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A first-principles study of gas molecule adsorption on borophene

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Borophene, a new two-dimensional material, was recently synthesized. The unique anisotropic structure and excellent properties of borophene have attracted considerable research interest. This paper presents a first-principles study of the adsorption of gas molecules (CO, CO_2, NH_3, NO, NO_2 and CH_4) on borophene. The adsorption configurations, adsorption energies and electronic properties of the gas molecules absorbed on borophene are determined, and the mechanisms of the interactions between the gas molecules and borophene are evaluated. We find that CO, CO_2, NH_3, NO and NO_2 are chemisorbed on borophene, while CH_4 is physisorbed on borophene. Furthermore, our calculation also indicate that CO and CO_2 are chemisorbed on borophene with moderate adsorption energy and NO, NO_2 and NH_3 are chemisorbed on borophene via strong covalent bonds. Moreover, CO is found as an electron donor, while CO_2 an electron acceptor. The chemisorption of CO and CO_2 on borophene increases the electrical conductivity, so It seems that borophene has the potential to be used in high-sensitivity CO and CO_2 gas sensors. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5005959

I. INTRODUCTION

With the rapid development in modern industrial technology, environmental pollution caused by harmful gases is becoming increasingly serious. Therefore, research on the adsorption and detection of harmful gases has become more and more important. Graphene, a new two-dimensional (2D) material that was first deposited by Novoselov et al.[1] through mechanical exfoliation in 2004, has become one of the most exciting research topics. Because 2D materials exhibit high surface areas, special structural characteristics and excellent performance, they have been widely used in materials adsorption, gas sensors and other fields.[2,3] Schedin et al.[4] experimentally studied the adsorption properties of NO_2, CO, H_2O and NH_3 individual gas molecules on graphene and found that graphene is sufficiently electronically quiet to be used in single-electron detectors operational at room temperature and in ultrasensitive sensors of magnetic field or mechanical strain. Leenaerts et al.[5] used first-principles calculations to study the adsorption of H_2O NH_3 CO and NO on graphene and found that all the gases physisorbed on graphene, and only a weak charge transfer occurs between the small gas molecules and graphene. The adsorption of small gas molecules on MoS_2, another 2D material, has also been extensively studied;[6,7] the interactions between gas molecules and MoS_2 were found to be weak, and the electronic properties of MoS_2 did not change obviously after adsorption. A first-principles study of the adsorption of small gases molecule on the 2D material phosphorene[8,9] revealed that NO is chemisorbed on phosphorene, suggesting that phosphorene has potential applications in the detection of harmful gases. Xia et al.[10] studied the adsorption of gas

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molecules on the 2D material germanene using density functional theory (DFT); they found that CO, CO_2 and H_2O are physisorbed on germanene, while NH_3, NO and NO_2 are chemisorbed on germanene. The chemisorption of NH_3 and NO on germanene has moderate adsorption energy, and few electrons transfer in different directions, making germanene a candidate for NH_3 and NO sensing.

Boron is the fifth element in the periodic table and is adjacent to carbon. Because of their unique electronic properties, boron clusters have attracted the attention of many researchers, the structures and adsorption properties of boron clusters have been studied extensively. The adsorption of CO, N_2, NO and other molecules on the boron cluster B36 was studied by Valadbeigi et al. using DFT.[11] The thermodynamic data show that the B36 cluster is a good adsorbent for CO and NO molecules. Sun et al.[12] used first-principles DFT calculations to study the adsorption of CO_2, CH_4, and other gas molecules on B80 fullerene. They found that CO_2 is chemically adsorbed on B80 fullerene, while the other studied molecules are physically adsorbed. This study also provided insight into the mechanism of CO_2 capture and separation by the electron-deficient B80 fullerene. Previous theoretical calculations showed that boron clusters have potential applications as gas sensors. Thus, theoretical studies on the structures and properties of 2D boron materials have also been carried out.[13–15] Recently, 2D boron sheets (borophene) with rectangular structures were successfully grown on single-crystal Ag (111) substrates by Mannix et al.[16] Borophene shows unique anisotropic metallic properties, mechanical properties, and large specific surface area,[17–21] which are similar to the properties of graphene and other 2D materials formed from single elements. Therefore, there has been a great upsurge in research on the structure and properties of borophene. At present, no studies have been reported on the adsorption of gas molecules on borophene. Borophene and boron clusters are composed of the same elements, and their structural properties are similar to those of graphene and other 2D materials. Therefore, we speculate that borophene may have good adsorption properties for pollutant gas molecules. In this study, we performed first-principles calculations to investigate the adsorption of small gas molecules (CO, CO_2, NO, NO_2, NH_3 and CH_4) on borophene. The results are expected to provide theoretical support for the application of borophene in the adsorption of polluted gases, gas sensors, surface catalysis and so on.

