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INSIGHTS INTO INTERACTION OF CO_2 WITH N AND B-DOPED GRAPHENES

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Abstract. *Graphene is a promising candidate for CO_2 capture, storage, and sensor. Doping graphene with other elements is an effective way to modify its CO_2 storage ability. The literature has shown that the N and B dopants could change the adsorption strength of CO_2 on the graphene substrate. However, there is no research available to elucidate adsorption sites and physical properties underlying the interaction of CO_2 with the N and B doped systems. Therefore, this paper is devoted to clarifying the current topic using the self-consistent van der Waals density functional theory calculations. The results showed that the N and B dopants increase and decrease the adsorption energy of CO_2 in the most favorable configurations, respectively. The reason is that the N p orbital is more active than the B p orbital in the interaction with the electronic density of states of CO_2.*

Keywords: 2D materials, gas storage, interface, computation, toxic gases.

Classification numbers: 82.45.Jn; 82.47.-a; 68.35.bd; 82.30.-b.

I. INTRODUCTION

Carbon dioxide is a major gas causing global warming. At present, when sustainable energy technologies such as fuel cells are not yet matured, the CO_2 emission becomes more and more serious due to the constant escalation of energy demand from fossil fuels. Therefore, the reduction of the CO_2 concentration by the capture based on the adsorption process has attracted much attention. Different adsorbents such as metal-organic frameworks [1–3], zeolites [4], activated carbons [5], and carbon nanotubes [6] have been studied for CO_2 capture. Especially, graphene and graphene-based materials with two-dimensional structures and large surface area are promising candidates due to their high mechanical stability, thermal, and electrical conductivity. Therefore, they have potential applications in fuel cells, gas sensors, and supercapacitors [7]. Understanding the adsorption of CO_2on the materials also plays a crucial role in the applications.

The CO_2 adsorption on graphene has been studied by both experiment and theory. The graphene was found to have a higher CO_2 capacity at ambient temperature and pressure than other carbon nanostructures and zeolites [8]. The density functional theory (DFT) calculations have found favorable adsorption sites and configurations of CO_2 on graphene and graphene nanoribbon [9, 10]. The modification of graphene by doping with electron-donating and electron-withdrawing elements like N and B is a useful method to alter the interaction of gases with the graphene substrate [11]. Boron and nitrogen-doped graphene have been used for hydrogen storage [12] and adsorption of various gases [13]. The studies showed that the B dopant increases and the N dopant decreases the binding energy of hydrogen and COOH groups, which implies that the doping can vary the surface reactivity of graphene and modifies the storage capacity [12,13]. Kemp et al. found that the N dopant can affect the adsorption capacity of CO_2 more profoundly than other gases [14]. Besides, the effects of three types of nitrogen doping have been clarified by experiments that the reactivity toward the CO_2 adsorption is in the following order: pristine graphene < graphitic N-doped < pyrrolic N-doped < pyridinic N-doped graphene and the N doping in graphene significantly improves the CO_2 adsorption capacity [15]. The thermodynamic study has shown that the graphitic N doping has higher stability than the pyrrolic and pyridinic N dopings, but the adsorption energy of CO_2 on the graphitic N doped graphene is lower than the others [16]. Although the adsorption energy of CO_2 on the N and B-doped graphenes has been calculated [17], the underlying mechanisms have not been clarified yet. Therefore, this paper is devoted to solving the above problem by comparing the adsorption energy and the electronic structure of CO_2 on the N and B-doped graphene with that on the pristine graphene case. We then highlighted the differences in the electronic structure properties of the N and B-doped substrate toward the CO_2 adsorption. The self-consistent van der Waals density functional theory calculations will be used in this work. We only consider the single-site graphitic dopings of N and B by replacing one C atom in the unit cell of graphene, respectively.

