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First-principle investigation of CO, CH₄ and CO₂ adsorption on Cr-doped graphene-like hexagonal borophene

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Abstract

It is important for life safety and scientific research to design new sensing materials for detecting CO, CH₄ and CO₂ from environment. We theoretically designed a new Cr-doped graphene-like hexagonal borophene (CrB₆) as potential sensor material for these gases. Carrying out first-principles density-functional calculations, we calculated the adsorption energy, band structure, adsorption distance, charge transfer, charge density difference, density of states and partial density of states of CO, CH₄ and CO₂ gas molecules adsorbed on CrB₆ monolayer. The calculated results show that the adsorption behavior of CO is different from those of CH₄ and CO₂. CO adsorbed on CrB₆ monolayer prefers chemisorption while CH₄ and CO₂ adsorbed on CrB₆ monolayer prefers physisorption. As a result, the different adsorption behaviors have significant influence on the band structures and density of states of CrB₆ monolayer. We hope that our results can help experimentalists synthesize better sensor materials based on hexagonal borophene.

Keywords: 2D material; hexagonal borophene; sensor material; gas adsorption; first-principles calculations

1. Introduction

Over the past few years, scholars have shown great interests in the identification and detection of toxic gases by developing sensitive gas sensors^{1, 2}. Among these hazardous gases, the common air pollutants CO and CO₂ are mainly produced in industry and automobile exhaust, which causes a great threat to the natural environment and human security. For example, CO is a colorless, tasteless and difficult to distinguish toxic gas³. Exposure to the low concentration (~35 ppm) of CO would result in headache, dizziness and nausea⁴. However, when the concentration of CO is higher than 150 ppm, CO inhaled by human body will combine with hemoglobin, destroy the ability of blood to transport oxygen, even lead to death⁵. CO₂ and CH₄ are two representative greenhouse gases (GHG). The continuous rise of CO₂ concentration is mainly due to the burning of carbon fuel in industry and the destruction of vegetation caused by deforestation, which is the major contributor of global warming. But in terms of unit molecular number, the greenhouse effect of CH₄ is 25 times greater than CO₂. Therefore, seeking for potential materials as highly effective gas sensors to detect CO, CO₂ and CH₄ is highly demanded.

Since the discovery of graphene, it has attracted the research climax of two-dimensional (2D) materials because of its high surface-to-volume ratio, good conductivity, distinctive surface morphology and low Johnson noise⁶⁻⁹. The high sensitivity and excellent performance of the 2D materials to gas molecules make them promising for gas sensing application^{10, 11}. Therefore, lots of 2D materials have been extensively studied for gas adsorption and detection both in theoretical and experimental aspects, such as Fe-doped graphene, silicene, MoS₂, C₂N and Phosphorene¹²⁻¹⁶. Although the layered 2D materials possess outstanding mobility and sensing performance, some intrinsic drawbacks still exist in 2D materials. For example, the main

shortcoming of graphene is its zero-gap, which makes it difficult to adsorb more gases¹⁷. Besides, silicon shows poor stability and a relatively low mobility was found in MoS₂^{18,19}. All these shortcomings force us to actively look for new 2D materials with good performance as gas sensors.

Due to the distinctive electronic properties of boron, the structure and adsorption characters of 2D boron materials have been widely studied^{20, 21}. Recently, Mannix et al. experimentally proved single layered borophene sheet (BS) can be successfully synthesized on single-crystal Ag (111) substrates under ultra-high vacuum conditions²¹. There are also many theoretical studies which predicted a variety of possible 2D configurations of BS. For example, buckled triangular BS^{22, 23}, α/β -BS²⁴ and graphene-like hexagonal BS (HBS)^{25,26}. Among these BS, HBS is the most promising candidate because it provides superconductivity and can be applied in fabricate Dirac fermion devices²⁷. But the HBS was found to be unstable by Evans et al²⁸, because the π -bonds cannot be formed in HBS due to boron atom with one electron less than carbon atom²⁴. Metal doping is considered to be one of the most effective methods to improve the stability of HBS. Li, Be, Mg, Cr and Mn have been attempted to dope in HBS²⁹⁻³³. These metal atoms can provide electrons to the π -valence orbitals of HBS, and then maintain the stability of HBS.

In this paper, we theoretically designed a 2D Cr-doped graphene-like hexagonal borophene (CrB₆) in which Cr atoms are doped partially on center of boron-ring to make hexagonal borophene stable. And then, using first-principles density-functional calculations, some properties of CO, CH₄ and CO₂ gas molecules absorbed on CrB₆ monolayer, such as adsorption energy, band structure, adsorption distance, charge transfer, charge density difference, density of states and partial density of states, have been studied to explore the possibility of CrB₆ monolayer as gas

sensor material. Our calculated results show that the three gas molecules prefer to be adsorbed on Cr atom. What's different is that the adsorption of CO is relatively strong chemisorption with adsorption energy of 2.59 eV and the adsorptions of CH₄ and CO₂ are relatively weak physisorption with adsorption energy of 0.72 and 0.69 eV, respectively. Considering the reversibility property of gas sensor, the CrB₆ monolayer is more suitable for a promising candidate for CH₄ and CO₂ sensor.