II. COMPUTATIONAL METHOD AND MODELS

First-principles DFT calculations were implemented using the Cambridge Sequential Total Energy Package (CASTEP)[22] in Materials Studio 6.1. The calculations employed periodic boundary conditions and plane-wave expansion of the wave function. The generalized gradient approximation in the scheme of the Perdew–Burke–Ernzerhof function was used for the exchange-correlation potential,[23] and the ultrasoft pseudopotential[24] was used to describe electron–ion interactions. Electronic structure methods, such as DFT, can be used to study the interaction of materials with adsorbed molecules from first principles. An essential detail is the inclusion of dispersion interactions, which are omnipresent in adsorption phenomena. As these interactions are not adequately indicated in standard DFT, various methods have been proposed to incorporate them.[25] Particularly, a posteriori correction using predefined dispersion coefficients, such as the schemes devised by Grimme (often named DFT-D).[26,27] In this work, dispersion-corrected density-functional theory (DFT-D) methods are employed to calculate the interaction energies for small molecules adsorbed on the borophene. The internal coordinates and lattice constants were optimized until the Hellman–Feynman forces acting on each atom were less than 0.01 eV/Å. The energy convergence was chosen as 10^{-6} eV between two steps, and a vacuum of 20 Å was employed along the Z direction of the porous borophene sheet to eliminate interactions between borophene sheets. All calculations were done with an energy cutoff of 500 eV and a $25 \times 25 \times 1$ k-point mesh in the Brillouin zone. The model is shown in Fig. 1. The optimum lattice parameters were $a = 1.617$ Å and $b = 2.871$ Å, in agreement with previous experimental[11] and theoretical results.[28,29] This agreement indicates that the model can guarantee accurate calculations. The initial positions of the gas molecules on borophene as shown in Fig. 1: B1-B2 bridge, B2-B3 bridge, B1-B3 bridge, B top. The small gas molecules were placed parallel and vertical to these four highly symmetrical adsorption sites, and the best adsorption sites were obtained after structural optimization.
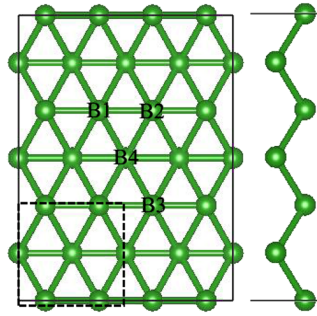
FIG. 1. Top and side views of the optimized structure of borophene. The unit cell of borophene is denoted by black lines.

Adsorption energy[10] is defined as

$$E_{\text{ads}} = E_{\text{borophene/gas}} - (E_{\text{borophene}} + E_{\text{gas}}), \tag{1}$$

where $E_{\text{borophene/gas}}$, $E_{\text{borophene}}$, and E_{gas} are the total energy of the relaxed configuration of the gas and borophene sheets, the total energy of an isolated borophene sheet, and the total energy of the gas molecules in the ground state, respectively.

