flat band near the Fermi level, which indicates that the combination of the P-G and ZnO-ML introduces impurity states. Thus, the energy gap is increased to 0.57 eV. Also, the interaction between the NO₂ molecule and heterojunction are considered. In Figure 2 (c)-(d), the band structure of the NO₂ molecule adsorbed by B-G/ZnO and P-G/ZnO heterojunction are calculated, respectively. In Figure 2 (c), there is a flat band above the Fermi level, indicating the impurity is introduced due to the interaction between B-G/ZnO and NO₂. In Figure 2 (d), the flat band disappeared and the valence band is close to Fermi level. Meanwhile, the conduction band gradually approaches the Fermi level. The band gap of the NO₂ molecule adsorbed on B-G/ZnO and P-G/ZnO heterojunction are 0.556 eV and 0.331 eV, respectively. Compared with that before adsorption, the band gap of B-G/ZnO increases, but P-G/ZnO does the opposite. These results indicate that the heterojunction based on the ZnO-ML have great adsorption properties.

![Figure 2](image_url). The band structures of (a) B-G/ZnO, (b) P-G/ZnO, (c) B-G/ZnO adsorbing NO₂ and (d) P-G/ZnO adsorbing NO₂, the Fermi level is set to zero energy and indicated by the red dashed line.
To further explore the adsorption mechanism, DOS and PDOS of B-G/ZnO and P-G/ZnO heterojunction before and after adsorbing NO\(_2\) molecule are calculated, as displayed in Figure 3. The PDOS of the B, C, N, O and P atoms’ electron orbitals are analyzed. For B-G/ZnO heterojunction, the number and the maximum of peaks are almost unchanged (Figure 3a and 3c). After adsorbing NO\(_2\), there are two weak peak with high energy state near the Fermi level, which is consistent with its band structure. It is explained that the impurity is introduced. The B-G/ZnO heterojunction has a maximum peak at -5.1 eV, which is mainly contributed by \(d\) orbital of Zn atom. The peak of the high energy state is contributed by the \(p\) orbital of B atom. After adsorbing NO\(_2\), it is observed that the \(s\) and \(p\) orbitals of O atom affect the small peak near the Fermi level and low energy state in total DOS. Besides, the other orbitals are similar with that before adsorption. For the P-G/ZnO heterojunction, the small peak disappear near the Fermi level, at the same time, there is a new weak peak in -21.4 eV after adsorption. It is mainly contributed by the \(s\) orbital of O atom, \(s\), \(p\) and \(d\) orbitals of P atom, respectively. It is proved that graphene is effectively doped. Besides, there appear some new peaks, including the peak near -12.1 eV attributed to \(s\) orbitals of O and P atoms, and the peak near -9.3 eV belonged to \(p\) orbital of O atom. The maximum peak in B-G/ZnO and P-G/ZnO heterojunction are different, one is in the right of -5 eV, and the other is in the left of -5 eV. However, the maximum peak are almost same. In summary, due to a number of great electrical properties, B-G/ZnO and P-G/ZnO heterojunction can be considered as excellent gas sensitive materials.

![Figure 3.](image)

**Figure 3.** The DOS and PDOS of (a) B-G/ZnO, (b) P-G/ZnO, (c) B-G/ZnO adsorbing NO\(_2\) and (d) P-G/ZnO adsorbing NO\(_2\) based on the most stable configurations.

4. Conclusion

The adsorption and electronic properties of B-G/ZnO and P-G/ZnO heterojunction with the most stable configurations are investigated using the DFT. The most stable sites that NO\(_2\) molecules can be effectively absorbed are the T site of B-G/ZnO heterojunction and the T\(_0\) site of P-G/ZnO heterojunction, respectively. They have the largest adsorption energies and the shortest adsorption heights than other cases. The adsorption capacity of pristine graphene can be greatly enhanced by
doping and constructing heterojunction. It implies that B/P atom doping can modulate the band gap and the electronic structure more flexibly. Finally, these results can provide more theoretical support for the adsorption properties of heterojunction based on the ZnO-ML, which could become a promising gas sensitive materials.

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