Sensing of NO, NO₂, and SO₂ on two dimensional WS₂ doped with Al, P, and Fe: An ab initio study

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Abstract

Owing to their harmful and polluting the environment, nitrogen oxides and sulfur dioxide are expected to monitor when they are used. However, the widespread use of gas sensing methods presents obstacles in terms of portability or stability. Hence, a better detect way needs to be found urgently. The success of graphene-based gas sensors has stimulated interest in two-dimensional (2D) materials in the gas sensing area. Transition metal dichalcogenides (TMDs), such as MoS₂ or WS₂, are considered to have the high-performance potential for gas sensors. Unfortunately, when used as a gas sensor, the sensing response of the pristine TMDs is greatly affected by a number of gas molecules that are too weak to be detected. Herein, to evaluate the sensing capability of Al, P, and Fe-doped WS₂ to NO, NO₂, and SO₂, the molecular model of the adsorption systems was constructed, and density functional theory (DFT) was used to calculate the adsorption behavior of these gases. The binding force of all the doped-WS₂ to the harmful gas molecules is much stronger than that of the pristine WS₂. According to the results of adsorption energy, band structure, and state density, Al-doped WS₂ has the potential to be used as NO and SO₂ gas sensor, while P-doped WS₂ is selective to NO. This work opens up a new reference for choosing appropriate doping types on 2D materials for noxious gas sensing.

1. Introduction

Nitrogen oxide and sulfur dioxide are widely used in industrial production. For example, nitric oxide (NO) could be used as an N source for doping in the semiconductor industry, and sulfur dioxide (SO₂) could be used to prevent grape from deterioration[1, 2]. However, these gases are not only harmful but also could cause serious environmental problems, such as acid rain or photochemical smog[3, 4]. It is necessary to monitor the industrial application of these gases for leakage. The widely used metallic oxide sensors also have the disadvantages of instability and limited working conditions[5]. Finding new materials to detect these gases is therefore significant. In order to effectively detect gas molecules, the materials used should have a large surface volume ratio and sufficient binding force on adsorbed gas molecules[6]. The two-dimensional (2D) material proved by the preparation of graphene just meets these requirements[7, 8]. In particular, 2D graphene has become a research hotspot of gas sensors because of its moderate interaction with gas molecules. When the gas molecules are attached to graphene, their resistance changes with the energy band structure [5, 9].

The excellent gas sensing properties of graphene have motivated researchers to put their attention on 2D materials, such as III-V nitrides or transition metal dichalcogenides (TMDs)[10–12]. Among these 2D materials, TMDs caught a lot of concern in gas sensors because of its stable semiconducting property, high thermal stability, and appropriate carrier mobility[13–15]. For example, SnS₂ or MoS₂ could be used to sense NO₂, WS₂ is an excellent candidate to be applied in a dissolved gas analyzer (DGA)[16–18].

However, the pristine TMDs had some problems when used as a gas sensor, such as weak adsorption force that unable to effectively capture gas molecules[19]. In this case, doping is widely used in 2D materials to adjust the surface properties and bonding force between materials and gas molecules, and

improve the gas adsorption properties and the sensing capability[20]. For example, Pd-doped WS₂ or Co-doped MoS₂ have already shown their improvement than their pristine counterparts in gas sensing[6, 21, 22]. Nevertheless, most previous studies on doped TMDs as a gas sensor only considered the attachment of dopants to the monolayer surface, while few studies on the substitution of doped atoms for atoms in the pristine material. Furthermore, different atoms doped in the materials have the different gas sensing capability. Therefore, it is necessary to discuss the atom which is most suitable for doping into 2D materials by atom substitution method.

In this paper, we take WS₂ as a case and study the influence of doping by atom substitution on its gas sensing properties based on density functional theory (DFT). Three atoms, Al Fe P, were selected as alternative impurities in WS₂ supercells to investigate their effects on gas sensing properties of NO NO₂ and SO₂. The three atoms were chosen because gas sensing property can be significantly enhanced when these elements are doped in other gas sensing materials, such as metal oxides[23–25]. The adsorption energy, band structure, and density of state (DOS) of the adsorption systems consist of the pristine or doped WS₂ with harmful gas molecules of NO, NO₂ and SO₂ were evaluated and compared respectively. It proves that WS₂ doped with Al or P atoms has obvious advantages over the pristine WS₂ in sensing these gases, while the Fe-doped one cannot be the suitable gas sensor candidate. This work provides a new perspective to choose appropriate doping types on 2D materials for harmful gas sensing.