III. RESULTS AND DISCUSSION

A. Analysis of borophene adsorption

The calculated adsorption energies and atomic distances are shown in Table I, and the optimized structures of CO, CO_2, NO, NO_2, NH_3 and CH_4 adsorbed on borophene are shown in Fig. 2. The main conclusions are as follows. The calculated adsorption energies by DFT-D method were larger than GGA functional conclusions, which are consistent with the conclusions that the GGA PBE functional may underestimate the adsorption energies and the DFT-D methods could give a satisfied description of such van der waals interaction,[30,31] but the overall adsorption way has not changed. There are

TABLE I. Adsorption energy for gases on borophene (E_{ads}), adsorption energy for gases on borophene by DFT-D method (DFT-D E_{ads}/eV) and adsorption energy of gases on graphene (E_{graphene}) along with the distances of the gases above borophene (r) and graphene ($r_{\text{gas-graphene}}$).

gas		r(gas)/Å	$r_{\text{gas-graphene}}$/Å[33,38]	E_{ads}/eV	DFT-D E_{ads}/eV	E_{graphene}/eV[33,38]
CO	a1	1.166(C-O)	1.499(C-B)	3.74	-0.557	-0.761	-0.014
	a2	1.205(C-O)	1.591(C-B)		-0.395	-0.641	
CO_2	b1	1.426(C-O)	1.425(O-B)		-0.707	-0.898	
	b2	1.182(C-O)	3.680(O-B)		-0.110	-0.092	
NH_3	c1	3.418(N-H)	1.414(N-B)/ 1.198(H-B)	3.81	-1.992	-1.963	-0.031
	c2	1.040(N-H)	1.597(N-B)		-1.190	-1.246	
NO_2	d1	1.346(N-O)	1.465(O-B)		-2.594	-2.836	
	d2	1.366(N-O)	1.446(O-B)	3.61	-2.505	-2.756	-0.067
	d3	2.604(N-O)	1.435(O-B)		-2.157	-2.288	
NO	e1	3.061(N-O)	1.415(N-B)/ 1.419(O-B)		-3.803	-4.043	
	e2	1.415(N-O)	1.433(N-B)/ 1.459(O-B)	3.76	-2.157	-2.307	-0.029
	e3	1.368(N-O)	1.463(N-B)/ 1.446(O-B)		-2.233	-2.363	
CH_4		1.097(C-H)	3.461(H-B)		-0.059	-0.156	

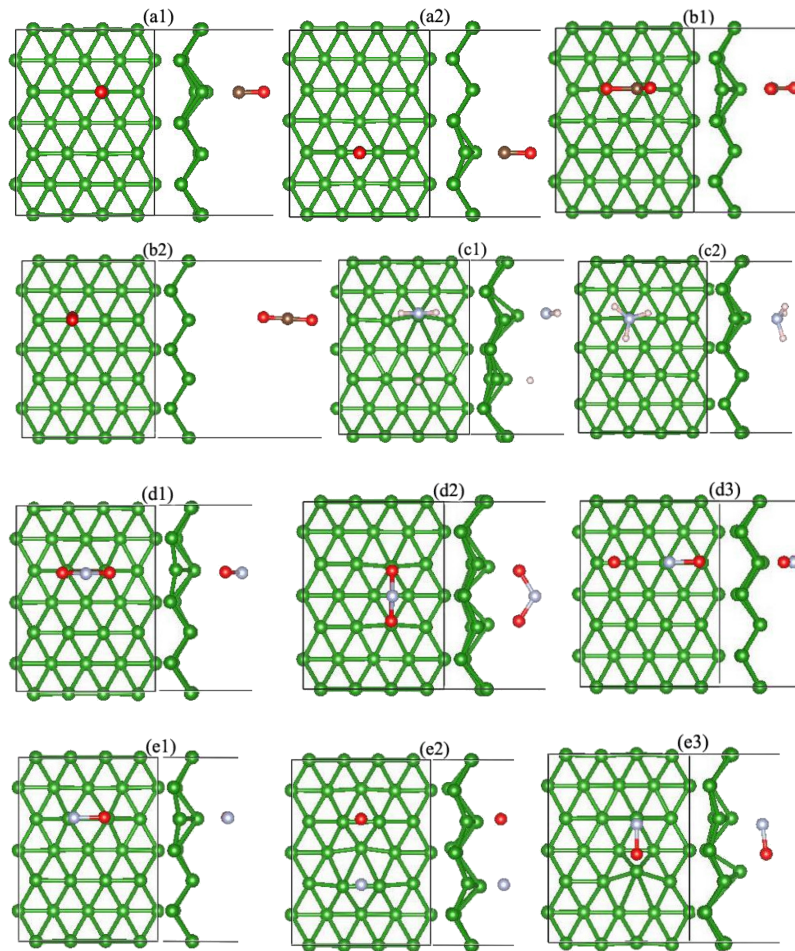FIG. 2. Atomic structures of the most stable configurations for small gas molecules adsorbed on borophene: (a1, a2) CO, (b1, b2) CO_2, (c1, c2) NH_3, (d1, d2, d3) NO_2, and (e1, e2, e3) NO. The green, red, brown, light-purple and light-pink balls denote boron, oxygen, carbon, nitrogen, and hydrogen atoms, respectively.

