



Original Article

# Toxic Gases on $\beta_{12}$ Borophene: the Selective Adsorption

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**Abstract:** Borophene, a new member of the 2D material family, was proven theoretically and empirically in many recent studies that it has a unique structure and promising properties applied in batteries and electronic devices. In this work, the adsorption ability of  $\beta_{12}$  borophene towards some main harmful gases was investigated. The first-principles calculations were employed to obtain the adsorption configurations and the adsorption energies of CO, NO, CO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> on  $\beta_{12}$  borophene. The vdW interactions are taken into account by using three functionals: revPBE-vdW, optPBE-vdW, and vdW-DF2. The most stable configurations and diffusion possibilities of the gas molecules on the surface of  $\beta_{12}$  borophene were determined visually by using our Computational DFT-based Nanoscope. The nature of bonding and interaction between gas molecules and  $\beta_{12}$  borophene were disclosed by using the density of states analysis and Bader charge analysis. Remarkably, borophene exhibits as a highly selective adsorbent when having great interactions with NO<sub>x</sub> gases outweigh the others.

**Keywords:**  $\beta_{12}$  borophene, DFT, adsorption, toxic gases, 2D materials.

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## 1. Introduction

When industrialization and urbanization are increasing sharply, air pollution becomes a severe global problem. Air pollution can affect human health directly or indirectly. According to WHO (2017) data, air pollution causes 1 in 9 deaths worldwide while ambient air pollution caused 7.6% deaths over the world in 2016, which includes 4.2 million premature deaths [1].

To decrease the impacts of air pollution, detecting pollutants is the first work needed to do before carrying out the subsequent processing procedures [1]. Hence, the thing here is discovering good material that has high sensitivity and selectivity with toxic gases, which are the significant pollutants causing air pollution, aiming to create an effective sensor to detect these pollutants.

Overall, low-dimensional materials are potential adsorbents on gas adsorbing applications due to their high surface-to-volume ratio. Together with growing concern for two-dimensional, we carried out theoretical research on the adsorption of toxic gases on  $\beta_{12}$  borophene, which is a novel 2D material.

Borophene is expected to have intriguing characteristics similar to graphene. It exhibits outstanding mechanical and electronic performance such as existing spin gapless Dirac cone [2]. Borophene thus is a promising candidate for adsorption of poisonous applications. Recently, borophene has been successfully synthesized by the chemical vapor deposition method in ultrahigh vacuum conditions on silver (111) substrate [3], [4].  $\beta_{12}$ , as a line-defective phase of borophene, has been depicted to have unusual mechanical, electronic, and chemical properties, materializing its potential in practical applications [5]–[8]. This research aims to discover whether  $\beta_{12}$  borophene is a potential material for filtering or sensing toxic gases in the ambient atmosphere for the purpose of mitigating air pollution effects and enhancing community health. First-principles calculations were systematically employed to obtain the adsorption configurations, adsorption energies, and electronic structures of CO, NO, CO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> on  $\beta_{12}$  – borophene.

## 2. Computational Methods

All our Density Functional Theory (DFT) calculations were performed by using the Vienna Ab initio Software Package (VASP) [9]. The periodic boundary conditions and plane-wave expansion of the wave function were employed. The generalized gradient approximation in the scheme of the Perdew–Burke–Ernzerhof function was used to calculate the exchange-correlation potential and the PAW pseudopotential was applied to describe electron-ion interactions. Three van der Waals (vdW) correlation functionals, namely revPBE-vdW [10], optPBE-vdW [11] and vdW-DF2 [12] are implemented to calculate the interaction energies for small molecules adsorbed on borophene. The electronic calculation convergence reaches if the energy difference between two self-consistent function steps is smaller than  $10^{-5}$  eV, and the internal coordinates and lattice constants were optimized until the Hellman–Feynman forces acting on each atom were less than 0.01 eV/Å. To eliminate interactions between borophene sheets, a vacuum of 20 Å was employed along the z-direction of the borophene sheet. The cut-off energy was determined to be 500 eV by using the fixed K-point at  $12 \times 12 \times 1$ . Then the K-point mesh in the Brillouin zone was investigated and optimized at  $3 \times 3 \times 1$  at cut-off energy 500 eV for the  $4 \times 3$  supercell. To optimize the gas-borophene geometries, we fixed the z-coordinate of boron atoms and optimize all the other degrees of freedom.