2. Computational details

We used the DMol³ module of Material Studio software³⁴ to perform the density functional theory calculations for the optimized structures and the electronic properties of CrB₆ monolayer. The Perdew-Burke-Ernzerhof (PBE)³⁵ generalized gradient approximation (GGA) which is embedded in DMol³ was chosen. And the double-numerical properties plus polarization (DNP) was selected as basis set. To make the calculated results accurate, the global orbital cutoff radius in real-space was set as 5.2 Å. In the convergence tolerance, the energy, force, and displacement were set as 10⁻⁵ Ha, 0.002 Ha/Å, and 0.005 Å, separately. For the calculation of the optimized structures, the Monkhorst-Pack k-mesh was set to 3×3×1 and for the calculation of energy band and density of states, the k-point was set to 6 × 6 × 1. To prevent the adjacent layers from interacting, a vacuum layer of 20 Å was added in the direction of vertical substrate plane. To accurately evaluate the interactions between gases and CrB₆ monolayer, the Grimme dispersion correction³⁶ was applied in the calculations of the adsorption of CO, CH₄ and CO₂ on CrB₆ monolayer. The adsorption energy is defined as the change of the total energy before and after adsorption, the size of which can be used to determine the stability of the structure after

adsorption. The adsorption energy (E_{ads}) of these gas molecules on CrB₆ monolayer is defined as follows:

$$E_{ads} = E_{total} - E_{monolayer} - E_{gas} \quad (1)$$

where E_{total} is the total energy of the gas molecule adsorbed on CrB₆ monolayer, $E_{monolayer}$ is the energy of isolated CrB₆ monolayer, and E_{gas} is the energy of a single gas molecule. According to our definition, a larger negative E_{ads} represents the more stable adsorption of gas molecule on CrB₆ monolayer.

3. Results and discussions

3.1. Structural and electronic properties of CrB₆ monolayer

The optimized unit cell of CrB₆ is shown in Fig. 1(a). The calculated lattice parameters of CrB₆ unit cell are $a = b = 5.35 \text{ \AA}$, which is slightly shorter than the lattice parameter of FeB₆³⁷. The bond lengths of B-B and Cr-B in Cr doped six membered rings are 1.85 \AA and 1.91 \AA , respectively. The bond length of B-B in B₆ six membered rings is 1.65 \AA . Unlike the completely planar structure of FeB₆ monolayer, the Cr atom is not in the plane of borophene and the distance from the Cr atom to the plane is 0.49 \AA . Besides, the band structure of the CrB₆ is also calculated and shown in Fig. 1(b). It can be seen that the CrB₆ monolayer has a small bandgap of 0.851 eV , which indicates that the CrB₆ exhibits semiconductor characteristic. As a promising gas sensor/capture material, excellent dynamical stability is essential. The structural stability of CrB₆ can be examined by phonon dispersion. As shown in Fig. 1(c), there is no

