

First-principles study of sulfur dioxide sensor based on phosphorenes

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Abstract—The adsorption behaviors of sulfur dioxide (SO₂) gas molecule over pristine, boron-, silicon-, sulfur-, and nitrogen-doped phosphorenes are theoretically studied using first-principles approach based on density-functional theory (DFT). The adsorption energy (E_a), adsorption distance (d) and Mulliken charge (Q) of SO₂ molecules adsorbed on the different phosphorenes are calculated. The simulation results demonstrate that pristine phosphorene is sensitive to SO₂ gas molecule with a moderate adsorption energy and an excellent charge transfer, while evidence of negative effect is observed during doping with S and N. We also observe that B- or Si-doped phosphorene exhibits extremely high reactivity towards SO₂ with a stronger adsorption energy, indicating that they are not suitable for use as SO₂ sensors, but have potential applications in the development of metal-free catalysts for SO₂. Therefore, we suggest that pristine phosphorene could be an excellent candidate as sensor for the polluting gas SO₂.

Index Terms—Density-functional theory, phosphorene, sulfur dioxide, gas sensors.

I. INTRODUCTION

SENSING gas molecules, especially toxic gases, is critical in environmental pollution monitoring and agricultural and medical applications [1]. SO₂ is one of the main atmospheric pollutants. In many industrial processes, coal and oil burning will generate a large volume of SO₂. It is a colorless, corrosive and strong excitant odor which is easily oxidized in air. When dissolved in water, it forms sulfuric acid which has a strong stimulation and corrosion to human skin, mucous membrane of eyes and nose, and other organizations. Much efforts have been devoted to the development of SO₂ sensors as

The research is co-supported by National Natural Science Foundation of China under Grant Nos. 51303033 and 61434001, the Guangxi Natural Science Foundation under Grant No. 2011GXNSFD018027, the Guangxi's Key Laboratory Foundation of Manufacturing Systems and Advanced Manufacturing Technology under Grant No. 15-140-30-002Z, the Guilin Science and Technology Development Foundation under Grant No. 20140103-3, and the Guangxi Universities' Scientific Foundation under Grant No. YB2014116.

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a safety precaution device [2, 3]. However, most of the commercially available SO₂ sensors based usually on metal oxides show either low sensing response or high operating temperature [4, 5]. Therefore, it is in great need of gas sensors for SO₂ detection. Recently, a new category of layered direct-bandgap semiconductor, phosphorene, with high-mobility transport anisotropy and linear dichroism, has been theoretically discovered [6] and successfully fabricated by micromechanical exfoliation methods [7-9]. It has been theoretically reported that phosphorene is sensitive to the toxic gases, such as NO and NO₂ [7]. Nevertheless, we note that no prior works have been conducted on phosphorene-based SO₂ sensors and much work is needed. Some studies have reported that sensitivity of graphene sensor can be further improved through the introduction of the dopants in graphene [10], [11]. Motivated by these studies, we take great interest in developing phosphorene and dopants decorated-phosphorenes as SO₂ sensors. We are aware of no *ab initio* calculations of the properties of SO₂ adsorbed on different phosphorenes.

II. THEORY AND SIMULATIONS

All the calculations were carried out in DMol³ code based on DFT [12]. Many previous works [13] have proven that generalized gradient approximation (GGA) tend to neglect of van der Waals interaction. In contrast, local-density approximation (LDA) appeared to be more appropriate to study weakly interacting systems [14, 15]. Therefore, LDA was employed in our work. The system consisting of a 3×3 supercell of phosphorene monolayer with the lattice constant of $a = 13.50 \text{ \AA}$ and $b = 9.96 \text{ \AA}$ was used, in good agreement with previous report [16]. A vacuum space of 20 Å is placed to avoid interaction between the adjacent layers in the direction perpendicular to the infinite plane of phosphorene. The Brillouin zone was sampled using a 20×20×1 Monkhorst-Pack \mathbf{k} -point grid for both geometry optimization and electronic properties calculations. All of the atomic positions were optimized until the maximum force was less than 0.001 a.u.