II. COMPUTATIONAL DETAILS

We used the vdW-DF version [18–20] of the van der Waals corrected density functional theory, which was implemented in the Vienna ab initio simulation package [21, 22], to optimize the geometry and calculate the total energy. The Perdew-Burke-Ernzerhof functional [23–25] and the projector-augmented-wave method [26, 27] have been employed for treating the exchange-correlation energy and the valence electron-ion interactions, respectively. The plane-wave basis set was expanded at the cutoff energy of 400 eV. The integrations in the Brillouin zone were performed with the *k*-point grid of $5 \times \times 1$ by the Monkhorst-Pack sampling technique [28]. We used the Gaussian smearing with the smearing width of 0.1 eV to aid the convergence speed of the geometric optimization and the total energy calculations. The graphene sheet was modeled by the supercell approach with the unit cell of 4×4 and the vacuum space of 18 Å along the normal direction of the graphene surface. The N and B-doped graphenes denoted by NG and BG were simulated by replacing one C atom in the unit cell of the graphene sheet with the N atom and B atom, respectively. The substrate was fully optimized before loading the CO_2 molecule on it. During the geometry optimization of CO_2, all positions of CO_2 and the substrates were allowed to fully relax until satisfying the upper criterion of 10^{-3} eV/A for the interatomic forces. The chosen cutoff energy, the k-point mesh, and the smearing width ensured the convergence of the adsorption energy. This work focused on the electronic effects of CO_2 adsorption and ignored other factors such as temperature, etc.

The adsorption strength of CO_2 on the pristine graphene, NG, and BG has evaluated via the adsorption energy E_a as follows:

$$E_a = E_{[\text{sub + gas}]} - E_{\text{sub}} - E_{\text{gas}}, \tag{1}$$

where $E_{[\text{sub + gas}]}$, E_{sub}, and E_{gas} are the total energy of the substrate - CO_2 system, the isolated substrate, and the isolated CO_2, respectively.

III. RESULTS AND DISCUSSION

The CO_2 molecule was initially located in various configurations with its C-O bond vertical, parallel, slanted to the plane of the graphene sheet. For each configuration of CO_2, we positioned CO_2 at hollow, top, and C-C bridge sites of the substrate. After performing the geometry optimization, we found the most favorable adsorption structure for each site, which was shown in Figure 1 for the pristine graphene, based on the negative adsorption energy. The stable structure was named by the configurational type with the specific position on the surface of the substrate, i.e., the parallel over the hollow of the benzene ring (PH), the parallel over the C-C bridge (PB), the vertical over the top site (VT), and the vertical over the hollow of the benzene ring (VH). The adsorption energy of CO_2 and the vertical bond distance from the C atom of CO_2 to the surface of the substrate for each structure were listed in Table 1.

Table 1. Adsorption configuration, adsorption energy, and vertical bond length (h) from the C atom of CO_2 to the surface of the pristine substrate.

Configuration	Position	Abbreviation	E_a (meV)	h (A)
Parallel	Hollow	PH	-271.1	2.92
Parallel	**Bridge**	**PB**	**-288.6**	**2.90**
Vertical	Top	VT	-95.4	3.49
Vertical	**Hollow**	**VH**	**-128.9**	**3.49**

We found that CO_2 adsorbs stably at the parallel configurations (Figs. 1a and b), where the C-C bridge offers the most favorable adsorption position site due to the most negative adsorption energy as shown in Table 1. The vertical configurations are less favorable than the parallel ones, and the hollow site is more favorable than the top site. The order of the stability of CO_2 adsorption on the pristine graphene is PB $>$ PH $>$ VH $>$ VT. The parallel-bridge structure more stable than the vertical-hollow one is in good agreement with another theoretical work [9]. The adsorption energy of the most stable structure, -288.6 meV of PB, is a little bit lower than that of 300 meV obtained by Lee *et al.* in Ref. [9]. It must be noted that the graphene sheet of the present work is modeled in the periodic supercell with the inclusion of van der Waals correction, while the work of Lee is the isolated graphene sheet of 32 and 44 C atoms without van der Waals. Two works also used different basis sets and theory levels. The average vertical bond length of 3.2 A was found to be in good agreement with the theory [9].