The adsorption energy  $E_a$  is calculated by the following equation:

$$E_a = E_{\text{gas-borophene}} - (E_{\text{gas}} + E_{\text{borophene}}) \quad (1)$$

where  $E_{\text{gas-borophene}}$ ,  $E_{\text{gas}}$ , and  $E_{\text{borophene}}$  are the total energies of the gas-borophene system, isolated gas molecule, and isolated borophene, respectively.

The Computational DFT-based Nanoscope [13] was applied to determine the most stable configurations, diffusion possibilities, adsorption energy profile, and electronic attributes of the gas molecules on the  $\beta_{12}$  borophene surface visually. This tool has been utilized to simulate adsorption behaviors of organic gases on other 2D materials, namely graphene [14] or silicene [15].

The Bader charge analysis was executed using the code developed by Henkelman group from the University of Texas at Austin [16]. The following equation calculates the charge density difference:

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B \quad (2)$$

where  $\rho$  is the total charge of the system, AB is the complex system, A and B are two separate systems.

The visualization using in this work is VESTA developed by K. Momma and F. Izumi [17].

### 3. Results and Discussion

The lattice crystal of  $\beta_{12}$  borophene shown in Figure 1 has a flat structure. Along zigzag direction, there exists a mixture of boron-centered and vacant hexagons. The unit cell includes five boron atoms marked by the dashed line. The lattice constants of borophene are totally in agreement with empirical data [3], [4], [18] and previous theoretical studies [19]–[21] as shown in Table 1. The electronic structure of  $\beta_{12}$  borophene is calculated as well, indicating that  $\beta_{12}$  borophene has a metallic structure with the absence of bandgap, which is consistent with other studies.

Table 1. Lattice constants of  $\beta_{12}$  borophene

	<b>a</b> (Å)	<b>b</b> (Å)
GGA	2.921	5.083
revPBE-vdW	2.928	5.106
optPBE-vdW	2.931	5.075
vdW-DF2	2.913	5.070
Experimental data [3]	$2.9 \pm 0.2$	$5.1 \pm 0.2$

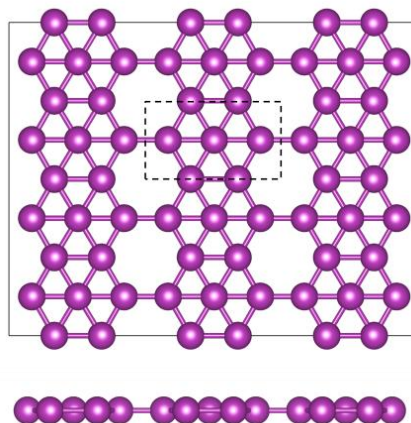


Figure 1. Top view (top) and side view (bottom) of the optimized supercell of the  $\beta_{12}$  borophene.

To compare the adsorption performance among these poisonous gases, we analyze the distance and the binding energy between these gas and the adsorbent materials when the geometries were fully optimized by employing optPBE-vdW correlation functional, as shown in Figure 2. Thereby, the energetically favorable configuration of  $\text{NO}_2$  is closest to the surface ( $d_z = 1.7 \text{ \AA}$ ). On the other hand,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{NH}_3$  favorably locate quite far from the surface at approximately  $3 \text{ \AA}$ . Besides, the adsorption energy of  $\text{NO}_2$  system is the highest value; almost two times larger than the second strongest binding energy for  $\text{NO}$ .

