

# A first-principles study of gas molecule adsorption on two-dimensional borophene

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**Abstract.** The effect of two-dimensional borophene on the adsorption properties of gas molecules was studied by first-principles method. The adsorption energies of gas molecule on the four adsorbed site were first computed. Through compare these adsorption energies of different adsorbed site, the most stable of adsorption configuration were determined. In order to confirm the interaction mechanism of gas molecule and borophene, the charge population of borophene-gas molecule were computed. The calculated shows that the CO, NO and NO<sub>2</sub> molecule are adsorbed on the borophene nanosheet with chemical adsorption. The further charge population analysis of the borophene-CO and the borophene-NO adsorption system shows that the electrons transfer from borophene nanosheet to CO and NO molecule. It is can be seen that the borophene acts as electron donor and gas molecule acts as electron acceptor. Based on the above the calculation and analysis, we concluded that the borophene materials is an excellent candidates to detect gas molecules.

**Keywords:** First-principles calculation; borophene; gas molecule; adsorption.

## 1. Introduction

Graphene, a new type of 2-D single-atom layer material, was first synthesized in 2004 by Novoselov<sup>[1]</sup> make use of mechanical stripping. From then on, the structures, properties, applications and the interaction relationship of new 2-D single-atom nanomaterials has become one of the most amusing fields of research, such as silicene, germanene, stanene and 2-D transition metal sulfide. Borophene is a new type of 2-D monolayer nanomaterial, which has been successfully prepared on monocrystal Ag (111) crystallographic plane<sup>[2]</sup> at the condition of ultrahigh vacuum degree. It has particular geometrical configuration and unique electronic structure, which make it possesses outstanding physical, chemical, and mechanical properties<sup>[3-8]</sup>. The outstanding properties of borophene is suitable for many types of applications, for instance, Lithium ion batteries<sup>[9, 10]</sup>, hydrogen-storage<sup>[11,12]</sup>, capacitors<sup>[13]</sup>, and toxic gas sensors<sup>[14-16]</sup>. So more and more researcher studied the effects of surface modification on the physical, chemical and mechanical properties of borophene nanosheet, for example, doping technology (heteroatom doping and vacancy doping), heteroatom adsorption (hydrogen or group functionalization), and so on. Besides, with the environmental pollution caused by the toxic gases (CO, NO, NO<sub>2</sub>, and so on) is becoming more and more serious. The research on the detection and adsorption of toxic gas molecules is of great significance, and the development of new high sensitivity and large capacity of gas molecular sensors has attracted the attention of many researchers. Because of the 2-D borophene has unique wrinkle geometrical configuration<sup>[2]</sup> (which has peak of wave and trough of wave, shows in Figure 1), large surface-volume ratio and excellent electronic conductivity, indicating that the electron state of the borophene nanosheet can be easily altered by gaseous molecular adsorption, which allows it for use in sensor and gas detection. Many colleagues studied the adsorption performance of gas molecule on the borophene nanosheet through the calculational and experimental methods. Based on the calculational and experimental methods, researchers developed a series of theoretical achievements and high-performance gas molecule sensors. Huang<sup>[14]</sup> et al. studied the adsorption properties of gas molecules absorbed on borophene. They discovered that CO molecule were chemically adsorbed to borophene nanosheet with large adsorption energy, but other gas molecule has minor interaction with

the borophene nanosheet. Their results shows that the borophene nanosheet can be used to develop high sensitivity gas molecule sensor to detect NO molecule. In this work, based on the first-principles study, we study the adsorption properties of CO, CO<sub>2</sub>, NO, and NO<sub>2</sub> molecules on pristine borophene nanosheet. By analyzing the adsorption energy, adsorption configuration, charge population of gas molecules on pristine borophene, we come to the conclusion that the borophene materials is suitable for the gas detection applications.

## 2. Computational method and details

The CASTEP software package based on density functional theory (DFT) was used for all the studies in this paper. The PBE functional in GGA is used to deal with the exchange-correlation energy between electrons, and the ultrasoft pseudopotential was used to depict the interactions between the ion nuclei and electron. The calculation were performed make use of about energy cutoff = 400 eV and a  $4 \times 4 \times 1$  of Brillouin zone k-point. The geometric structure model of borophene is present in Figure 1. The calculation model composed of 24 boron atoms, and the bond length of TB site and T-V bond is 1.6258 Å and 1.86874 Å, respectively. Since the three dimensional periodic boundary condition, it is necessary enlarge the Z-direction thickness to avoid the interaction between the layer, so we choose the lattice parameters were  $c = 20$  Å. The gas molecule are then vertically adsorbed directly above the borophene nanosheet in the four adsorbed sites, and the best adsorbed site and adsorption energy were calculated after geometry optimization. The adsorption energy ( $E_{ad}$ ) of the gas molecule on borophene was defined by:

$$E_{ad} = E_{\text{molecule/borophene}} - E_{\text{borophene}} - E_{\text{molecule}} \quad (1)$$

where  $E_{\text{molecule/borophene}}$ ,  $E_{\text{borophene}}$ , and  $E_{\text{molecule}}$  are the total energy of the optimized adsorption configuration, the energy of the pristine borophene sheet, and the energy of the isolated gas molecule, respectively.