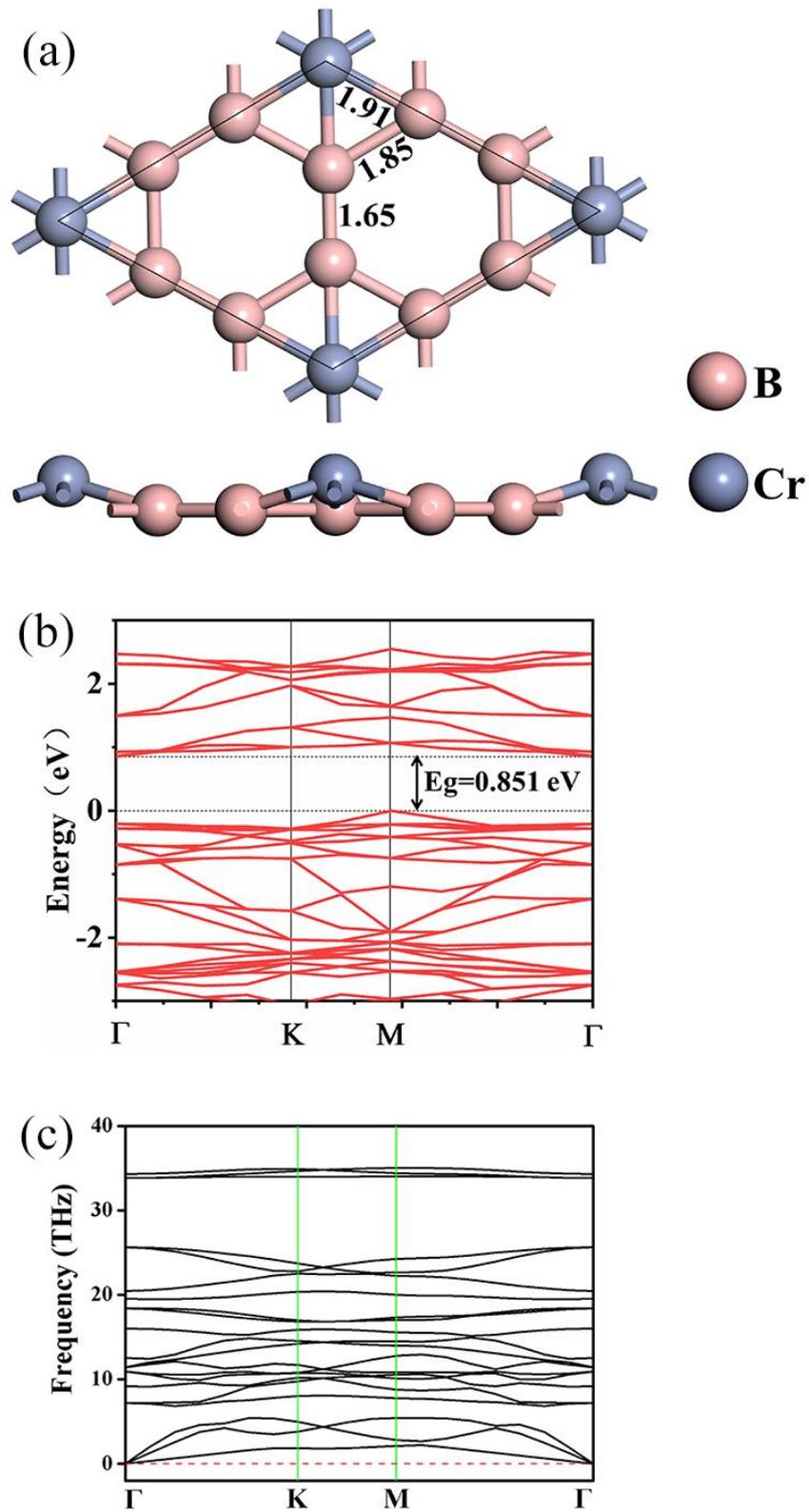


Fig. 1. (a) Top view and side view of the optimized CrB₆ monolayer (bond lengths in angstroms). (b) Band structure and (c) phonon dispersion plot of the CrB₆ structure.

imaginary frequency, which means that the structure of CrB₆ monolayer has a good dynamical stability.

3.2. Adsorption of gas molecule on CrB₆ monolayer

To fully comprehend the feasibility of CrB₆ as a gas sensor material, we researched the adsorption behaviors of CO, CH₄ and CO₂ molecules on the CrB₆ monolayer. Three possible adsorption sites are considered by us, and they are T_{Cr} site (the top site on Cr atom), B site (above the B-B bond bridge) and H site (above the center of boron-ring), respectively, as shown in Fig. 2.

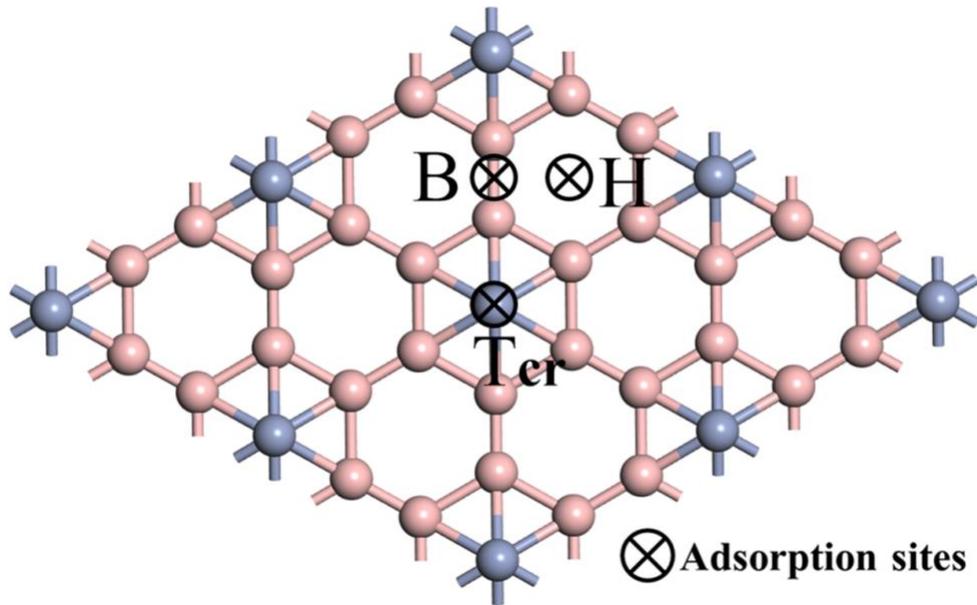


Fig. 2. The three possible adsorption positions of CrB₆ monolayer.

We used a 2×2×1 supercell, consisting of 28 atoms, to calculate the E_{ads} of gas molecules on CrB₆ monolayer. In order to find the most stable adsorption configuration, we placed the gas molecules with different orientation on the three possible adsorption sites in CrB₆ monolayer. For each gas molecule adsorption on CrB₆ monolayer, the optimized structures of the two largest E_{ads} are presented in Fig. 3. And the E_{ads} , charge transfer

(Q) and the distance between the nearest atom of gas molecules and CrB_6 monolayer (d) are listed in Table 1. For CO, it is