Compared with other 2D materials, the borophene has a superior adsorption performance. For example,  $\text{MoS}_2$  exhibits smaller binding energy for all the gases ( $< -0.3 \text{ eV}$ ) [22]. Similarly, the adsorption energies of graphene toward these gases are much lower than those of the borophene. Although graphene is most sensitive to  $\text{NO}_2$  like the borophene, its adsorption energy, is only  $-67 \text{ meV}$  [23]. These values of phosphorene are also smaller than the borophene with the adsorption energies for  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  are  $-0.31$ ,  $-0.18$ ,  $-0.32$ , and  $-0.5 \text{ eV}$ , respectively [24].

The adsorption profiles of  $\beta_{12}$  borophene suggest that this material might be a sensitive and selective adsorbent towards  $\text{NO}_x$  gases. Thus, we intensively investigate the adsorption behavior of system  $\text{NO}_x$  (i.e.,  $\text{NO}$  and  $\text{NO}_2$ ) on borophene. Figure 3 compares the adsorption energies as a function of  $\text{NO}_x$ –borophene separations among three vdW correlation functionals. In this figure, the lowest peak corresponds to the most stable position of the molecule along the z-direction. Considerably, the difference in adsorption energy of  $\text{NO}_2$  is significant among these methods. By using optPBE-vdW, the binding energy is much higher than using two remaining functionals, which is  $1.5 \text{ eV}$  comparing to around  $0.7 \text{ eV}$ . Correspondingly, the space between gas and borophene is narrower with optPBE-vdW method. In particular, the shortest distance between  $\text{NO}_2$  molecule and the substrate is  $1.7 \text{ \AA}$  when employing optPBE-vdW while this figure for two other functionals is  $2.2 \text{ \AA}$ .

In the case of  $\text{NO}$ , among three employed functionals, optPBE-vdW estimates the highest adsorption energy while the others give similar results at smaller values. Also, the distance between the gas molecule and the adsorbent is expected to be rather independent to employed vdW correlation functionals. In particular, the adsorption energy varies from almost  $-0.5 \text{ eV}$  to  $-0.7 \text{ eV}$ . This adsorption energy of  $\text{NO}$  on borophene is higher than that on graphene ( $-0.03 \text{ eV}$ ) and silicene ( $-0.35 \text{ eV}$ ) [25]. For all three methods, the shortest distance from the adsorbent to the gas molecule is  $2.3 \text{ \AA}$ .

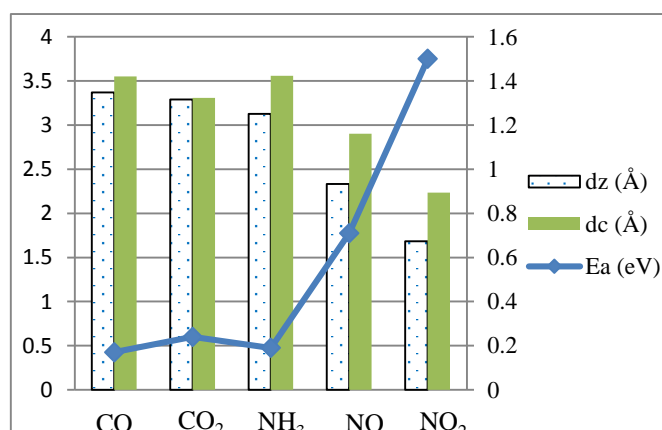


Figure 2. The shortest distance ( $d_z$ ), the distance from the mass center of gas molecules to borophene ( $d_c$ ), and absolute values of adsorption energy ( $E_a$ ) using optPBE-vdW functional.