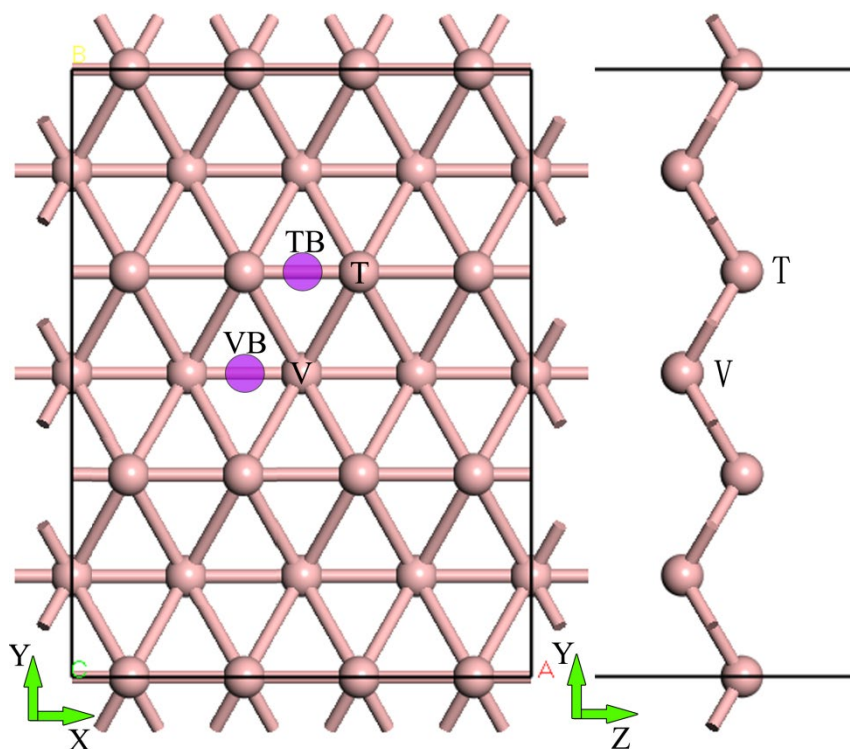


Figure 1. The configuration of the borophene, and the adsorbed sites (TB site, T site, VB site and V site).

### 3. Results and Discussion

#### 3.1 Adsorption energy ( $E_{ad}$ ) and Adsorption configuration

The  $E_{ad}$  change of the CO, CO<sub>2</sub>, NO, and NO<sub>2</sub> molecule on borophene with adsorbed sites variation are present in Figure 2, and the optimized adsorption configuration are present in Figure 3.

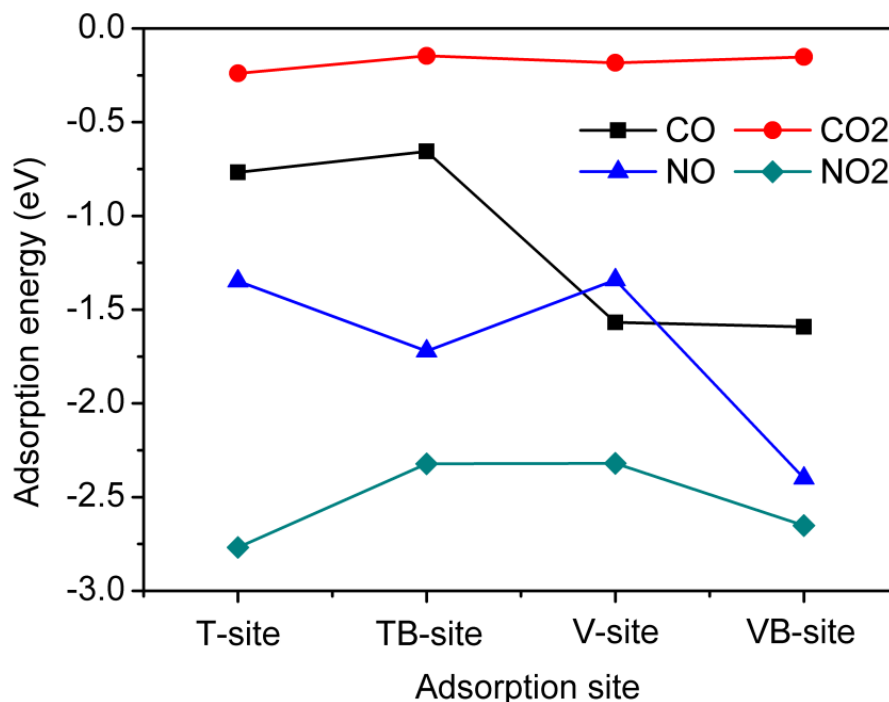


Figure 2. The  $E_{ad}$  change of the gas molecules on borophene with the adsorbed site variation.

