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First-Principles Study of Gas Molecule Adsorption on C-doped Zigzag Phosphorene Nanoribbons

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Abstract: Phosphorene, due to its large surface-to-volume ratio and high chemical activity, shows potential application for gas sensing. In order to explore its sensing performance, we have performed the first-principles calculations based on density functional theory (DFT) to investigate the perfect and C-doped zigzag phosphorene nanoribbons (C-ZPNRs) with a series of small gas molecules (NH₃, NO, NO₂, H₂, O₂, CO, and CO₂) adsorbed. The calculated results show that NH₃, CO₂, O₂ gas molecules have relatively larger adsorption energies than other gas molecules, indicating that phosphorene is more sensitive to these gas molecules. For C-ZPNRs configuration, the adsorption energy of NO and NO₂ increase and that of other gas molecules decrease. Interestingly, the adsorption energy of hydrogen is -0.229 eV, which may be suitable for hydrogen storage. It is hoped that ZPNRs may be a good sensor for (NH₃, CO₂ and O₂) and C-ZPNRs may be useful for H₂ storage.

Keywords: phosphorene; carbon doping; gas adsorption

1. Introduction

As an important 2D material, when phosphorene is exposed to the air, it will be unstable and it has an inherent, direct and appreciable band gap [1]. It has attracted extensive research owing to its ambipolar behavior with drain current modulation up to $\sim 10^5$ and a field effect mobility value up to 1000 cm²·V⁻¹·s⁻¹ at room temperature [2]. It also has a considerable band gap that varies from 1.5 eV to 0.3 eV depending on the number of layers and the strain within the layer [1,3–11]. Phosphorene has linear dichroism and direction-dependent phononic anharmonicity because its electronic [1,12–15] and optical [9,16] properties are highly anisotropic. Meanwhile, it has many other applications, such as photovoltaics [17] and synthesizing quantum dots [18], based on phosphorene. The detection of gas molecules is extremely important for environmental monitoring, chemical process control, space missions and medical applications [19]. In recent years, two-dimensional materials have been proved to be suitable for gas sensing due to their large surface-to-volume ratio [20,21]. Previous studies indicate that the feasibility of pristine graphene couldbe a good sensor for CO₂, O₂ and nitrogen-based gases [19,22]. It is shown that the sensitivity of blue-phosphorene to volatile organic molecules, such as acetone, can be improved by introducing single vacancy and S-doping [23]. Meanwhile, some studies have also confirmed that nonmetallic and metallic atoms doping is an



effective method for enhancing the sensitivity of graphene to gas molecules [22,24–26]. Compared with graphene and blue phosphorene, phosphorene can be an excellent gas sensor due to its sensitivity and selectivity to gas molecules [27–33], the sensitivity of phosphorene to gas molecules could be further enhanced by substitution doping and vacancy. For example, S-doped phosphorene is more sensitive to organic gases such as methane [34–39]. Although there are many studies on transition metal (TM)-doped phosphorene. Inspired by C-doped armchair phosphorene nanoribbons (APNRs) with edge Cl passivation is proper to fabricate the lower power consumption electronic devices [40], we chose C-doped zigzag phosphorene nanoribbons (ZPNRs) in this paper. As far as we know, the investigation of systematically examining the gas-sensing ability of C-doped ZPNRs is still lacking.

In this paper, we have investigated the sensing properties of perfect and C-doped ZPNRs for seven gas molecules (NH₃, CO, CO₂, H₂, O₂, NO, and NO₂). The calculated results show that these gases induce the recognizable states in these adsorption configurations. This paper will focus on the adsorption energy (E_a), binding energy (E_b), magnetic moments and charge transfer between seven gas molecules and phosphorene. In order to provide a more obvious comparison, we have also investigated the perfect phosphorene with gas molecules adsorbed. The calculated results reveal that the binding strength is closely related to the charge transfer between these molecules and phosphorene. It can be found that the adsorption of some selected gas molecules will cause significant changes, which makes it possible for perfect and C-doped ZPNRs to be used in gas sensors, capture and storage application.