Understanding the sensing properties of materials depends on understanding the interactions between sensing material and targeted analyte [17]. In order to characterize the substrate-SO₂ interaction, the adsorption energy (E_a) is defined as Eq. (1):

$$E_a = E_{\text{sub} + \text{so}_2} - E_{\text{sub}} - E_{\text{so}_2} \quad (1)$$

where $E_{\text{sub} + \text{so}_2}$, E_{sub} and E_{so_2} are the total energies of substrate-SO₂ adsorption adducts, isolated substrate and SO₂ molecule, respectively.

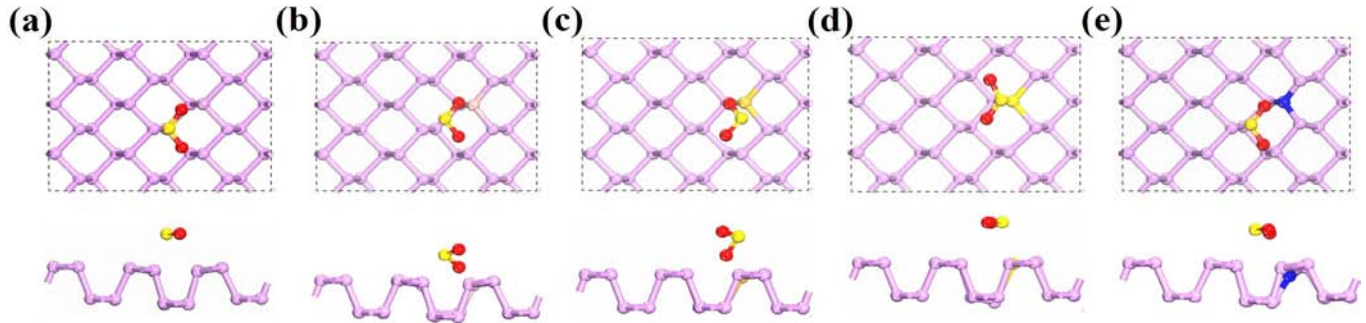


Fig. 1. The most favorable configurations for SO_2 adsorbed on pristine (a) and the B (b), Si (c), S (d), N (e) doped phosphorene. The purple, red, yellow, deep yellow, dark blue balls represent P, O, S, Si and N atoms, respectively.

III. RESULTS AND DISCUSSION

In order to understand the sensing mechanism, it is necessary to investigate the phosphorene- SO_2 interactions. This investigation is started by comparing the SO_2 adsorption capability of B-, Si-, S-, and N-doped phosphorenes. The most stable configurations of SO_2 molecule adsorbed on different phosphorenes are presented in Fig. 1. It is evident that the positions and the orientations of SO_2 are variant depending on the dopant types. Towards a better understanding of the adsorption of SO_2 on these different phosphorenes, the adsorption energy (E_a), adsorption distance (d), and the Mulliken charges (Q) are calculated and listed in Table 1. The adsorption distance d is defined as the shortest distance between the impurity atom (for doped phosphorene) or the phosphorus atom (for the pure phosphorene) and the atom of SO_2 molecule. A positive value of Q means the charges transfer from phosphorene to SO_2 molecule. The high E_a of -0.748 eV is calculated in the SO_2 on pristine phosphorene associated with the d of 2.591 Å, which is much larger than the sum of the covalent radii of the P and O atom (1.74 Å) or P and S atom (2.14 Å), indicating a physisorption nature. Besides, the Q between SO_2 and pristine phosphorene is 0.192 e , which will benefit for sensor detection. When SO_2 adsorbed on B- and Si-doped phosphorenes, the d are found to be 1.476 Å and 1.674 Å, respectively, which are within the limit of the sum of the covalent atomic radii of B-O (1.48 Å) and Si-O (1.79 Å) [18]. In other words, the adsorption of SO_2 on B (or Si) doped phosphorene is chemisorption with a much stronger E_a of -1.820 eV (or -1.554 eV). Although the B and Si doped phosphorenes are not suitable for using as SO_2 sensors, they still have great potential in the application of metal-free catalysts for SO_2 degradation in environmental protection and the industrial waste gas recovery process. N-doped phosphorene exhibits a similar E_a , Q , and d upon adsorption of SO_2 in comparison to the case of pristine phosphorene because the N and P elements belong to the same family in the periodic table. Contrasting to other impurity-doped phosphorenes, the smallest E_a (-0.477 eV) and Q (0.122 e) together with the largest d (2.778 Å) are observed in S-doped phosphorene. Therefore, we come into the conclusion that there will be a repulsive effect between the substrate and the SO_2 molecule when the phosphorene is doped with S atom.