For the type of CO<sub>2</sub> molecule adsorbed on the borophene, the effect of change of adsorption site on the  $E_{ad}$  is not obvious, such as -0.24 eV of T-site, -0.15 eV of TB-site, -0.18 eV of V-site and -0.15 eV of VB-site (the red cycle point and line in Figure 2). The interaction between CO<sub>2</sub> molecule and pristine borophene nanosheet is weak, it may be result of the CO<sub>2</sub> is a nonpolar molecule. But for the CO and NO molecule, the  $E_{ad}$  gradually decreased with the adsorbed site from the T-, TB-, V-, to the VB-site, from -0.76 eV and -1.35 eV reduce to -1.59 eV and -2.40 eV, respectively. When NO<sub>2</sub> molecule adsorbed on borophene nanosheet, with the change of adsorbed site from T- to VB-site, the  $E_{ad}$  first increased and then decreased, and the  $E_{ad}$  of NO<sub>2</sub> molecule on borophene nanosheet of T-site is smallest, indicated that the T-site is the most stable adsorbed site. Furthermore, the  $E_{ad}$  of the most stable adsorption configurations of CO, CO<sub>2</sub>, NO and NO<sub>2</sub> on borophene are -1.59 eV, -0.24 eV, -2.40 eV and -2.69 eV, respectively.

When the gas molecule interacted with pristine borophene nanosheet, especially for the condition of chemical interaction, the bond length and bond angle will changed since the charge transfer from ppriestine borophene nanosheet to gas molecule. Therefore, in order to analysis the intensity of the interaction, the changes of bond length and bond angle before and after gas molecule adsorption were systematically compared, the data shown as present in Table 1. The bond length of CO molecule of free condition is 1.154 Å, but the adsorption condition is 1.202 Å, it is can be seen that the bond length minor increase after adsorption. These data indicated that CO is vertically adsorbed on borophene by chemical adsorption, and the adsorption configuration is present in Figure 3(a1, a2). When CO<sub>2</sub> molecule interacted with the borophene, the C-O bond is obviously stretched (both the length of C-O1 and C-O2 bond extends to 1.315 Å from 1.161 Å (free CO<sub>2</sub> molecule). Besides, the

bond angle of the CO<sub>2</sub> molecule decreases from 180° to 135.176°(from the line type of molecule to the large angle V-type molecule, Figure 4(a1, a2)). Prior to adsorption, the bond length of NO molecule is 1.151 Å. And its extends to around 1.261 Å after adsorbed on borophene. After NO<sub>2</sub> absorbed on borophene, the bond length N–O increased obviously (the length of N–O1 and N–O2 bond extends to 1.480 Å from 1.197 Å (free NO<sub>2</sub> molecule)), indicating that there has a strong interaction for the NO<sub>2</sub> molecule and pristine borophene nanosheet, which accordance with the results of large adsorption energy. The bond angle of the NO<sub>2</sub> molecule decreased from 142.357° to 121.912° (Figure 4(d1, d2)).

Table 1. The change of bond length, bond angle of gas molecule before and after adsorption.

Gas molecule	Bond	Bond length (Å)		Bond Angle	
		Before adsorption	After adsorption	Before adsorption	After adsorption
CO	C–O	1.154	1.202	—	—
CO <sub>2</sub>	C–O1	1.161	1.315	180°	135.176°
	C–O2	1.161	1.315		
NO	N–O	1.151	1.261	—	—
NO <sub>2</sub>	N–O1	1.197	1.480	142.357°	121.912°
	N–O2	1.197	1.482		