2. Calculation Methods

Structural relaxation and electronic properties calculations are performed by using First-principles calculations based on the density functional theory (DFT), which are implemented by using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA-3.2) programand the Vienna ab initio simulation package (VASP-5.4.1) [41,42]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional ischosen [43]. The double zeta polarization (DZP) basis set is used to optimize all the systems. During the optimization, all atoms in the unit cell are relaxed until the residual force on each atom is smaller than 0.01eV/Å. The mesh cutoff energy is 200 Ry and a $1 \times 11 \times 1$ Monkhorst-Pack k-point grid is applied, the direction of 1D nanoribbon is the Y axis (zigzag direction). In order to obtain more accurate results, the DFT-D3 method of Grimme is performed to correct the Van der Waals interactions between ZPNRs and gas molecules [44], the projector augmented wave (PAW)-Perdew-Burke-Ernzerhof (PBE) pseudopotentials is chosen. The cutoff for the kinetic energy of the plane waves is 520 eV. The vacuum layers along the two finite directions is 15 Å. The 3×4 rectangular supercell with 48 atoms is used to simulate the ZPNRs. The lattice constant of the single layer phosphorene is a = 4.63 Å and b = 3.29 Å along the armchair and zigzag directions, which is in accordance with the existing parameters [45].

When we substitute carbon atom for phosphorus atom in phosphorene, the system is completely relaxed. The binding energy (E_b) is calculated to investigate the stability of the system, the calculation formula is:

$$E_{\rm b} = E_{\rm ZPNRs+C} - E_{\rm ZPNRs} - E_{\rm C},\tag{1}$$

where $E_{ZPNRs+C}$ represents the total energy of C-ZPNRs, E_{ZPNRs} is the total energy of ZPNRs with vacancy and E_C is the total energy of the C atom in its ground state, respectively [46].

To describe the strength of the interaction between these molecules and ZPNR, the $E_{C+ZPNRs+gas}$ is defined as the energy of the ZPNRs or C-doped ZPNRs with a gas molecule adsorbed, $E_{C+ZPNRs}$ is the total energy of the ZPNRs or C-doped ZPNRs and E_{gas} is total energy of an isolated gas molecule, respectively. The adsorption energies (E_a) are calculated by using the formula [29]:

$$E_{\rm a} = E_{\rm ZPNRs+C+gas} - E_{\rm C+ZPNRs} - E_{\rm gas}.$$
 (2)

3. Results and Discussion

For the optimized phosphorene, each phosphorus atom forms a covalent bond with three adjacent phosphorus atoms, similar to the honeycomb structure of graphene but with wrinkles. Figure 1a,c show top and side schematic views of optimized perfect ZPNRs and C atom doped ZPNRs, respectively. For comparison, the electronic structure of the pristine ZPNRs is calculated. According to the density of states (DOS) of the system, it can be seen that the bare ZPNRs are metallic, which is consistent with the previous results [47].



Figure 1. (**a**) Refers to the pristine zigzag phosphorene nanoribbons (ZPNRs); (**b**) refers to the most energetically favorable perfect ZPNRs with NO adsorbed; (**c**) refers to the C doped ZPNRs; (**d**) refers to the C-ZPNRs with NO adsorbed. The N, C, O and P atoms are represented by blue, gray, red, and purple spheres, respectively.