two stable models of CO adsorption on borophene. In both models, CO adsorbs on the borophene sheets by the vertical. The first adsorption structure is shown in Fig. 2(a1). After adsorption, r_{C-O} is 1.166 Å, which is longer compared to in free CO molecules (r_{C-O} = 1.129 Å).[32] C atom at the below, which is adsorbed on a borophene bulge of the top B atom. The distance between the CO molecules and the borophene sheets is 1.499 Å, larger than the corresponding distance for CO adsorbed on graphene ($r_{CO-graphene}$ = 1.41~1.43 Å).[33] The adsorption energy is −0.761 eV, corresponding to chemical adsorption, which is the most stable type of adsorption. In general, chemisorption is considered when the adsorption energy is greater than 0.2 eV and the distance between two atoms is less than 3.0 Å.[34–36] The second adsorption structure is shown in Fig. 2(a2). The distance between CO and borophene also increases after adsorption in this structure. The C atom is adsorbed onto two adjacent B atoms. The adsorption energy is −0.641 eV, larger than those for the adsorption of CO on germanene (−0.16 eV)[10] and the adsorption of CO on graphene (−0.12 eV).[33] In addition, CO is physisorbed on borophene.

There are two stable adsorption models of CO_2 on borophene. In the first structure [Fig. 2(b1)], which is similar to the structure for CO_2 adsorption on β_{12} borophene,[37] $r_{CO2-borophene}$ is 1.423 Å after adsorption, and CO_2 is parallel adsorption on borophene. The C and O atoms are adsorbed on two B atoms. The distance between CO_2 and borophene is 1.425 Å, similar to the distance between CO_2 and β_{12} borophene but smaller than CO_2 adsorption on negative electricity β_{12} borophene.[37] The adsorption energy is −0.898 eV, which is chemisorbed on borophene with moderate adsorption

energy. In the second adsorption structure [Fig. 2(b2)], CO_2 is physisorbed on borophene. The CO_2 molecule is adsorbed perpendicularly onto borophene, and the distance between CO_2 and borophene is 3.680 Å.

NH_3, NO_2 and NO are chemisorbed on borophene with strong adsorption energy. Two mechanisms of chemical adsorption are observed between NH_3 and borophene. In the first mechanism, NH_3 dissociates into H and NH_2, which are then adsorbed on two B atoms [Fig. 2(c1)]; the corresponding adsorption energy is −1.963 eV. In the second mechanism, NH_3 adsorbs on borophene with $r_{NH3-borophene} = 1.597$ Å [Fig. 2(c2)]. The adsorption energies for NH_3 adsorption on graphene, perforated graphene, B-doped graphene and N-doped graphene are −0.11∼0.50 eV,[38] indicating that NH_3 adsorption on borophene is more stable. In other words, NH_3 is not easily desorbed from borophene. NO_2 and NO are chemisorbed on borophene with strong adsorption energy between −2.288 and −4.043 eV, greater than the energies for NO_2 and NO adsorption on graphene.[5] CH_4 is physisorbed on borophene.