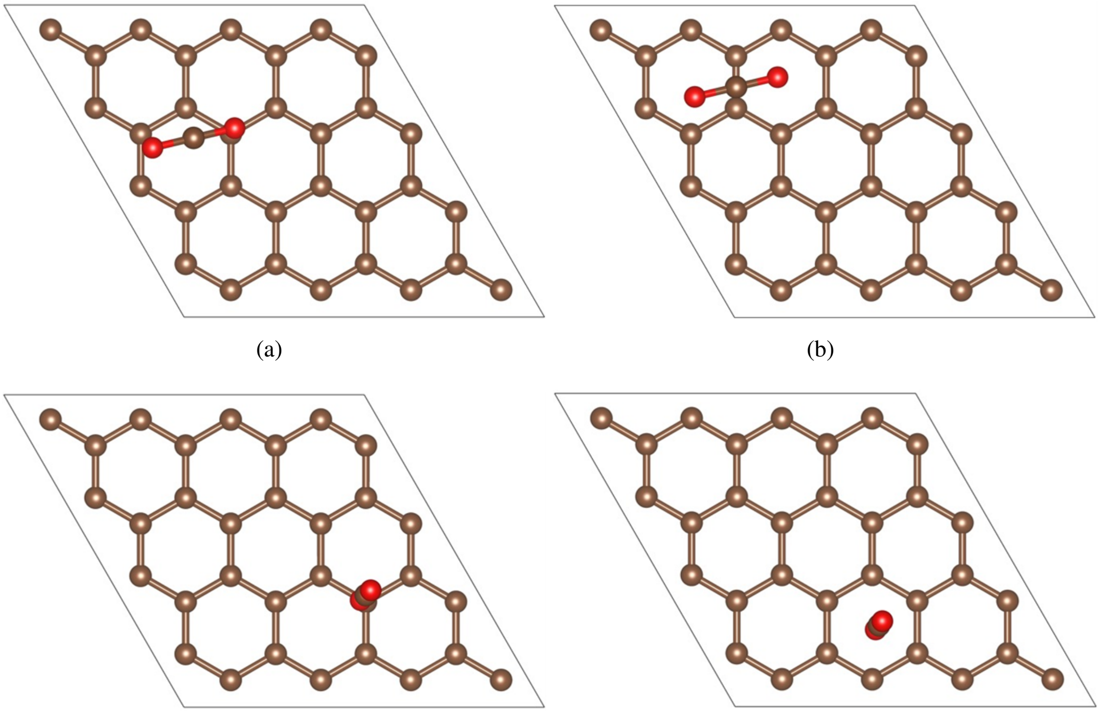
(a) (b) (c) (d)

Fig. 1. (color online) Adsorption configurations of CO_2 on graphene: PH (a), PB (b), VT (c), and VH (d). Color scheme: Brown (C), Red (O).

Figure 2 describes the optimized structure of CO_2 on the doped graphene. The corresponding adsorption energy and the vertical bond length from the C atom of CO_2 to the surface of the doped substrates were listed in Table 2. The more negative the adsorption energy, the more stable the structure of CO_2 should be. We found that the parallel configuration over the C-C bridge (PB1) is more favorable than that over the C-N bridge for the NG substrate (PB2). Contrastingly,

Table 2. (color online) Adsorption configuration, adsorption energy (E_a), and the vertical bond length (h) from the C atom of CO_2 to the surface of the doped substrate.