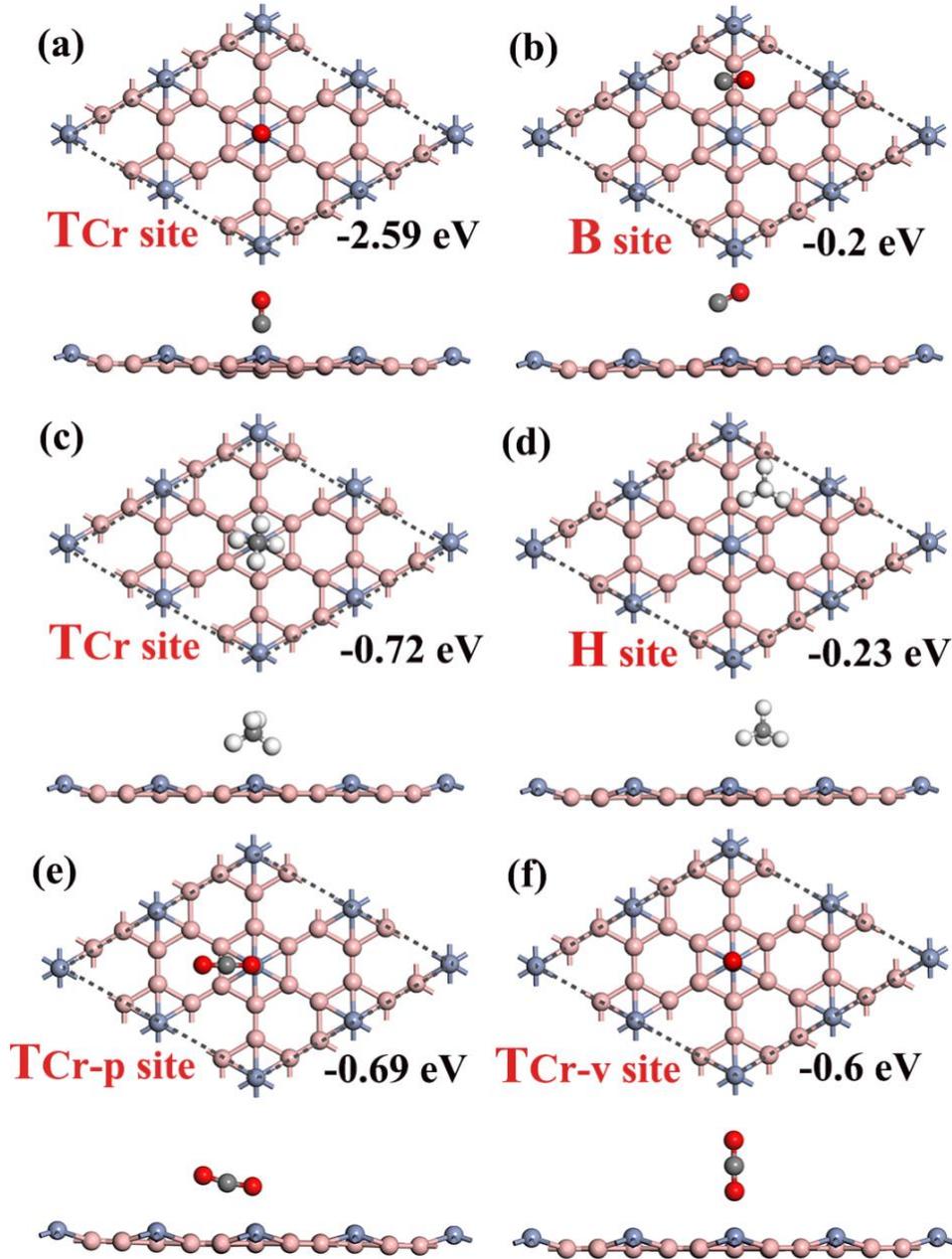


Fig. 3. The top and side views of the two most stable adsorption configuration of (a, b) CO, (c, d) CH₄, (e, f) CO₂.

preferably adsorbed on the T_{Cr} site. The CO is vertical to the CrB_6 monolayer and the distance between C and Cr is 1.87 Å which is shorter than the sum

of radii of C (0.70 Å) and Co (1.35 Å)³⁸. Such short C-Co bond length indicates that the interaction between C and Cr atoms is very strong, leading to the large E_{ads} (-2.59 eV) and Q (-0.03 e). For CH₄, it is also preferly adsorbed on the T_{Cr} site, corresponding to the E_{ads} of -0.72 eV. The C atom is on the top of the Co atom and the nearest distance from H atom to the Co atom is 1.98 Å. And for CO₂, the adsorption sites of the two largest E_{ads} are all on the T_{Cr} site. The difference is the orientation of CO₂. One is vertical to the CrB₆ monolayer, denoted by T_{Cr-V}; the other is almost parallel to the CrB₆ monolayer, denoted by T_{Cr-P}.

Table 1 Adsorption energies (E_{ads}), charge transfer (Q) and the distance between the nearest atom of gas molecules and substrate (d) of the two most stable adsorption configuration of CO, CH₄ and CO₂.

Gas molecule	Adsorption sites	E_{ads} (eV)	Q (e)	d (Å)
CO	T _{Cr}	-2.59	-0.03	1.87
	B	-0.2	0.01	3.72
CH ₄	T _{Cr}	-0.72	0.06	1.98
	H	-0.23	-0.03	3.26
CO ₂	T _{Cr-P}	-0.69	0.10	2.18
	T _{Cr-V}	-0.6	0.14	2.11

For CO and CH₄, the shorter d and larger Q indicate a larger E_{ads} (see Table 1). However, contrary to CO and CH₄, the E_{ads} of CO₂ on T_{Cr-P} is larger than that on T_{Cr-V}, although the value of d (Q) of CO₂ on T_{Cr-P} is longer (less) than that on T_{Cr-V}. The reason may be attributed to the distance (2.67 Å) between C in T_{Cr-P} and Co is shorter than that (3.28 Å) between C in T_{Cr-V} and Co, which increases the interaction between CO₂ on T_{Cr-P} and the CrB₆ monolayer. In fact, according to the evaluation standard proposed by Rouquerol et al, the surface binding energy of gas molecules determines

the type of gas adsorption³⁹. Usually when the $E_{ads} < 1$ eV, physisorption takes place between gas molecules and surface, but the chemisorption occurs when the $E_{ads} > 1$ eV. Therefore, CO₂ and CH₄ belong to physisorption on CrB₆ monolayer. In contrast, CO gas molecule on substrate is chemisorption.