Materials used in gas sensors for gas adsorption and detection have several requirements: high sensitivity so that the material adsorbs to the target gas; good long-term stability to require moderate adsorption energy, which results in easy gas adsorption and desorption and is conducive to recycling. The calculated adsorption characteristics between the gas molecules and borophene reveal that NH_3, NO_2 and NO are chemisorbed on borophene with strong adsorption energy; thus, desorption does not occur easily. Therefore, from the point of view of recycling, borophene is not suitable as a gas sensor for the detection of NH_3, NO_2 and NO. CH_4 is physisorbed on borophene; thus, borophene is not suitable for use as a sensor for detecting CH_4 from a sensitivity point of view. CO and CO_2 molecules are chemisorbed on borophene with more moderate adsorption energies. Therefore, borophene shows potential as a gas sensor for the detection of CO and CO_2. In the following sections, we analyze the electronic structure and properties of the most stable borophene/CO and borophene/CO_2 systems and further discuss their adsorption properties.

B. Electronic properties of the borophene/CO and borophene/CO_2 systems

Bonding strength among atoms can be quantitatively analyzed based on the Mulliken charge population and bond population.[39] The formation of a chemical bond occurs via the redistribution of electron density among atoms such that the entire system achieves the lowest-energy state.[40] The change in the charge population for the most stable borophene/CO adsorption system is shown in Table II, which shows that the C and O atoms lose electrons (0.06 and 0.09 e, respectively), while the B atom gains electrons (0.12 e). Charge transfer occurs mainly in the 2s and 2p orbitals. The CO molecules are electron donors, while borophene is an electron acceptor. The analysis of charge population indicated that the C and O2 atoms (linked to the B atoms) gained electrons (0.46 e and 0.03 e, respectively), while the B atoms lost electrons (0.51 e and 0.06 e). Charge transfer occurs mainly in the 2s and 2p orbitals. The O1 atom (far from the B atoms) loses electrons (0.02 e), and the charge transfer occurs mainly in the 2p orbital. The CO_2 molecules act as electron acceptors, and

TABLE II. Calculated electron populations for the most stable structures of the borophene/CO and borophene/CO_2 systems.

atom		Mulliken 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	2.43	0.48
	O	1.83	4.58	-0.42	1.83	4.50	-0.33
	B	0.78	2.22	0.00	0.73	2.39	-0.12
	B	0.78	2.22	0.00	0.68	2.28	0.04
Borophene/CO_2	C	0.68	2.34	0.98	1.01	2.47	0.52
	O1	1.83	4.66	-0.49	1.83	4.63	-0.47
	O2	1.83	4.66	-0.49	1.82	4.70	-0.52
	B1	0.78	2.22	0.00	0.63	1.86	0.51
	B2	0.78	2.22	0.00	0.76	2.17	0.06

TABLE III. Calculated bond populations for the most stable structures of the borophene/CO and borophene/CO_2 systems.

| | Bond | After adsorption | |
		Population/e	Length/Å
Borophene/CO	C–B	1.07	1.50
	C–O	1.24	1.16
Borophene/CO_2	C–O1	1.12	1.20
	C–O2	0.53	1.42
	C–B2	0.89	1.61
	O2–B1	0.77	1.43

borophene is an electron donor. The bond population analysis of the borophene/CO system indicated bond populations of 1.07 and 1.24 e for C–B and C–O, respectively (Table III). It is shown that C–B, C–O and C–O are all covalent bonds. The covalent nature of the C–O bond is greater than that of the C–B bond, which explains the dissociation of CO. In the borophene/CO_2 structure, the bond populations of C–B2 and O2–B1 are 0.89 and 0.77 e, respectively, indicating that both C–B and O–B are covalent bonds. The bond populations of C–O1 and C–O2 are 1.12 and 0.53 e, respectively. This shows that the two C–O bonds in the CO_2 molecule are covalent, but adsorption weakens the covalent nature of the C–O2 bond.