TABLE I
ADSORPTION ENERGY, PHOSPHORENE- SO_2 DISTANCE, AND MULLIKEN CHARGE OF SO_2 ON DIFFERENT PHOSPHORENES

Model	E_a (eV)	d (Å)	Q (e)
Pristine	-0.748	2.591	0.192
B-doped	-1.823	1.476	0.147
Si-doped	-1.554	1.674	0.402
S-doped	-0.477	2.778	0.122
N-doped	-0.673	2.653	0.196

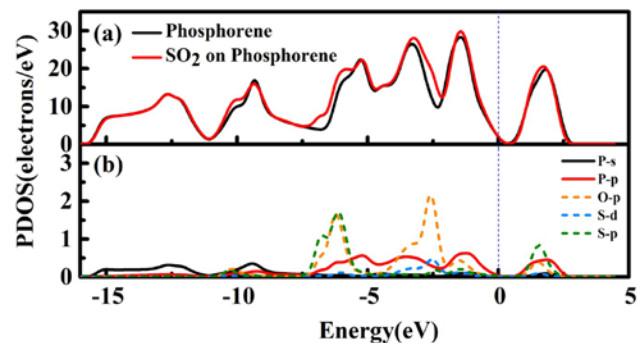


Fig. 2. (a) The total DOS of phosphorene with and without SO_2 adsorption; (b) The PDOS of the SO_2 on the pristine phosphorene.

Because pristine phosphorene exhibits excellent SO_2 gas sensing performance, so in this section, we focus primarily on exploring its deeper interaction mechanism with SO_2 . The total electronic densities of states (DOS) and atom projected density of states (PDOS) are plotted in Fig. 2. The DOS of SO_2 on pristine phosphorene is analogous to that of the pristine one, which means that the superior electronic properties of free-standing phosphorene can be well preserved after SO_2 adsorption. Furthermore, the result further strengthens the evidence of incapability of chemisorption between SO_2 molecule and phosphorene. Besides, the P p and O p orbitals of the SO_2 /phosphorene structure respectively share the similar states within the range of -2 to 3 eV, indicating the slight orbital hybridization. It should be noted that the orbital hybridizations existed in this system is not rather strong, so the E_a is moderate and incapable of chemical bond forming.

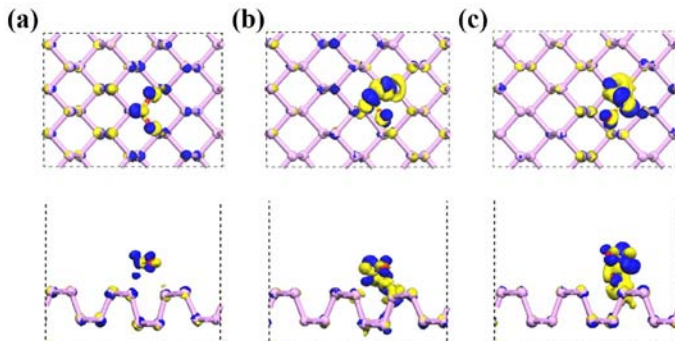


Fig. 3. Charge density difference for SO₂ on (a) pristine, (b) B-, and (c) Si-doped phosphorene. The isosurface value is 0.03 e/Å³.