Configuration	Position	Abbreviation	E_a (meV)/NG	h (A)/NG	E_a(meV)/BG	h (A)/BG
Parallel	C-C Bridge	PB1	**-292.8**	**2.67**	-274.4	2.85
Parallel	C-N (B) Bridge	PB2	-282.3	2.76	**-282.6**	**2.62**
Vertical	C Top	VT1	-78.9	3.44	-84.7	3.41
Vertical	N (B) Top	VT2	**-152.3**	**3.46**	**-101.7**	**3.47**
Vertical	Hollow of benzene ring	VH1	-152.3	3.57	**-161.4**	**3.57**
Vertical	Hollow of benzene ring with doped atom	VH2	**-187.1**	**3.56**	-144.0	3.58

the parallel configuration over the C-B bridge (PB2) is more favorable than that over the C-C bridge (PB1) for the BG substrate. For the vertical on top sites, CO_2 prefers to adsorb on the N and B atoms (VT2) rather than the C atoms (VT1). For the vertical configuration on hollow sites, the favorable trend for NG is in opposite direction with that for BG, i.e., the better one is VH2 and VH1 for the N and B-doped graphene, respectively. Overall, the most favorable adsorption structure of CO_2 on NG and BG was found to be PB1 and PB2, respectively. The adsorption energy of CO_2 is more negative on the N-doped graphene than on B-doped graphene, which is in good agreement with another DFT investigation [17]. The average vertical bond length from the C atom of CO_2 to the surface of both the