Density of states (DOS) reflects the number of states for the until energy and is important in analyzing bonding among atoms and material properties. The partial DOS (PDOS) before and after adsorption was analyzed for the most stable borophene/CO model [Fig. 3(a)]. When the CO molecule adsorbs on borophene, the DOS changes significantly; DOS moves to a deep level after adsorption, and the energy is −16.5~10.1 eV, indicating that CO is interacting with the surface (an energy of zero corresponds to the Fermi level). There is no band gap near the Fermi level of borophene before or after adsorption, indicating that borophene displays metal properties. This finding is similar to the conclusion of a previous work,[28,29] which found that "there is no band gap in the borophene." Moreover, C, B and O atoms 2s, 2p orbitals overlap, and apparent resonance after adsorption indicates covalent bonds between C and B and between C and O. After adsorption, the peak DOS value increases obviously, indicating the enhanced conductivity of the borophene/CO system. This finding is consistent with CO adsorption on graphene[33] and with the bond population analysis results in this study. The conclusions of analyzing the borophene/CO_2 system of PDOS [Fig. 3(b)] are similar to the conclusions of analyzing the borophene/CO system of PDOS. When the CO_2 molecule adsorbs on borophene, DOS moves to a deep level after adsorption, indicating that CO_2 is interacting with the surface. Obvious hybridizations between B1-p and O2-s,p orbitals can be found about −22.5 ∼ −20.0 eV and −10.0 ∼ −2.5 eV, which is shown interaction between B1–O2 by a covalent bond. Same as above the B–C and O–C are also forming covalent bonds. The conclusions of PDOS analysis are consistent with the conclusions of the Mulliken charge population and bond population.

The electron localization function (ELF) is a tool for discussing charge transfer. Beck et al.[41] presented a way to calculate the local electron distribution that can be represented by graphs. The electrons near the nuclear area combination bonding area and the lone-pair electrons of a system, and then further analyzes the characteristics and types of chemical bonds analyzed by this method.[42–44] The range of ELF is 0–1. An ELF value of 0.75<ELF<1 (red parts) indicates obvious electron localization and strong covalent bond property. An ELF of 0.5~0.75 indicates a metallic bond, and $0 \leq ELF \leq 0.5$ (blue parts) indicates strong ionic bonding.[45] As shown in Fig. 4(a), the electron density is high between C and B and biased clearly towards the B atom. This shows that the C atom loses charge, while the B atom gains charge; thus, the C and B atoms act as charge donor and acceptor, respectively. Moreover, overlap in electron density clearly exists between C and O and between C and B. C–O and C–B are in the red parts. Therefore, the C–B and C–O bonds are typical covalent bonds. The ELF for the borophene/CO_2 structure [Fig. 4(b)] is similar to those for the borophene/CO structure, which indicate that the O2–B1 and C–B2 are covalent bonds. This conclusion is agreeing with the results of the PDOS and bond population analyses.
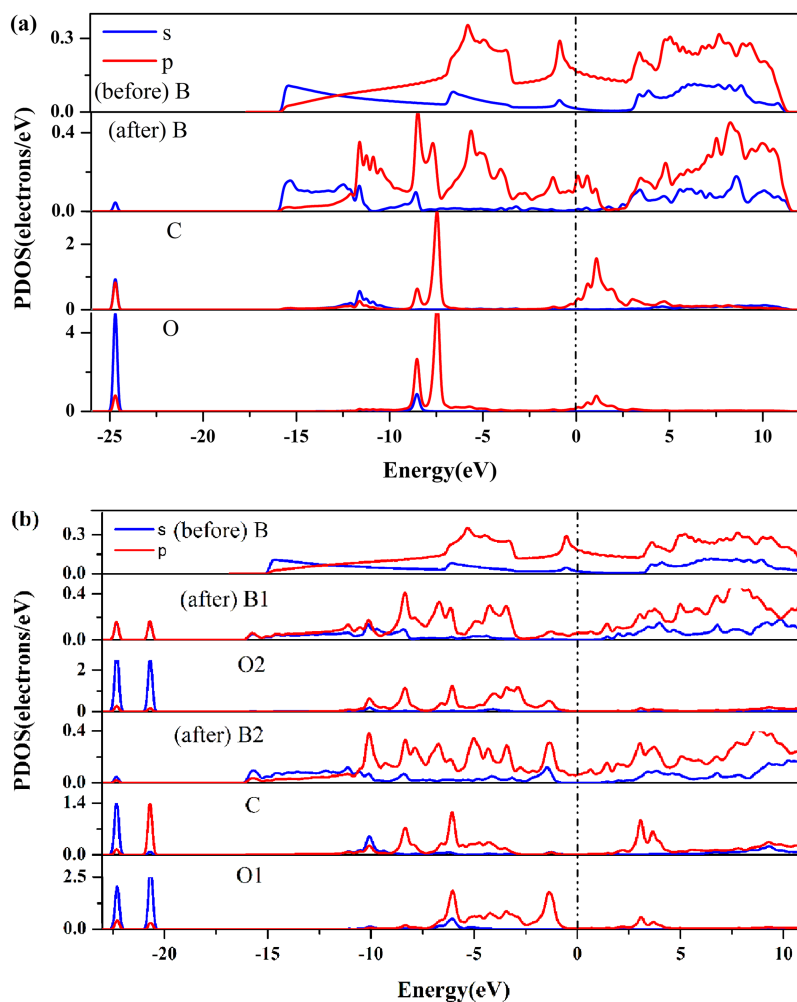
FIG. 3. (a) Partial density of states (PDOS) of the most stable structure of the borophene/CO system. (before) B is DOS before adsorption; (after) B is DOS after adsorption. (b) PDOS of the most stable structure of the borophene/CO_2 system.