The adsorption capacity and the diffusing ability might be obtained from the potential energy surface (PES) of  $\text{NO}_x$  gas adsorbed on borophene, as shown in Figure 4. The gap of binding energy in the case of  $\text{NO}_2$  is significant of nearly 600 meV. The adsorption of  $\text{NO}_2$ , nevertheless, is comparatively delocalized, which means  $\text{NO}_2$  might move smoothly along the armchair direction. This diffusion is illustrated by quite flat purple routes in Figure 4a. This gas has to overcome a  $\sim 600$  meV-potential barrier to diffuse along the other direction (i.e., zigzag direction). In the case of  $\text{NO}$  interacting with borophene, the adsorption is quite localized because of the large gap of binding energy between where the gas molecule is trapped and neighboring areas, illustrated in Figure 4b. That is, once the  $\text{NO}$  molecule is adsorbed on borophene, it would rather be stationary than diffuse along the surface.

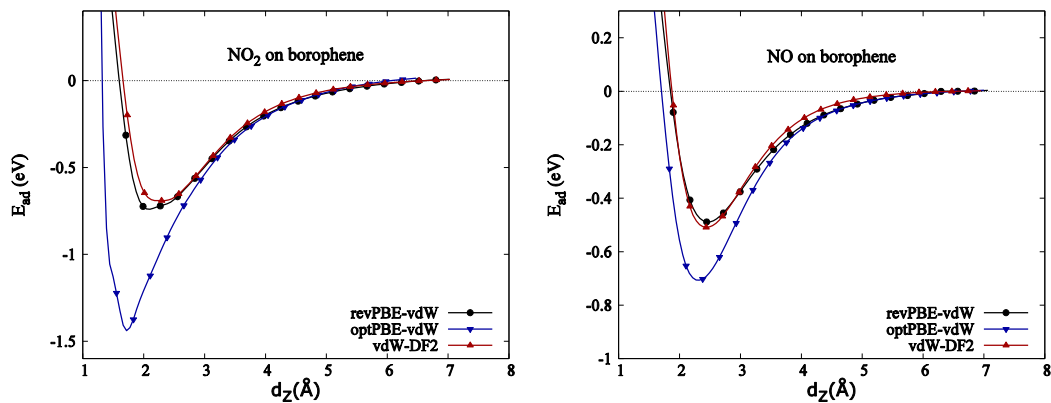


Figure 3. Adsorption energy vs. distance of  $\text{NO}_2$  – borophene (left) and  $\text{NO}$ -borophene (right) using revPBE-vdW, optPBE-vdW, and vdW-DF2 functionals.

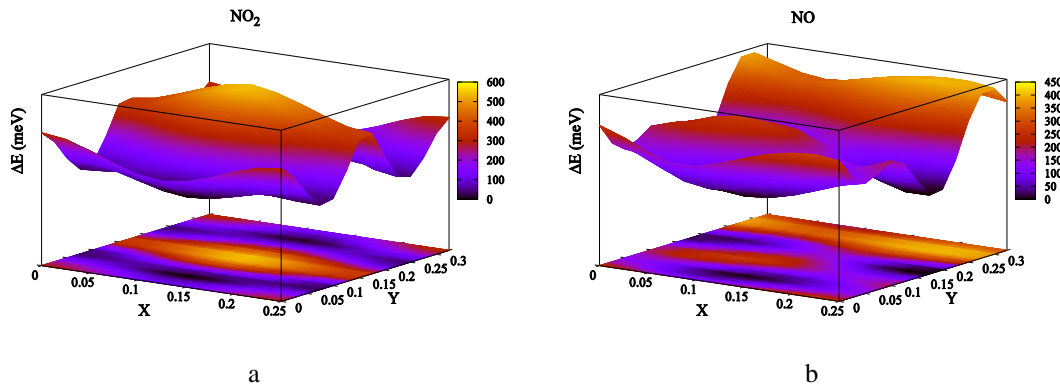


Figure 4. The PES of  $\text{NO}_2$  (a) and  $\text{NO}$  (b) adsorbed on borophene

The electronic structure of the two systems ( $\text{NO}$  – borophene) and ( $\text{NO}_2$  – borophene) are plotted in Figure 5, where the black line is the total density of state (DOS) of the system, the colored lines are the partial DOS classified into elements. The displayed contribution to DOS of nitrogen and oxygen are multiplied by three. Borophene remains metallic property after adsorbing both  $\text{NO}$  and  $\text{NO}_2$

molecules. Significantly, NO contributes states close to Fermi energy, which possibly affects the transport properties of borophene.