Fig. 4 shows the charge density difference between the gas molecule and CrB₆ monolayer in the most stable adsorption site, which is defined by

$$\Delta\rho = \rho_{total} - \rho_{monolayer} - \rho_{gas} \quad (2)$$

where ρ_{total} , $\rho_{monolayer}$ and ρ_{gas} are the charge density distributions of the gas molecule adsorbed on CrB₆ monolayer, pristine CrB₆ monolayer and an isolated gas molecule, respectively. The charge accumulation is represented by yellow, whereas blue represents the charge depletion region. It can be seen that there are a lot of electron depletion/accumulation between CO and CrB₆ monolayer, which reflects the chemisorption between CO and CrB₆ monolayer. While there are less electron depletion/accumulation between CH₄/CO₂ and CrB₆ monolayer, which is consistent with the physisorption between CH₄/CO₂ and CrB₆ monolayer.

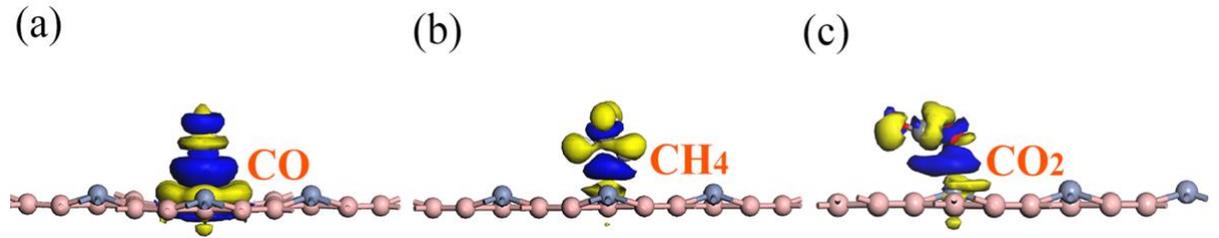


Fig. 4. The side views of charge density difference plot of (a) CO, (b) CH₄ and (c) CO₂ on the most stable adsorption site.

3.3. Band structures

To investigate the adsorption effect of three gas molecules on CrB₆, the band structures of CO, CH₄ and CO₂ adsorbed on the most stable adsorption site are shown in Fig. 5. It can be seen that the band gap of CrB₆

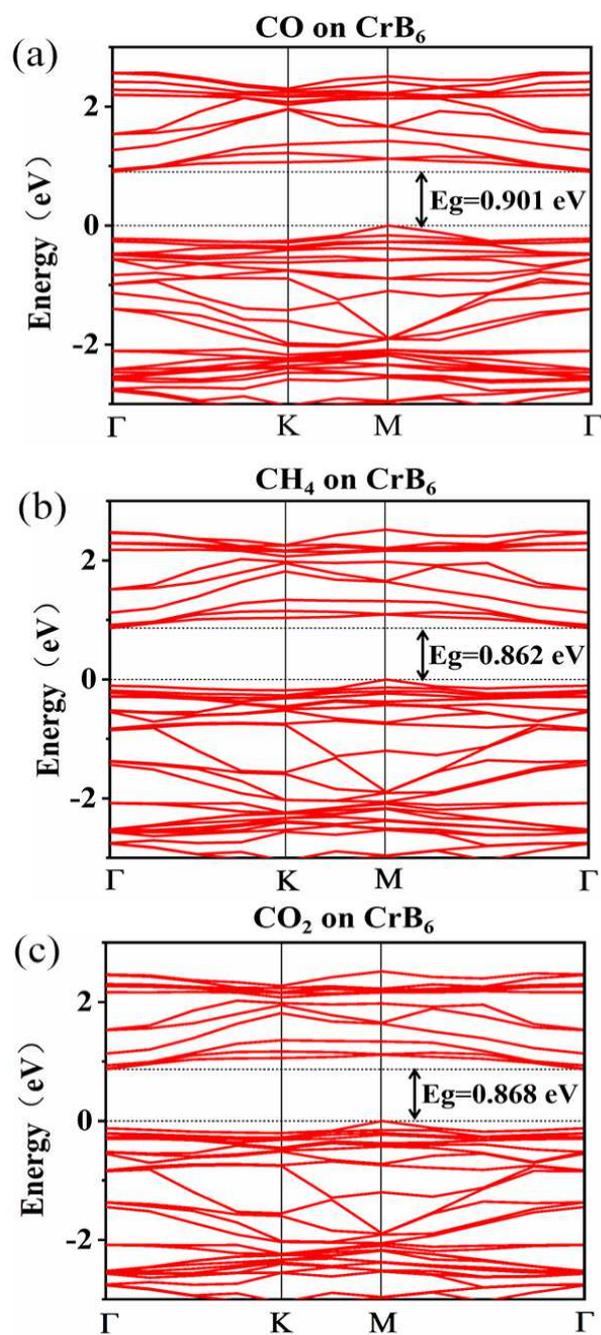


Fig. 5. The band structures of (a) CO, (b) CH₄ and (c) CO₂ adsorbed on the most stable adsorption site.

monolayer will increase when the gas molecules is adsorbed on the surface of CrB₆ monolayer. Compared with the band gap (0.851 eV) of CrB₆ monolayer, the band gap (0.901 eV) of CrB₆ monolayer absorbed by CO increases obviously while the band gap (0.862/0.868 eV) of CrB₆ monolayer absorbed by CH₄/CO₂ increases slightly. These results agree well with the type of gas adsorption on CrB₆ monolayer. Similar conclusions have been reported in previous study¹².