N and B doped substrate is 3.25 (A), which is a little bit longer than 3.2 (A) for the pristine graphene. Noticeably, we found that the N doping increases and the B doping decreases the magnitude of the adsorption energy, and hence the binding strength of CO_2 relative to the pristine graphene. The effect found here is in opposition to that found for the adsorption of hydrogen and COOH groups in the literature [12,13].

The electronic structure and Bader point charge can elucidate the physical properties underlying the CO_2-substrate interaction. The Bader charge partition technique is based on the minimum charge density surface to separate the atoms in a complex structure. We first calculated the total charge inside the volume made of the minimum charge density surface, we then took the obtained charge subtracts the total charge of the neutral atom to obtain the Bader charge exchange for each atom. The point charge in Table 3 shows that the C atom and O atoms of CO_2 always lose and gain negative charge, respectively. The N atom gains and the B atom loses negative charge, which agrees with then-type andp-type doping nature of these elements [29]. The final result is

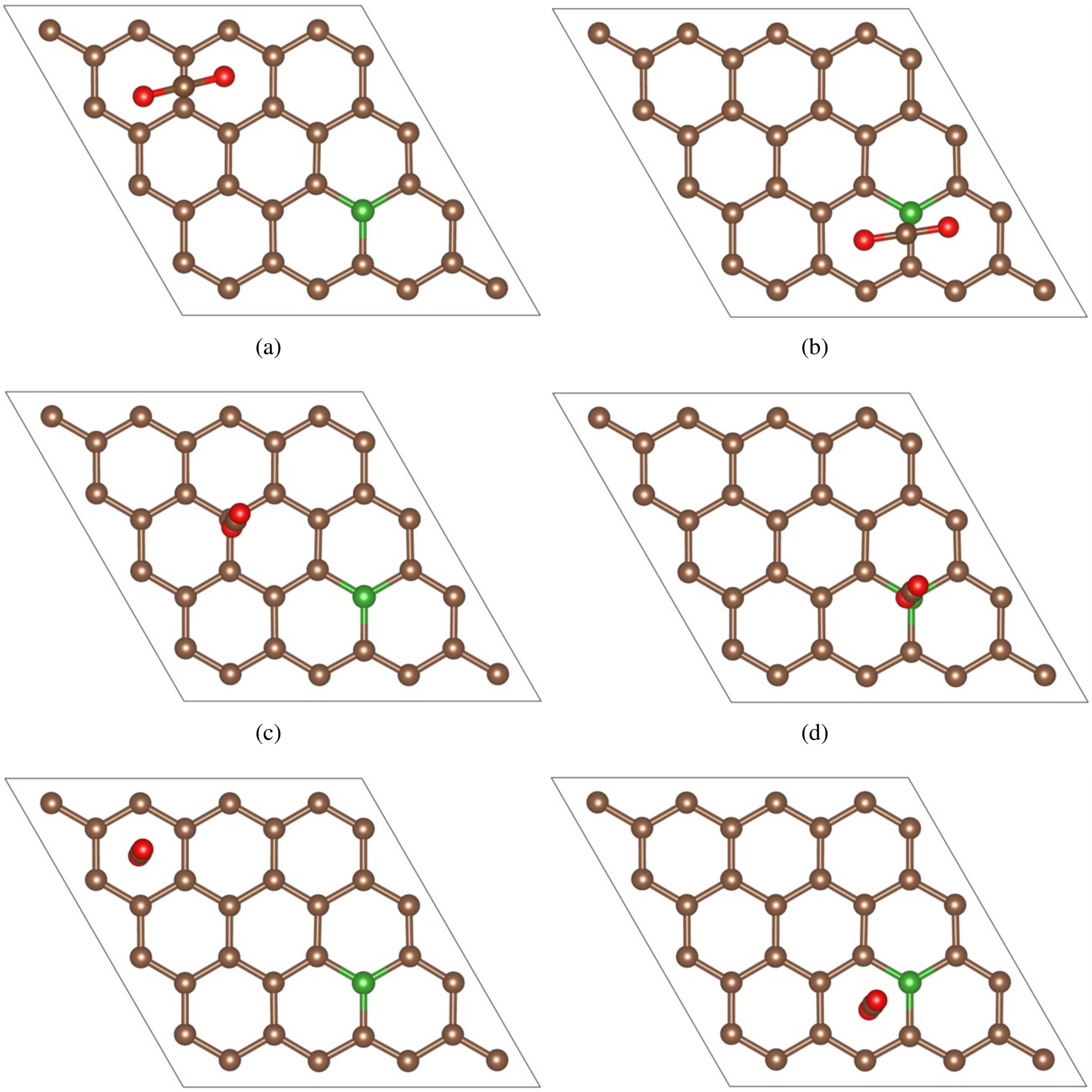
(a)
(b)
(c)
(d)
(e)
(f)