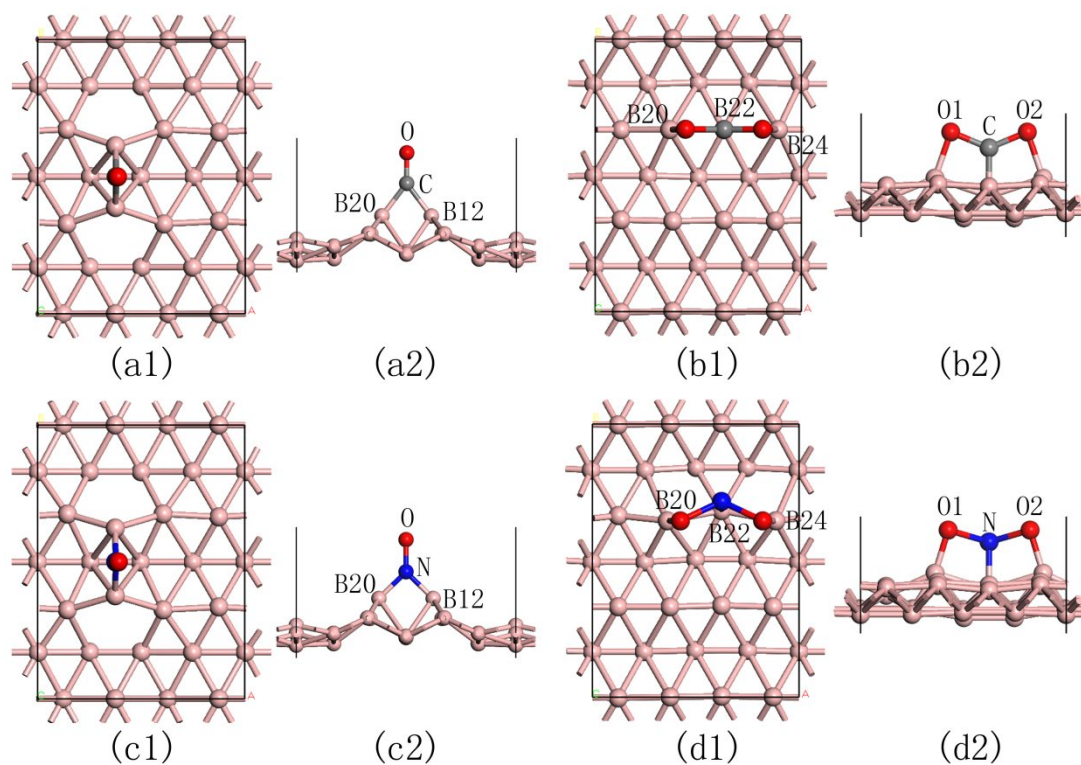


Figure 3. Atomic configurations of borophene-gas molecule.

The calculated data presented that CO, NO, and NO<sub>2</sub> molecule is chemically adsorbed on borophene with a large adsorption energy value compared to CO<sub>2</sub> molecule (−0.240 eV). Therefore, CO, NO, and NO<sub>2</sub> chemisorbed on borophene with stronger adsorption capacity.

### 3.2 Electronic properties of borophene-gas adsorption configurations

On the basis of the Mulliken populations algorithm, the charge population of the borophene-CO and borophene-NO adsorption configuration was computed, and the data are shown in Table 2.

Table 2. The computed charge populations of the most stable borophene-gas configurations.

Atom	Charge population						
	Before adsorption/e			After adsorption/e			
	s	p	Charge	s	p	Charge	
Borophene-CO	C	1.68	1.91	0.42	1.09	2.68	0.23
	O	1.83	4.58	-0.42	1.84	4.55	-0.39
	B12	0.78	2.22	0.0	0.87	2.02	0.11
	B20	0.78	2.22	0.0	0.87	2.02	0.11
Borophene-NO	N	1.79	3.07	0.14	1.45	3.68	-0.13
	O	1.84	4.31	-0.14	1.87	4.43	-0.30
	B12	0.78	2.22	0.0	0.84	1.87	0.28
	B20	0.78	2.22	0.0	0.84	1.87	0.28

The charge population variations of the minimum  $E_{ad}$  borophene-CO adsorption configuration were indicated in the first portion of Table 3, which presented that the C atoms in CO achieved 0.08 e, but the O atom lost 0.03 e. And both the B12 and B20 atoms in borophene lost 0.11 e. When NO molecule absorbed on the VB-site of borophene sheet, the N and O atom in the NO molecule achieved 0.27 and 0.44 e, respectively, but the B12 and B20 atoms lost 0.28 e. These data presented that borophene nanosheet acts as electron donor and gas molecule acts as electron acceptor.

## 4. Conclusions

We calculated the adsorption capacity of CO, CO<sub>2</sub>, NO, and NO<sub>2</sub> molecule on borophene nanosheet based on first-principle study. The  $E_{ad}$  and charge population of the borophene-gas molecule configuration were computed. The interaction mechanism between the gas molecule and the borophene were further analyzed. Through compare these adsorption energies of different adsorbed site, the most stable of adsorption configuration were determined. In order to confirm the interaction mechanism of gas molecule and borophene, the charge population of borophene-gas molecule were computed. The calculated shows that the CO, NO and NO<sub>2</sub> molecule are adsorbed on the borophene nanosheet with chemical adsorption. The further charge population analysis of the borophene-CO and the borophene-NO adsorption system shows that the electrons transfer from borophene nanosheet to CO and NO molecule. It is can be seen that the borophene acts as electron donor and gas molecule acts as electron acceptor. Based on the above the calculation and analysis, we concluded that the borophene materials is an excellent candidates to detect gas molecules.

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