3.4. Density of states and partial density of states

To further explore the effect of adsorbed gas molecules on the electronic structures of CrB₆ monolayer, we analyzed the density of states (DOS) and

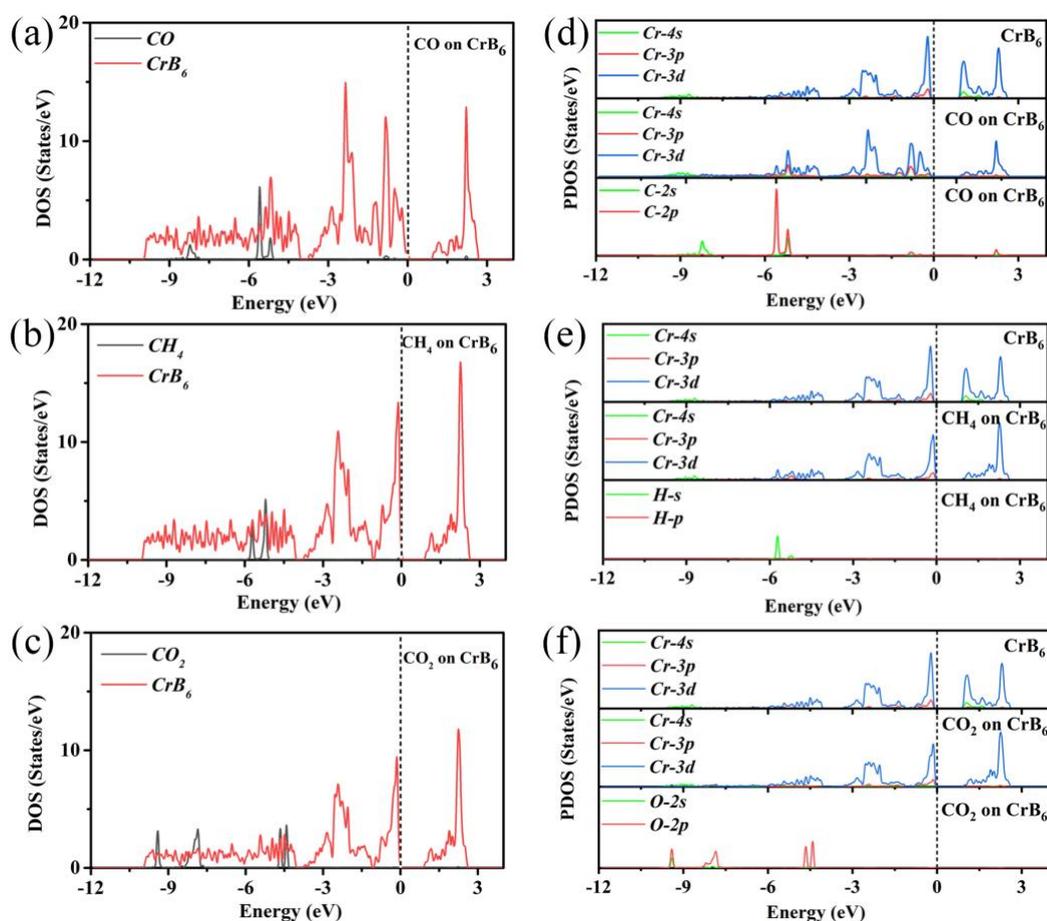


Fig. 6. The DOS and PDOS of (a and d) CO, (b and e) CH₄ and (c and f) CO₂ molecules adsorption on the most stable adsorption site.

partial density of states (PDOS) of the gas molecules adsorbed on the most stable adsorption site, which are shown in Fig. 6. As can be seen from Fig. 6 (a-c), the DOS of CrB₆ monolayer in CH₄ on CrB₆ is same as that in CO₂ on CrB₆ in the range of -3 to 3 eV. While the DOS of CrB₆ monolayer in CO on CrB₆ is obviously different from the former in the range -3 to 0 eV, which indicates the effect of the physisorption on DOS of CrB₆ monolayer is less than the effect of the chemisorption. It is interesting that there are more overlaps between the DOS of the three gas molecules and the DOS of the CrB₆ in the range of -10 to -4 eV in both chemisorption and physisorption.