2. Computational Details

In this work, all first principle calculations are based on DFT[26, 27]. The local density approximation (LDA) with the PWC function was selected to address the electron exchange and correlation. For alleviating the burden of computation, kernel (DFT semi-core Pseudopots) was replaced by a single effective potential. Dual numerical orbital basis set and orbital polarization function (DNP) was chosen. The global orbital cutoff radius was set to 4.9 Å to ensure enough accuracy. The Monkhorst-Pack k-points was set as 4 × 4 × 1 after a convergence test, with a vacuum layer of 13.4 Å to avoid the interaction between adjacent units. The energy convergence precision for geometric was 1.0 × 10⁻⁵ Hartree, while the maximum displacement was 0.005 Å, and the maximum force was 0.002 Hartree/Å.

A 4 × 4 × 1 supercell, which contains 16 W atoms and 32 S atoms were established after the lattice parameters were calculated, as shown in Fig. 1 (a). For building models of doped WS₂, a W atom was replaced by a Fe atom and an S atom was replaced by a P or Al atom[28], as shown in Fig. 1 (b), (c) and (d). Then a geometry optimization was given. After that, the gas molecule was set above the WS₂ plane to build the gas adsorption model. Three sites for the adsorbed gas molecule were chosen. They were: just above the S or dopant atoms, just above the midpoint of the bond between the doped atom and the W or S atom and in the center of the hexagon structure, which is marked as (a), (b), and (c). (Fig. 1 (a)-(d)) After geometry optimizations for every adsorption system, the models with the most stable adsorption systems were chosen. Then the adsorption energy (E_{ad}), which could reflect the interaction between the material and the adsorbed gas molecule was calculated by the following function:

$$E_{ad} = E_{tot} - E_m - E_{gas}$$

where E_m represents the energy of the material without adsorbing gas molecules; E_{tot} represents the total energy of the material and the gas molecules; E_{gas} represents the energy of the isolated gas molecule[29]. A larger absolute value of E_{ad} represents a stronger interaction force between the material and gas molecules.

3. Results And Discussion

(i) Geometric and electronic structure of pristine or Al-, Fe-, and P-doped WS_2 and gas molecules

At first, a geometry optimization was given to the models of pristine and doped WS_2 , and the three kinds of gas molecules. The optimized models of these three gas molecules are shown in Fig. 1 (e), (f), and (g). The bond length of NO, NO_2 , and SO_2 are 1.16 Å, 1.21 Å, and 1.46 Å, respectively. And in the pristine and doped WS_2 models, the bond length of W-S, Al-W, P-W, and Fe-S bonds is around 2.43 Å, 2.86 Å, 2.45 Å, and 2.31 Å, respectively (Fig. 2 (a)-(d)). Then, the most stable adsorption sites of the Al-, P-, and Fe-doped WS_2 and the pristine WS_2 towards all the three gas molecules were chosen according to their E_{ad} . As marked in Fig. 1, the most stable sites for Al-doped WS_2 towards NO, NO_2 , and SO_2 were (⊗), (⊗), and (⊗), while for Fe-doped WS_2 or P-doped WS_2 , they were (⊗), (⊗), and (⊗). It can be found that the E_{ad} absolute values of the three gases adsorbed on the pristine WS_2 are very small (Table S1), which means the interaction between the NO, NO_2 , and SO_2 gas molecule and the pristine WS_2 was so weak that the pristine WS_2 could not capture these gas molecules well and detect them effectively.

Then, the DOS results of pristine WS_2 and Al-, Fe- or P-doped WS_2 are shown in Fig. 2 (a), (b), and (c). It can be seen from Fig. 2 (a) and (c) that the DOS curves of Al or Fe doping system are significantly different from that of the pristine WS_2 . There is a new peak appeared around the Fermi level due to the contribution of the Al or Fe dopant indicates a better conductivity. Furthermore, the DOS curves have an apparent shift to the lower area after the Al or Fe doped. While in the P doped system, the DOS curve has no evident change, and the left shift is also slight. That is because P and S are adjacent elements of the same period that their electronic structure is similar. In addition, the DOS of the doped Al, Fe, and P atoms mainly contributed by Al-p, P-p, and Fe-d orbitals. They have a prominent overlap with that of the W-d and S-p orbitals (Fig. 2 (d), (e), and (f)), which means a robust hybrid between them[16]. It also confirms with the above discussion that there is a strong interaction between doped Al, P, and Fe atom and WS_2 . Indicating the Al, P or Fe atoms could be a stable dopant.

(ii) NO adsorption on pristine or Al-, Fe-, and P-doped WS_2

The most stable adsorption sites of NO molecule adsorbed on the doped WS_2 were shown in Fig S1 (a), (b), and (c). It observed that the length of the N-O bond in NO molecule has the most significant change when it is adsorbed on Al-doped WS_2 . It turned from 1.16 Å to about 1.20 Å. When the NO molecule is

adsorbed on Fe-doped WS₂, the N-O bond length has almost no change. On the other hand, when the NO molecule is adsorbed on P-doped WS₂, the N-O bond length varies between the first two adsorption systems.