The charge transferring behaviors of these gases and borophene were summarized in Table 2. The positive sign indicates the accumulation of electrons whereas the negative sign represents the depletion of electrons after adsorbing processes. Thus, NO is an electron donor while NO<sub>2</sub> is an acceptor. Notably, the amount of charge transferred in the case of NO and NO<sub>2</sub> (around 0.7 electrons) are higher by far than those of CO, CO<sub>2</sub>, and NH<sub>3</sub> gases, approximately 30 times larger than CO and CO<sub>2</sub>, and 100 times larger than NH<sub>3</sub>. This data shows an impressive adsorbing performance of borophene toward these gases even in comparison with other 2D materials. For example, in the case of phosphorene, NO<sub>2</sub> also has the greatest electronics interaction with adsorbent, but the charge transfer is only 0.185 e [24]. The charge transferred from WS<sub>2</sub> to CO and NO, are smaller than those of borophene as well, at 0.0078 and 0.0096 e, respectively [24].

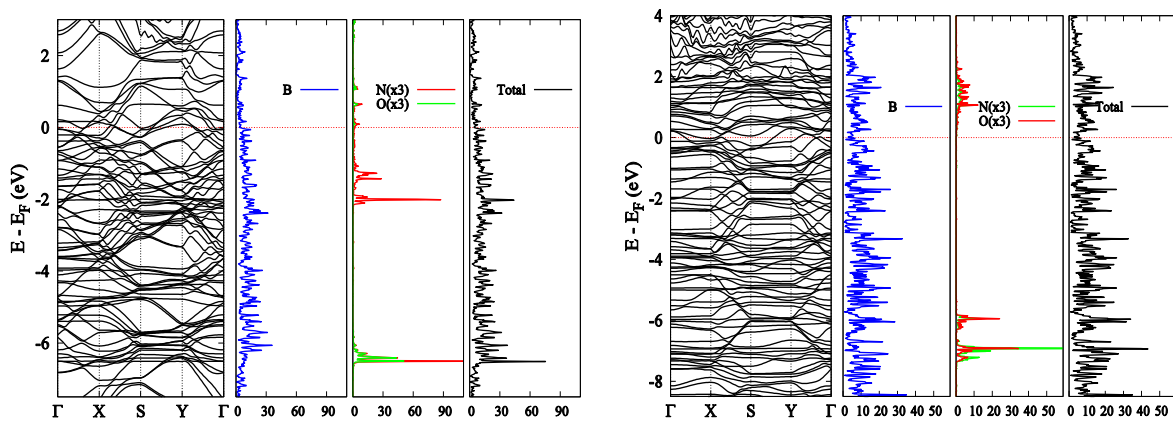


Figure 5. Band structure and DOS of NO<sub>2</sub> – borophene (left) and NO –borophene (right).

Table 2. The charge transferred to gas molecules

	Charge transferred $\Delta Q$ (e)
CO	+0.0236
CO <sub>2</sub>	+0.0268
NH <sub>3</sub>	-0.0066
NO	- 0.7686
NO <sub>2</sub>	+0.7522

The received or donated charge is expected to cause the change in resistivity of adsorbent;  $\beta_{12}$  borophene, therefore, is predicted to be a selective and sensitive material to NO<sub>x</sub> gases.

#### 4. Conclusion

Borophene exhibits as a material with high selectivity, which is much more sensitive to NO and NO<sub>2</sub> gases. Considerably, although the adsorption energy of NO on borophene is just in physical

adsorption range, which is neither too weak nor too strong for borophene as an adsorbent, NO has a great charge transfer with borophene. It is a potential characteristic for borophene to be an excellent sensing material, aiming to fabricate a sensitive and reusable sensor.

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