As can be seen from Fig. 6 (d-f), we found that the main contribution of the DOS of CrB₆ monolayer with the adsorbed gas molecule comes from the *Cr-3d* orbitals through comparing with the corresponding DOS. In Fig. 6 (d), comparing with the PDOS of CrB₆ monolayer with and without CO, we observed that the peaks of *Cr-3d* orbitals near the Fermi level become obviously weak after CO is adsorbed on CrB₆ monolayer, which indicates that the electrons transfer from the *Cr-3d* orbitals in the conduction band of CrB₆ monolayer to the CO molecule due to the formation of C-Cr bond. While in Fig. 6 (e and f), the peaks of *Cr-3d* orbitals near the Fermi level show little change after CH₄/CO₂ is adsorbed on CrB₆ monolayer because of the physisorption for them. However, the changes of *Cr-3d* orbitals in the valence band are almost similar after the three gas molecules were adsorbed on CrB₆ monolayer, which indicates that the *Cr-3d* orbitals in the valence band is not sensitive to the type of gas adsorption. Besides, it can be found that the DOS overlaps between CO/CH₄/CO₂ and CrB₆ monolayer is contributed by the *C-2p*, *H-1s* and *O-2p* orbitals, respectively.

4. Conclusions

In summary, to search new sensor material for detecting CO, CH₄ and CO₂ from environment, we theoretically designed a 2D CrB₆ monolayer in which Cr atoms are doped partially on center of boron-ring to make hexagonal borophene stable. Performing first-principles density-functional calculations, the adsorption energy, band structure, adsorption distance, charge transfer, charge density difference, density of states and partial density of states of CO, CH₄ and CO₂ gas molecules absorbed on CrB₆ monolayer have been investigated to check the possibility of CrB₆ monolayer as gas sensor material. The adsorption energy and adsorption distance reveal that CO prefers to be chemically adsorbed on Cr atom while CH₄ and CO₂ prefer to be physically adsorbed on Cr atom. The analyses of density of states and partial density of states show that the conduction bands of CrB₆ monolayer near the Fermi level are affected obviously by the chemisorption but are affected less by the physisorption. Moreover, these gas molecules can lead to the increasing in band gaps in different extent after they are absorbed on CrB₆ monolayer. Considering the reversibility property of gas sensor, the CrB₆ monolayer is more suitable for a promising candidate for CH₄ and CO₂ sensors and deserves further experimental exploring.

Declarations

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Availability of data and material: Data generated or used during the study is available from the corresponding author by request.

Code availability: N/A.

Author contribution: Chao Wang: **Investigation, Data curation,**

Writing-Original draft. Caihong Gao: **Writing-Reviewing & Editing.**

Jianhua Hou: **Software, Writing-eviewing & Editing. Formal analysis.**

Qian Duan: **Writing- Reviewing and Project administration.**

Reference

1. Haija, M. A.; Ayesh, A. I.; Ahmed, S.; Katsiotis, M. S., Selective hydrogen gas sensor using CuFe₂O₄ nanoparticle based thin film. *Applied Surface Science* **2016**, *369*, 443-447.
2. Yang, S.; Jiang, C.; Wei, S.-h., Gas sensing in 2D materials. *Applied Physics Reviews* **2017**, *4* (2), 021304.
3. Zhou, Q.; Xu, L.; Umar, A.; Chen, W.; Kumar, R., Pt nanoparticles decorated SnO₂ nanoneedles for efficient CO gas sensing applications. *Sensors and Actuators B: Chemical* **2018**, *256*, 656-664.
4. Takeda, H.; Ueda, T.; Kamada, K.; Matsuo, K.; Hyodo, T.; Shimizu, Y., CO-sensing properties of a NASICON-based gas sensor attached with Pt mixed with Bi₂O₃ as a sensing electrode. *Electrochimica Acta* **2015**, *155*, 8-15.
5. Weiyun, Z.; Fam, D. W. H.; Zongyou, Y.; Ting, S.; Tan, H. T.; Weiling, L.; Tok, A. I. Y.; Boey, Y. C. F.; Hua, Z.; Hng, H. H., A carbon monoxide gas sensor using oxygen plasma modified carbon nanotubes. *Nanotechnology (Print)* **2012**, *23*.
6. Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E.; Blake, P.; Katsnelson, M.; Novoselov, K. S., Detection of individual gas molecules adsorbed on graphene. *Nature materials* **2007**, *6* (9), 652-655.
7. Dutta, P.; Horn, P., Low-frequency fluctuations in solids: 1/f noise. *Reviews of Modern physics* **1981**, *53* (3), 497.
8. Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P., Experimental observation of the quantum Hall effect and Berry's phase in graphene. *nature* **2005**, *438* (7065), 201-204.