Fig. 2. (color online) Adsorption configurations of CO$_2$ on the doped graphene. Green (B and N), Red (O), and Brown (C). Structure denotation is listed in Table 2: PB1 (a), PB2 (b), VT1 (c), VT2 (d), VH1 (e), and VH2 (f).

that the CO$_2$-substrate interaction was established in such a way that the CO$_2$ molecule gains and the substrates donate negative charge for all cases. However, the charge exchanges are small; therefore, the interaction between CO$_2$ and the graphene systems is physisorption.

Figure 3 shows the electronic density of states (DOS) of the CO$_2$ -substrate systems. The previous publication presented the denotation for the peaks of the DOS of CO$_2$ [30]. In this figure,

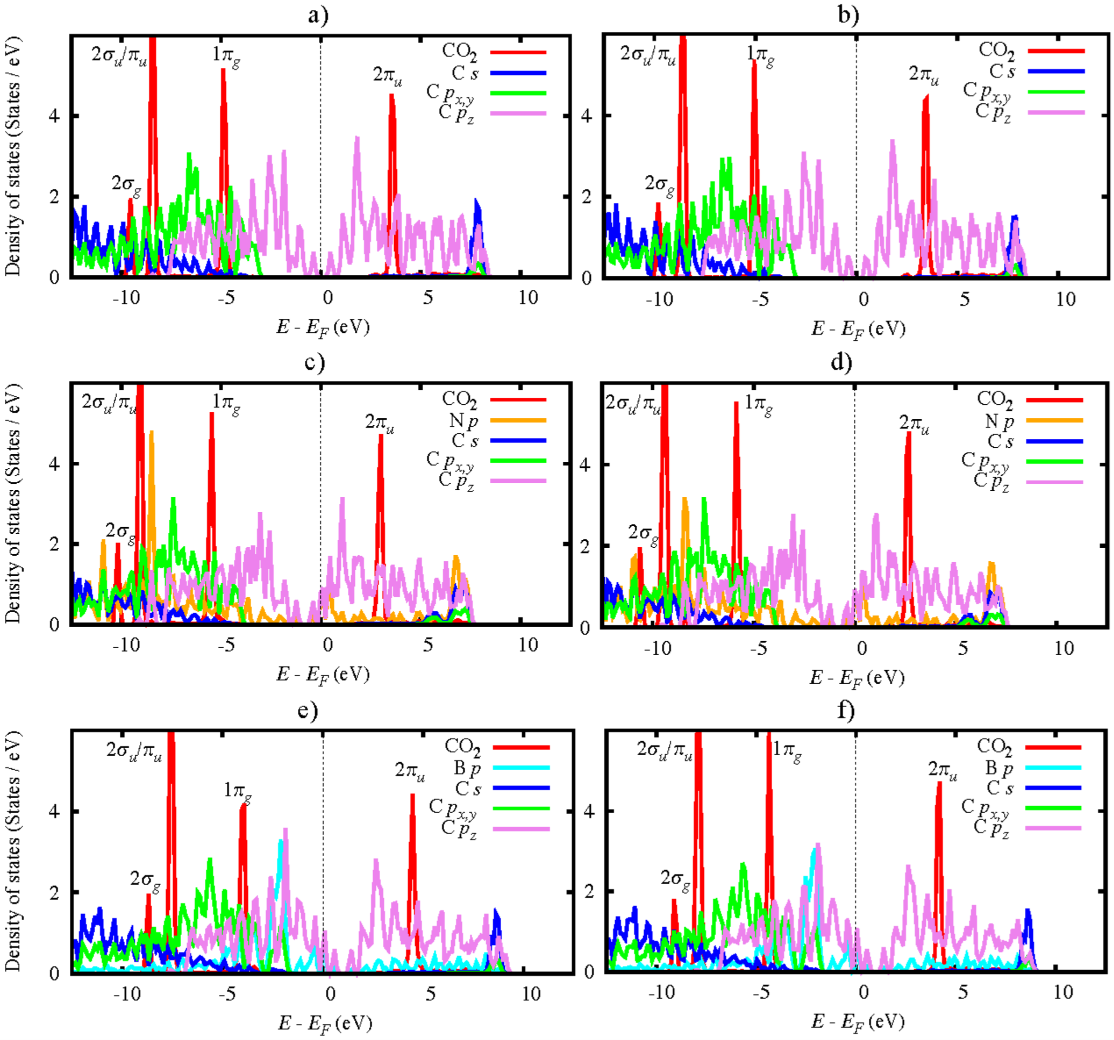

Fig. 3. (color online) The electronic density of states of CO_2 (red color), the p orbital of N and B dopants, the s orbital and the total orbital-projected density of states p_x, p_y, p_z of all the C atoms of the substrates. The structure PB (a) and VH (b) for the pristine graphene, PB1 (c) and VH2 (d) for the N-doped graphene, and PB2 (e) and VH1 (f) for the B-doped graphene. The p_x and p_y orbitals of the graphene are identical. The s orbital of N and B dopants is insignificant; therefore, it was not presented.

we separately described the s orbital and the total p_x,p_y ,p_z states of all the C atoms of the substrates with the p orbital of N and B dopants. Both the parallel (PB) and vertical (VH) configurations show a similar DOS structure and there is only a small shift in the absolute position of the p and s orbital of the substrates relative to the peaks' position of CO_2. The same property also holds for the systems of CO_2 on the N and B-doped graphene. The DOS overlapping between CO_2 and the substrate implies the interaction between two components leading to the Bader charge exchange as the above analysis. For CO_2 on the pristine graphene, the $2\pi_u$ state of CO_2 overlaps with the p_z orbital, the $1\pi_g$ state of CO_2 has the peak resonance with the p_x, p_y, and p_z orbitals, and the $2\sigma_g$ and $2\sigma_u/\pi_u$ states interact with the p_x, p_y, s orbitals of the graphene substrate. For CO_2 on the doped graphene, besides the peak resonance characteristics similar to the pristine graphene, the p orbital of N has interaction with all DOS peaks of CO_2 except for the unoccupied $2\pi_u$ state, while the B p orbital mainly overlaps with the $1\pi_g$ orbital of CO_2 . This result implies that the N doping could offer more active states than the B doping participating in the CO_2-substrate interaction.