To explore the sensing character, the pristine ZPNRs with seven common gas molecules adsorbed are considered. For these configurations, the vertical distance between all gas molecules and the phosphorene layer are set to 2.0 Å and the whole system are fully optimized. The shortest distance between the gas molecule and the phosphonene layer is defined as the adsorption distance. The most stable configuration of CO/H_2 —adsorbed on phosphorene are the same, from the top view (Figure S1a,c), they are located above the center of the honeycomb, the CO/H_2 molecules are nearly perpendicular to the phosphorene layer and the adsorption distances of the CO and H₂ are 2.92 and 2.69 Å, respectively(as shown in Figure 2). The relaxed NH₃ adsorption configuration is shown in

Figure S1d, where N atom points to the substrate, H atom points to the opposite direction, and its adsorption distance is 2.17 Å. The configuration of CO_2/O_2 —adsorbed on phosphorene are the same, the CO_2/O_2 molecules are almost parallel to the phosphorene layer (Figure S1b,f), the adsorption distancesare3.08 and 2.58 Å, respectively. The dipolar molecule NO₂ is shown in Figure S1e, where one O–N bond is approximately perpendicular to the phosphorene layer, the other is along the direction of the armchair. The O atom is closest to the P atom and its adsorption distance is 1.86 Å. For another dipolar molecule NO, the O–N bond is almost parallel to the phosphorene layer, as shown in Figure 1b, the distance between N and P is 2.17 Å.



Figure 2. Absorption distance of gas molecules on ZPNRs and C-doped ZPNRs.

To further illustrate the adsorption strength of these gas molecules on ZPNRs and C-doped ZPNRs. We have calculated the adsorption energy (*E*a), the calculated results are shown in Table 1. It can be found that the adsorption energy of H₂ is 0.464 eV and the minimum adsorption energy of NO is 0.11 eV, which is consistent with previous results [28]. The adsorption energy of H₂ is almost the same as that of other hydrogen storage materials [48]. The *E*a of CO, CO₂, NH₃, NO₂ and O₂ are -0.465, -0.864, -0.513, -0.223 and -0.963 eV, respectively. Interestingly, the adsorption energy of O₂, CO₂ and NH₃ is larger than that of other gas molecules, indicating that ZPNRs is more sensitive to these gases.

Gas Molecule	ZPNRs			C-Doped ZPNRs		
	E _a (eV)	Q (e)	Μ (μΒ)	$E_{\rm b}/E_{\rm a}$ (eV)	Q (e)	Μ (μΒ)
None	-	-	0	-8.266	0.136	0
CO	-0.465	0.042	0	-0.272	0.018	0
CO_2	-0.864	0.034	0	-0.557	0.024	0
H ₂	-0.464	-0.042	0	-0.229	-0.052	0
NH ₃	-0.513	0.078	0	-0.459	0.066	0
NO	-0.110	0.073	0.705	-0.204	0.093	1.161
NO ₂	-0.223	-0.028	0	-0.256	0.002	0
O ₂	-0.963	0.006	1.215	-0.734	0.027	2.008

Table 1. Adsorption energy (E_a)-VASP, Charge transfer (Q), and Magnetic moment (M) of gas molecules on ZPNRs and C-doped ZPNRs.

Previous studies of gas adsorption on phosphorene have shown that charge transfer plays an important role in the adsorption energy [28]. In order to further study the adsorption mechanism between gas molecules and phosphorene, the charge transfer is calculated by performing the Mulliken population analysis. As can be seen in Table 1, the CO, CO_2 , NH_3 , NO, and O_2 molecules are charge donors. The charge transfer of CO adsorption configuration is 0.042 e, while the electron transfer of CO_2 adsorption configuration is 0.034 e but its adsorption energy is large. Next, we turn tonitrogen-based gas molecules. For NO and NH_3 adsorption configurations, the corresponding charge transfer are

0.078 and 0.073 e (Table 1), respectively. For the O₂ adsorption configuration, its charge transfer is only 0.006 e, the smallest charge transfer in all gas molecules but its adsorption energy is relatively large. It may be attributed to that charge transfer and covalent interactions occur simultaneously.