9. Xia, F.; Perebeinos, V.; Lin, Y.-m.; Wu, Y.; Avouris, P., The origins and limits of metal–graphene junction resistance. *Nature nanotechnology* **2011**, *6* (3), 179-184.
10. Liu, T.; Chen, Y.; Zhang, M.; Yuan, L.; Zhang, C.; Wang, J.; Fan, J., A first-principles study of gas molecule adsorption on borophene. *Aip Advances* **2017**, *7* (12), 125007.
11. Zhang, L.; Zhang, Y.; Camacho, J.; Khodas, M.; Zaliznyak, I., The experimental observation of quantum Hall effect of $l=3$ chiral quasiparticles in trilayer graphene. *Nature Physics* **2011**, *7* (12), 953-957.
12. Zhang, C.-P.; Li, B.; Shao, Z.-G., First-principle investigation of CO and CO₂ adsorption on Fe-doped penta-graphene. *Applied Surface Science* **2019**, *469*, 641-646.
13. Prasongkit, J.; Amorim, R. G.; Chakraborty, S.; Ahuja, R.; Scheicher, R. H.; Amornkitbamrung, V., Highly sensitive and selective gas detection based on silicene. *The Journal of Physical Chemistry C* **2015**, *119* (29), 16934-16940.
14. Shokri, A.; Salami, N., Gas sensor based on MoS₂ monolayer. *Sensors and Actuators B: Chemical* **2016**, *236*, 378-385.
15. Yong, Y.; Cui, H.; Zhou, Q.; Su, X.; Kuang, Y.; Li, X., C₂N monolayer as NH₃ and NO sensors: A DFT study. *Applied Surface Science* **2019**, *487*, 488-495.
16. Kou, L.; Frauenheim, T.; Chen, C., Phosphorene as a superior gas sensor: selective adsorption and distinct I–V response. *The journal of physical chemistry letters* **2014**, *5* (15), 2675-2681.
17. Dai, J.; Yuan, J.; Giannozzi, P., Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study. *Applied Physics Letters* **2009**, *95* (23), 232105.
18. Zhao, J.; Liu, H.; Yu, Z.; Quhe, R.; Zhou, S.; Wang, Y.; Liu, C. C.; Zhong, H.; Han, N.; Lu, J., Rise of silicene: A competitive 2D material. *Progress in Materials Science* **2016**, *83*, 24-151.

19. Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S., Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature nanotechnology* **2012**, *7* (11), 699-712.
20. Zhou, X.-F.; Oganov, A. R.; Wang, Z.; Popov, I. A.; Boldyrev, A. I.; Wang, H.-T., Two-dimensional magnetic boron. *Physical Review B* **2016**, *93* (8), 085406.
21. Mannix, A. J.; Zhou, X.-F.; Kiraly, B.; Wood, J. D.; Alducin, D.; Myers, B. D.; Liu, X.; Fisher, B. L.; Santiago, U.; Guest, J. R., Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science* **2015**, *350* (6267), 1513-1516.
22. Kunstmann, J.; Quandt, A., Broad boron sheets and boron nanotubes: an ab initio study of structural, electronic, and mechanical properties. *Physical Review B* **2006**, *74* (3), 035413.
23. Lau, K. C.; Pandey, R., Stability and electronic properties of atomistically-engineered 2D boron sheets. *The Journal of Physical Chemistry C* **2007**, *111* (7), 2906-2912.
24. Tang, H.; Ismail-Beigi, S., Novel precursors for boron nanotubes: the competition of two-center and three-center bonding in boron sheets. *Physical review letters* **2007**, *99* (11), 115501.
25. Zhang, L.; Yan, Q.; Du, S.; Su, G.; Gao, H.-J., Boron sheet adsorbed on metal surfaces: Structures and electronic properties. *The Journal of Physical Chemistry C* **2012**, *116* (34), 18202-18206.
26. Zhu, L.; Zhao, B.; Zhang, T.; Chen, G.; Yang, S. A., How is honeycomb borophene stabilized on Al (111)? *The Journal of Physical Chemistry C* **2019**, *123* (23), 14858-14864.
27. Liu, C.-C.; Jiang, H.; Yao, Y., Low-energy effective Hamiltonian involving spin-orbit coupling in silicene and two-dimensional germanium and tin. *Physical Review B* **2011**, *84* (19), 195430.

28. Evans, M. H.; Joannopoulos, J.; Pantelides, S. T., Electronic and mechanical properties of planar and tubular boron structures. *Physical Review B* **2005**, *72* (4), 045434.
29. Martínez-Guerra, E.; Ortíz-Chi, F.; Curtarolo, S.; de Coss, R., Pressure effects on the electronic structure and superconducting critical temperature of Li₂B₂. *Journal of Physics: Condensed Matter* **2014**, *26* (11), 115701.
30. John, D.; Nharangatt, B.; Chatanathodi, R., Stabilizing honeycomb borophene by metal decoration: a computational study. *Journal of Materials Chemistry C* **2019**, *7* (37), 11493-11499.
31. Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J., Superconductivity at 39 K in magnesium diboride. *nature* **2001**, *410* (6824), 63-64.
32. Cadeville, M., Propriétés magnétiques des diborures de manganèse et de chrome: MnB₂ et CrB₂. *Journal of Physics and Chemistry of Solids* **1966**, *27* (4), 667-670.
33. Ma, S.; Bao, K.; Tao, Q.; Xu, C.; Feng, X.; Zhu, P.; Cui, T., Investigating robust honeycomb borophenes sandwiching manganese layers in manganese diboride. *Inorganic chemistry* **2016**, *55* (21), 11140-11146.
34. Delley, B., From molecules to solids with the DMol 3 approach. *The Journal of chemical physics* **2000**, *113* (18), 7756-7764.
35. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Physical review letters* **1996**, *77* (18), 3865.
36. Grimme, S., Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of computational chemistry* **2006**, *27* (15), 1787-1799.
37. Wu, Y.; Li, H.; Hou, J., A first-principle study of FeB₆ monolayer as a potential anode material for Li-ion and Na-ion batteries. *Computational Materials Science* **2021**, *190*, 110273.
38. Slater, J. C., Atomic radii in crystals. *The Journal of Chemical Physics* **1964**, *41* (10), 3199-3204.

39. Rouquerol, J.; Rouquerol, F.; Llewellyn, P.; Maurin, G.; Sing, K. S.,
Adsorption by powders and porous solids: principles, methodology and applications.
Academic press: 2013.