It can reflect that in the Al-, Fe-, P-doped, and pristine WS₂, the interaction force between NO molecule and Al-doped WS₂ is the strongest. It was also consistent with the E_{ad} result (Table S1). Furthermore, in comparison with the adsorption model of the pristine WS₂, the E_{ad} of all the three doped WS₂ has a prominent enhancement, but the absolute value of E_{ad} of the Fe-doped WS₂ is still not large enough, especially compared with the other two kinds of doped WS₂.

Then the band structure of these Al-, Fe-, P-doped WS₂ adsorption systems for NO were calculated. As shown in Fig. 3, when NO is adsorbed, the Al-doped WS₂ changed from a zero-gap structure to a structure with a 0.502 eV bandgap. And a flat band around the Fermi level in the Al-doped system could lead to high sensitivity towards NO[30]. The bandgap of P-doped WS₂ also has a noticeable decrease from 1.822 eV to 0.653 eV. All these would lead to a remarkable change in conductivity. Resistance NO gas sensors could be made based on this change. While for the Fe doped system, the band structure has almost no difference. Although the Fe-doped WS₂ could capture NO molecules, the conductivity will make it difficult for sensing.

Then the DOS analysis was carried out. All the results are shown in Fig. 4. Around the Fermi level, the area formed by the DOS curve of NO molecules has the largest overlapping region created by the other atoms in the case of the Al-doped system, which is consistent with the E_{ad} result. And the relatively visible change of the DOS curve near the Fermi level also reflects the evolution of conductivity. And the curve of the DOS from the Al-doped system also has the most remarkable change in all these conditions, as shown in Fig. 4 (d). It could also reflect the most robust interaction that exists in the Al-doped NO adsorption system among the three adsorption systems.

All the above could prove that Al could be the best dopant for WS₂ to sense NO and P could also be appropriate, while Fe was not a suitable candidate.

(iii) NO₂ adsorption on the pristine or Al-, Fe-, and P-doped WS₂

Fig S2 shows the NO₂ is adsorbed on the Al-, Fe-, and P-doped WS₂ at the most stable position, respectively. It can be seen from Fig S2 (a), (b), and (c) that the bond length of NO₂ molecule changes obviously only when it is adsorbed by Al-doped WS₂. The N-O bond formed by the N atom and the O atom near the Al atom is lengthened to 1.52 Å, and the other N-O bond is shortened to 1.17 Å, while the length of both the N-O bonds in the Fe or P doped system lengthened slightly from 1.21 Å to 1.22 Å. It also agrees with the phenomenon that the largest absolute value of E_{ad} got in the Al-doped system. Besides, the same as NO, all these three kinds of atoms (Al, Fe, and P) doped in WS₂ could greatly strengthen the

binding force towards NO_2 molecule. And the Fe-doped system still has a relatively small E_{ad} in these doped materials.

Then the band structure of these three doped adsorption systems was calculated (Fig. 5 (a)-(f)). The new band could be found in all the doped WS_2 because of the adsorption of the NO_2 molecule.

However, in the NO_2 adsorption system, only the band structure of the P-doped system has some changes, which is different from the case where NO is absorbed by WS_2 . The bandgap decreased from 1.822 eV to 1.762 eV, but Al- or Fe-doped WS_2 still maintained a zero-gap structure with no significant change in conductivity.

The DOS analysis was given again (Fig. 6 (a)-(f)). From the overlap of the DOS curve of the NO_2 molecule and that of the atoms in doped WS_2 , the relatively stable interaction between NO_2 molecule and the Al or P doped WS_2 could be reflected. And it could also be indicated by the relatively visible change of the DOS curves between the original Al or P doped WS_2 and that with the NO_2 adsorbed. Since the bandgap changes of all the doped WS_2 are not obvious, and the conductivity changes are not significant, they cannot be used as an appropriate NO_2 sensor.

(iv) SO_2 adsorption on the pristine or Al-, Fe-, and P-doped WS_2

As mentioned above, the adsorbed SO_2 molecules are settled in the most stable positions (Fig S3 (a)-(c)). The Al-doped system has the most remarkable influence on the SO_2 molecule, which could be reflected by the most significant absolute value of the E_{ad} and the change of bond length in the SO_2 molecule (Table S1). The length of the S-O bond near the Al atom is lengthened from 1.46 Å to 1.60 Å, and others are lengthened to 1.48 Å. And the adsorption behavior of SO_2 on the P-doped WS_2 also shows a slight lengthen from 1.46 Å to 1.47 Å. In addition, the length of the S-O bond remains 1.46 Å in the Fe-doped adsorption systems (Fig S3). However, the adsorption of SO_2 is different from that of the above two gases. Although the three atoms doped with WS_2 can significantly enhance the adsorption capability of SO_2 , only Al-doped WS_2 has a relatively strong binding force for SO_2 molecules. The other two doped adsorption systems had lower E_{ad} values.