To get a deeper insight into the mechanism of SO₂ adsorbed on the substrates, we also calculated the charge density difference (CDD) of SO₂/phosphorene, SO₂/B-doped phosphorene and SO₂/Si-doped phosphorene systems. As presented in Fig. 3, the blue region shows the charge accumulation, whereas the yellow region represents the charge depletion. It is shown that for B (or Si) doped phosphorene, the charges are remarkably redistributed after adsorbing SO₂ and there is apparently large charge depletion between SO₂ and impurity atom indicating the strong hybridization of orbitals at the nanosensor surface. Such intense orbital hybridization is absent for physisorption of the SO₂ gas on pristine phosphorene [see Fig. 3(a)]. Extrapolating from the quantitative analysis of adsorption distance above, we consider this strong hybridization is due to the formation of covalent bonds between SO₂ and B (or Si) doped phosphorene, which gives a further explanation that B and Si doped phosphorenes are not suitable as the SO₂ sensor because of their slow desorption from substrate. Yet, they could activate or catalyze SO₂ due to the strong interaction, suggesting the possibility of B (or Si) doped phosphorene as a metal-free catalyst.

IV. CONCLUSION

In summary, the adsorption properties of SO₂ molecules on different phosphorenes are investigated by using density functional computations to exploit their potential applications as SO₂ sensors. The results show that different impurities doped phosphorenes exhibit different characteristics when exposed to SO₂ molecule. The pristine phosphorene is sensitive to SO₂ gas molecule with a moderate adsorption energy. By doping phosphorene with either B or Si atom, it exhibits significantly high reactivity towards SO₂ via strong chemisorption, thus presumably not suitable for usage as a SO₂ gas sensor. We conjecture that they can be applied as metal-free catalysts for activating or catalyzing SO₂ adsorbate. Doping with N or S is redundant without improving SO₂ sensing performance of phosphorene. Over all, we recommend that the pristine phosphorene has good potential as gas sensors for SO₂ detection.

REFERENCES

[1] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. J. Dai, "Nanotube molecular wires as chemical sensors," *Science*,

vol. 287, pp. 622-625, Jan. 2000. DOI: 10.1126/science.287.5453.622

[2] Q. Yue, Z. Shao, S. Chang, and J. Li, "Adsorption of gas molecules on monolayer MoS₂ and effect of applied electric field," *Nanoscale research letters*, vol. 8, pp. 1-7, Oct. 2013. DOI: 10.1186/1556-276X-8-425

[3] J. Dai, P. Giannozzi, and J. Yuan, "Adsorption of pairs of NO_x molecules on single-walled carbon nanotubes and formation of NO_x NO₃ from NO₂," *Surface Science*, vol. 603, pp. 3234-3238, Sep. 2009. DOI: 10.1016/j.susc.2009.09.010

[4] S. C. Lee, B. W. Hwang, S. J. Lee, H. Y. Choi, S. Y. Kim, S. Y. Jung, D. Ragupathy, D. D. Lee, J. C. Kim, "A novel tin oxide-based recoverable thick film SO₂ gas sensor promoted with magnesium and vanadium oxides," *Sensors and Actuators B: Chemical*, vol. 160, pp. 1328-1334, Sep. 2011. DOI: 10.1016/j.snb.2011.09.070

[5] Y. Shimizu, N. Matsunaga, T. Hyodo, and M. Egashira, "Improvement of SO₂ sensing properties of WO₃ by noble metal loading," *Sensors and Actuators B: Chemical*, vol. 77, pp. 35-40, Jun. 2001. DOI: 10.1016/S0925-4005(01)00669-4