Table 3. Bader charge (e^-) for the most stable structure of CO_2 on the pristine, N, and B doped graphene. The error in the point charge is 0.005 e^-.

Species/Structure	**PB**	VH	**N-doped PB1**	N-doped VH2	**B-doped PB2**	B-doped VH1
2O	4.014	4.012	4.020	4.007	4.028	4.010
C	-4.000	-4.000	-4.000	-4.000	-4.000	-4.000
CO_2	**0.014**	**0.012**	**0.020**	**0.007**	**0.028**	**0.010**
N, B	*	*	2.613	2.614	-3.000	-3.000
All C atoms in the unit cell of the substrate	-0.014	-0.012	-2.633	-2.621	2.972	2.990
Substrate	**-0.014**	**-0.012**	**-0.020**	**-0.007**	**-0.028**	**-0.010**

$*$The structures PB and VH belong to the pristine graphene. Therefore, they do not contain doping atoms.

IV. CONCLUSION

This paper used the van der Waals dispersion-corrected density functional theory calculations to elucidate the effects of the N and B doping in the graphene on the adsorption of CO_2. We found that the N doping increases and the B doping decreases the adsorption strength of CO_2 in the most favorable configuration compared to the pristine graphene. CO_2 adsorbs most favorably with the parallel configuration over the C-C and C-B bridge for the N and B doping, respectively. The second and third favorable configurations of CO_2 accordingly are the vertical one on the hollow of the benzene ring and the top of the doped atoms. The density of states showed that the N p orbital has the interaction with three states, i.e., $2\sigma_g$, $2\sigma_u/\pi_u$, and $1\pi_g$, and the B p orbital has the resonance with only one state, $1\pi_g$, of the CO_2 molecule.

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REFERENCES

[1] T. T. T. Huong, P. N. Thanh, N. T. X. Huynh and D. N. Son, *Metal organic frameworks: state-of-the-art material for gas capture and storage*, *VNU J. Sci.: Math. - Phys.* **32** (2016) 67.

[2] C. Pettinari and A. Tombesi, *Metalorganic frameworks for carbon dioxide capture*, *MRS Energy Sustain.* **7** (2020) 35.

[3] K. Sumida, D. L. Rogow, J. A. Manson, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Carbon dioxide capture in metalorganic frameworks*, *Chem. Rev.* **112** (2012) 724.

[4] S. Kumar, R. Srivastava and J. Koh, *Utilization of zeolites as CO_2 capturing agents: Advances and future perspectives*, *J. CO2 Util.* **41** (2020) 101251.

[5] S. Avevedo, L. Giraldo and J. C Moreno-Pirajan, *Adsorption of CO_2 on activated carbons prepared by chemical activation with cupric nitrate*, *ACS Omega* **5** (2020) 10423.

[6] J. M. Ngoy, N. Wagner, L. Riboldi and O. Bolland, *A CO_2 capture technology using multi-walled carbon nanotubes with polyaspartamide surfactant*, *Energy Procedia* **63** (2014) 2230.

[7] B. Szczniak, J. Choma and M. Jaroniec, *Gas adsorption properties of graphene-based materials*, *Adv. Colloid Interface Sci.* **243** (2017) 46.

[8] A. K. Mishra and S. Ramaprabhu, *Carbon dioxide adsorption in graphene sheets*, *AIP Advances* **1** (2011) 032152.

[9] K. J. Lee and S. J. Kim, *Theoretical investigation of CO_2 adsorption on graphene*, *Bull. Korean Chem. Soc.* **34** (2013) 3022.

[10] N. T. Cuong and N. M. Tien, *First-principles studies of CO_2 and NH_3 gas molecules adsorbed on graphene nanoribbons*, *VNU J. Sci.: Math. - Phys.* **32** (2016) 15.