 H_2 and NO_2 act as charge acceptors in all investigated systems. For the H_2 molecule, its charge transfer amount is -0.042 e and it behaves as a charge acceptor. Besides, its binding energy is relatively small, which is consistent with the previous results [28]. It may be attributed to the electrostatic attraction caused by the dipole dipole interaction polarization. Therefore, H_2 molecules are adsorbed on the phosphorene layer for physisorption. For the NO_2 molecule, it gets 0.028 e from surrounding P atoms.

To further study the changes in the electronic properties of ZPNR. The DOS of perfect ZPNR and seven common gas molecules adsorbed on the ZPNRs is shown in Figure 3a–h. The calculated results show that there is no obvious change for the DOS of ZPNR with CO, CO₂ and H₂ adsorbed (Figure 3b–d). Then we turn to analyzing the adsorption of nitrogen-based gas molecules; for NH₃ configuration, there is a significant change near the Fermi level. The main change is the appearance of two peaks around the energy of 0.2 eV (Figure 3e) but the value is smaller than that of the perfect ZPNR. For the case of NO₂ adsorption (Figure 3f), similar peaks appear in the energy of 0.2 and 0.4 eV near Fermi level, respectively. The difference is that a peak appears in 0.7 eV and it can be proved by PDOS that this peak is mainly caused by the interaction between NO₂ and ZPNR. It can be found that the adsorption of NO₂ gas molecules does not induce magnetic moment.

Next, the configurations of NO and O_2 adsorbed are discussed together and it can be seen that spin polarization appears (as shown in Figure 3g,h). For the case of NO configuration, the magnetic moment (M) is 0.705 µB. Around -0.5–0.5 eV, the impurity state of spin up appears, which can be identified in the PDOS analysis. Meanwhile, there are two spin-down peaks in the energy range of 0.5–1 eV, which may be attributed to the contribution of p orbital of the nitrogen. The magnetic moment of ZPNR with O_2 molecule adsorbed is 1.215 µB. It can be found that there is a spin-up peak around 0.7 eV (Figure 3h) and it has a significant change. It may be attributed to the p orbital of the oxygen atom.

Then we turn to the C-doped ZPNRs, as we all know that the coordination number of C is 3, it can be seen from Figure 1c that the three C–P bond lengths are approximately equal and the length is approximately 1.80 Å. We have calculated the binding energy of ZPNRs with C doping and $E_b = -8.266$ eV (Table 1), which is very close to the previous study [36], this indicates that the structure is stable after optimization.

The adsorption of these common gases on C-doped ZPNRs have been investigated, the vertical distances between all gas molecules and the C-doped ZPNRs are set to 2.0 Å and the system is fully optimized. The most stable configuration of $CO/CO_2/H_2/NH_3$ —adsorbed on C-doped ZPNRs are the same (Figure S2a–d), where the molecules are located at the center of the honeycomb. For these relaxed configurations, the adsorption distances of the CO, CO_2 , H_2 and NH_3 are 2.97, 3.05, 2.71 and 2.96 Å, respectively. As shown in Figure 2, the calculated results show that carbon doping has no significant effect on the electronic properties of ZPNR with four gases adsorbed. For the adsorption of paramagnetic molecules NO, NO₂ and O₂ on C-doped ZPNR (Figure 1d and Figure S2e,f), the corresponding distances are 2.13, 2.05 and 2.88 Å, respectively(as shown in Figure 2).By comparing the adsorption distance of NO₂ and O₂ on the pristine ZPNR, it can be found that the adsorption distance is significantly increasing. This may be attributed to the structure distortion, which is induced by the presence of carbon atoms.