[6] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, and W. Ji, "High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus," *Nature communications*, vol. 5, Jul. 2014. DOI: 10.1038/ncomms5475

[7] L. Kou, T. Frauenheim, and C. Chen, "Phosphorene as a superior gas sensor: Selective adsorption and distinct I-V response," *The Journal of Physical Chemistry Letters*, vol. 5, pp. 2675-2681, Jul. 2014. DOI: 10.1021/jz501188k

[8] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P. D. Ye, "Phosphorene: an unexplored 2D semiconductor with a high hole mobility," *ACS nano*, vol. 8, pp. 4033-4041, Mar. 2014. DOI: 10.1021/nn501226z

[9] E. S. Reich, "Phosphorene excites materials scientists," *Nature*, vol. 506, p. 19, Feb. 2014. DOI: 10.1038/506019a

[10] Y. H. Zhang, Y. B. Chen, K. G. Zhou, C. H. Liu, J. Zeng, H. L. Zhang, Y. Peng, "Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study," *Nanotechnology*, vol. 20, p. 185504, Apr. 2009. DOI: 10.1088/0957-4484/20/18/185504

[11] Z. Ao, J. Yang, S. Li, and Q. Jiang, "Enhancement of CO detection in Al doped graphene," *Chemical Physics Letters*, vol. 461, pp. 276-279, Jul. 2008. DOI: 10.1016/j.cplett.2008.07.039

[12] S. L. Zhang, M. Q. Xie, F. Y. Li, Z. Yan, Y. F. Li, E. Kan, W. Liu, Z. F. Chen, H. B. Zeng, "Semiconducting Group 15 Monolayers: A Broad Range of Band Gaps and High Carrier Mobilities," *Angewandte Chemie*, vol. 128, pp. 1698-1701, Jan. 2016. DOI: 10.1002/ange.201507568

[13] S. L. Zhang, Z. Yan, Y. F. Li, Z. F. Chen, and H. B. Zeng, "Atomically Thin Arsenene and Antimonene: Semimetal-Semiconductor and Indirect-Direct Band-Gap Transitions," *Angewandte Chemie International Edition*, vol. 54, pp. 3112-3115, Mar. 2015. DOI: 10.1002/anie.201411246

[14] X. P. Chen, N. Yang, J. M. Ni, M. Cai, H. Y. Ye, C. K. Wong, Y. Y. Leung, and Tian-Ling Ren, "Density-functional calculation of methane adsorption on graphenes," *Electron Device Letters, IEEE*, vol. 36, pp. 1366-1368, Oct. 2015. DOI: 10.1109/LED.2015.2492580

[15] X. P. Chen, N. Yang, J. K. Jiang, Q. H. Liang, D. G. Yang, G. Q. Zhang, and T. L. Ren, "Ab initio study of temperature, humidity, and covalent functionalization-induced bandgap change of single-walled carbon nanotubes," *Electron Device Letters, IEEE*, vol. 36, pp. 606-608, Jun. 2015. DOI: 10.1109/LED.2015.2425046

[16] A. Rodin, A. Carvalho, and A. C. Neto, "Strain-induced gap modification in black phosphorus," *Physical review letters*, vol. 112, p. 176801, Jan. 2014. DOI: http://dx.doi.org/10.1103/PhysRevLett.112.176801

[17] X.P. Chen, C.K.Y. Wong, C.A. Yuan, and G.Q. Zhang, Impact of the functional group on the working range of polyaniline as carbon dioxide sensors, *Sensors and Actuators B: Chemical*, vol. 175, pp. 15-21, Dec. 2012. DOI:10.1016/j.snb.2011.11.054

[18] P. Pekka and A. Michiko, "Molecular Single-Bond Covalent Radii for Elements 1-118," *Chemistry-A European Journal*, vol. 15, pp. 186-197, Dec. 2008. DOI: 10.1002/chem.200800987