Fig. 5 shows the total density of states (TDOS) and indicates that both the borophene and borophene/gas structures are metal systems.[19] The density peak of the borophene/gas structures has increased; thus, the electrical conductivity of borophene/gas has increased. For the borophene/NO and borophene/NO_2 systems, the DOS peak shifts to the right compared with pure borophene, indicating a decrease in the stability of the adsorption system. This suggests that borophene is not suitable as a
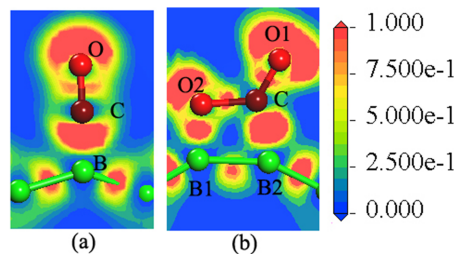

FIG. 4. (a), (b) represent Electron localization function for the most stable structure of the borophene/CO system and borophene/CO_2, respectively. The green, red and brown balls denote boron, oxygen and carbon atoms, respectively.

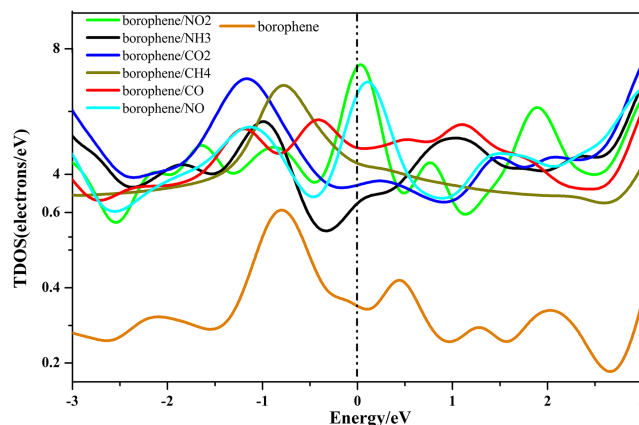FIG. 5. The total density of states (TDOS) for the most stable structures of the borophene/gas systems.

gas sensor for the detection of NO and NO_2. The DOS diagram indicates that CH_4 has little influence on the electrons of borophene.

III. CONCLUSION

In conclusion, we conducted a first-principles study of the adsorption of gas molecules (CO, CO_2, NH_3, NO, NO_2 and CH_4) on borophene. The results show that CO, CO_2, NH_3, NO and NO_2 are chemisorbed on borophene, while CH_4 is physisorbed on borophene. More importantly, our calculations indicate that borophene could be used as a gas sensor for detecting CO and CO_2 molecules. CO and CO_2 are chemisorbed on borophene via covalent bonds with moderate adsorption energies. Gas absorption increases the electrical conductivities of the borophene/CO and borophene/CO_2 structures. CO acts as an electron donor, and borophene as an electron acceptor. In contrast, in the borophene/CO_2 system, CO_2 is an electron acceptor, while borophene is an electron donor. Based on all these finding, it is apparent that 2D borophene can be a potentially important substrate for gas sensor.

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