The adsorption energy of C-doped ZPNRs with gas molecules adsorbed are also calculated, which can be found in Table 1. The values for CO, CO_2 and NH_3 are -0.272, -0.557 and -0.459 eV, respectively. The adsorption energies of these three gas molecules are smaller than that of pristine ZPNR. By performing the Mulliken population analysis, it is shown that the CO, CO_2 and NH_3 molecules act as charge donors. The corresponding charge transfer (Table 1) amounts are 0.018, 0.024 and 0.066 e, respectively. Compared with the perfect ZPNR with CO, CO_2 and NH_3 adsorbed, the amount of

charge transfer obviously decreases, which is consistent with the adsorption energy. Interestingly, the adsorption energy of hydrogen is -0.229 eV, which may be suitable for hydrogen storage materials [48]. For the case of NO, its adsorption energy slightly increases to -0.204 eV, but the charge transfer amount increases to 0.093 e and the magnetic moment increases to $1.161 \mu\text{B}$. For the case of NO₂, its adsorption energy increases to -0.256 eV but it changes from the charge acceptor to the charge donor after C-doping and the charge transfer amount is only 0.002 e. For the case of O₂, its adsorption energy is only -0.734 eV but its charge transfer amount increases to 0.027 e and the magnetic moment increases to $2.008 \mu\text{B}$.



Figure 3. Density of states (DOS) of ZPNR (**a**) and the projected density of states (PDOS) of CO (**b**), CO_2 (**c**), H_2 (**d**), NH_3 (**e**), NO_2 (**f**), NO (**g**) and O_2 (**h**) adsorbed on the ZPNRs.

To further investigate the effect of carbon-doping on the electronic properties of ZPNRs with gas molecules adsorbed. As shown in Figure 4b–h, there is no significant change in the DOS (Figure 4b–e) of C-ZPNRs, which means that carbon atom doping has no significant effect on them and it is still physisorption. For the case of NO₂ adsorption, it can be found that the DOS of C-ZPNRs have changed significantly near Fermi level (Figure 4f), which may be attributed to the interaction between C-dopant and NO₂. For the case of NO adsorption, there is also a large change near the Fermi level (Figure 4g). According to the PDOS of C-ZPNR with O₂ adsorbed, the peak near the Fermi level in Figure 4h is significantly smaller compared with the DOS (Figure 3h), and when the energy range is about 0.7 eV, the spin-down peak has a significant influence. When the energy range is about -1.8 eV, there is a sharp spin up peak, which may be attributed to interaction between C-dopant and O₂, and it is in accordance with the magnetic moment of C-ZPNR with O₂ adsorbed.



Figure 4. Density of states (DOS) of C-doped ZPNRs (**a**) and the projected density of states (PDOS) of the C-doped ZPNRs with CO (**b**), CO₂ (**c**), H₂ (**d**), NH₃ (**e**), NO₂ (**f**), NO (**g**) and O₂ (**h**) adsorbed. The Fermi energy is shifted to zero as indicated by the vertical dotted red line.

4. Conclusions

In summary, we have performed first-principles calculations based on density functional theory to investigate the electronic properties of ZPNRs and C-doped ZPNRs with adsorption of a series of small gas molecules (NH₃, NO, NO₂, H₂, O₂, CO, and CO₂). The electronic properties of ZPNR are obviously affected owing to the adsorption of nitrogen based gases. For C-doped ZPNRs, the sensitivity to NO, NO₂ and H₂ gas molecules are improved and the C-doped ZPNRs may be suitable for hydrogen storage. The calculated results suggest that ZPNRs and C-doped ZPNRs may be suitable for gas sensor, hydrogen storage material applications.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6412/9/11/763/s1, Figure S1: Models of the (a) CO, (b) CO₂, (c) H₂, (d) NH₃, (e) NO₂ and (f) O₂ gas adsorbed on the pristine phosphorene. The purple, red, gray, blue and white balls represent P, O, C, N and H atoms, respectively. Figure S2: Models of the (a) CO, (b) CO₂, (c) H₂, (d) NH₃, (e) NO₂ and (f) O₂ gas adsorbed on the C doped phosphorene. The purple, red, gray, blue and white balls represent P, O, C, N and H atoms, respectively. The purple, red, gray, blue and white balls represent P, O, C, N and H atoms, respectively.

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