Next, the band structure is analyzed, and the results are shown in Fig. 7 (a) to (f). New bands also appear in Fig. 7 (d) to (f) due to the adsorption of the SO_2 molecule. When SO_2 is adsorbed on the Al-doped WS_2 , a bandgap with a width of 0.193 eV appears. However, the bandgap of the P-doped WS_2 increased slightly from 1.822 eV to 1.939 eV, and the Fe doping system was still a zero-gap structure. It means that after adsorption of the SO_2 molecule, the conductivity of the Al doping system will change relatively significantly. The conductivity of the P-doped WS_2 also changes significantly after gas molecule adsorption.

Then the three adsorption systems were analyzed by DOS, and the results are shown in Fig. 8 (a) to (f). The DOS curves were in good agreement with the E_{ad} results. As shown in Fig. 8 (a), The DOS curve of the SO_2 molecule and the DOS curve of the atoms in the doped WS_2 formed a relatively large overlap region near the Fermi energy level, which only appeared in the Al doping system. In the other two doping systems, the overlap is quite small. In addition, the adsorption of the SO_2 molecules only had a relatively evident influence on the DOS curve of the Al-doped adsorption system (Fig. 8 (d)). Therefore, the strong interaction and the relatively visible conductivity changes indicate the potential of the Al-doped WS_2 as an SO_2 gas sensor.

4. Conclusion

In this work, using first-principles, theoretical calculations were carried out to evaluate the influence of the Al, Fe, or P atoms doped WS_2 on the gas sensing ability towards NO, NO_2 or SO_2 . The E_{ad} , band structure, as well as DOS, were considered to understand this question. Considering the E_{ad} results, all these kinds of doped WS_2 could capture these kinds of gas molecules far better than the pristine WS_2 . All the three gases could be stably adsorbed on the Al-doped WS_2 reflected by the E_{ad} and the DOS results. The conductivity of the Al-doped WS_2 could have a noticeable change after the NO or SO_2 molecules were adsorbed, reflected by the change of its bandgap. That means Al-doped WS_2 has the potential to be used as a resistance type gas sensor toward NO or SO_2 based on this change. For P-doped WS_2 , its gas sensing ability shows selectivity towards these gases because its bandgap has a far more significant change after NO molecule was adsorbed than the difference after the other two gases adsorbed. Thus, the P-doped WS_2 is most suitable to be used as a NO gas sensor that is less influenced by the possibly existed NO_2 or SO_2 in these three doped WS_2 materials. Our calculations evaluated the influence of these doped atoms (Al, P, and Fe) into WS_2 monolayer to its gas sensing capability towards the three kinds of gas (NO, NO_2 , and SO_2). It could give a reference to choose appropriate doping types on 2D materials for noxious gas sensing.

Declarations

Availability of data and material

All data are fully available without restriction.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

J. Cao and J. Zhou performed DFT calculations and drafted the manuscript; J. Shi performed DFT calculations; J. Chen helped in the English writing of this paper; W. Wang helped to process the graphs; Y. Zhang and X. Liu conceived of the study; All authors read and approved the final manuscript.

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Figures

Figure 1

The 4 × 4 × 1 supercell model of (a) pristine WS₂, (b) Al-doped WS₂, (c) P-doped WS₂, and (d) Fe-doped WS₂ with the three adsorption sites marked. And the models of (d) NO, (e) NO₂, and (f) SO₂ molecules. Yellow, light blue, dark red, violet, purple, blue, and red balls represent S, W, Al, P, Fe, and O, respectively.

Figure 2

The total and partial DOS of the three doped WS2 in comparison with the complete DOS of the pristine WS2. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system. The dash lines are the Fermi level.

Figure 3

Band structure of the three doped WS2 before and after the NO adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system. The dash lines are the Fermi level.

Figure 4

DOS of the atoms in the three doped NO adsorption systems and the DOS of the three adsorption systems before and after the NO adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system.

Figure 5

Band structure of the three doped WS2 before and after the NO2 adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system. The dash lines are the Fermi level.

Figure 6

DOS of the atoms in the three doped NO₂ adsorption systems and the DOS of the three adsorption systems before and after the NO₂ adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system.

Figure 7

Band structure of the three doped WS₂ before and after the SO₂ adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system. The dash lines are the Fermi level.

Figure 8

DOS of the atoms in the three doped SO₂ adsorption systems and the DOS of the three adsorption systems before and after the SO₂ adsorbed. (a) and (d) are the Al-doped system. (b) and (e) are the P-doped system. (c) and (f) are the Fe-doped system.

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