[11] S. Agnoli and M. Favaro, *Doping graphene with boron: a review of synthesis methods, physicochemical characterization, and emerging applications*, *J. Mater. Chem. A* **4** (2016) 5002.

[12] Y. G. Zhou, X. T. Zu, F. Gao, J. L. Nie and H. Y. Xiao, *Adsorption of hydrogen on boron-doped graphene: A first-principles prediction*, *J. Appl. Phys.* **105** (2009) 014309.

[13] N. A. Aqtash and I. Vasiliev, *Ab initio study of boron- and nitrogen-doped graphene and carbon nanotubes functionalized with carboxyl groups*, *J. Phys. Chem. C* **115** (2011) 18500.

[14] K. C. Kemp, V. Chandra, M. Saleh and K. S. Kim, *Reversible CO_2 adsorption by an activated nitrogen doped graphene/polyaniline material*, *Nanotechnology* **24** (2013) 235703.

[15] P. Tamilarasan and S. Ramaprabhu, *Sub-ambient carbon dioxide adsorption properties of nitrogen doped graphene*, *J. Appl. Phys.* **117** (2015) 144301.

[16] M. R. Fiorentin, R. Gaspari, M. Quaglio, G. Massaglia and G. Saracco, *Nitrogen doping and CO_2 adsorption on graphene: A thermodynamical study*, *Phys. Rev. B* **97** (2018) 155428.

[17] J. Dai, J. Yuan and P. Giannozzi, *Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study*, *Appl. Phys. Lett.* **95** (2009) 232105.

[18] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth and B. I. Lundqvist, *Van der Waals density functional for general geometries*, *Phys. Rev. Lett.* **92** (2004) 246401.

[19] T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard and D. C. Langreth, *Van der Waals density functional: Self-consistent potential and the nature of the van der Waals bond*, *Phys. Rev. B* **76** (2007) 125112.

[20] D. C. Langreth,B. I. Lundqvist,S. D. Chakarova-Kck,V. R. Cooper,M. Dion,P. Hyldgaard,A. Kelkkanen,J. Kleis,L. Kong,S. Li,P. G. Moses,E. Murray,A. Puzder,H. Rydberg,E. SchrderandT. Thonhauser, *A density functional for sparse matter*, *J. Phys.: Condens. Matter.* **21** (2009) 084203.

[21] G. Kresse and J. Furthmller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*, *Phys. Rev. B* **54** (1996) 11169.

[22] G. Kresse and J. Furthmuller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*, *Comput. Mater. Sci.* **6** (1996) 15.

[23] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation*, *Phys. Rev, B* **46** (1992) 6671.

[24] J. P. Perdew, K. Burke and M. Ernzerhof, *Generalized gradient approximation made simple*, *Phys. Rev. Lett.* **77** (1996) 3865.

[25] J. P. Perdew, K. Burke and M. Ernzerhof, *Generalized gradient approximation made Simple [Phys. Rev. Lett.* ***77*** *(1996) 3865]*, *Phys. Rev. Lett.* **78** (1997) 1396.
[26] P. E. Blochl, *Projector augmented-wave method*, *Phys. Rev. B* **50** (1994) 17953.
[27] G. Kresse and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*, *Phys. Rev. B* **59** (1999) 1758.
[28] H. J. Monkhorst and J. D. Pack, *Special points for Brillouin-zone integrations*, *Phys. Rev. B* **13** (1976) 5188.
[29] T. T. Pham, T. N. Pham, V. Chihaia, Q. A. Vu, T. T. Trinh, T. T. Pham, L. V. Thang and D. N. Son, *How do the doping concentrations of N and B in graphene modify the water adsorption?*, *RSC Adv.* **11** (2021) 19560.
[30] D. N. Son, T. T. T. Huong and V. Chihaia, *Simultaneous adsorption of* SO_2 *and* CO_2 *in an Ni(bdc)(ted)*$_{0.5}$ *metalorganic framework*, *RSC Adv.* **8** (2018) 38648.