Sensing Behavior of Two Dimensional Al- and P-Doped WS₂ Toward NO, NO₂, and SO₂: an Ab Initio Study

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Abstract

Two-dimensional transition metal dichalcogenides (2D TMDs), such as WS₂, are considered to have the potential for high-performance gas sensors. It is a pity that the interaction between gases and pristine 2D WS₂ as the sensitive element is too weak so that the sensor response is difficult to detect. Herein, the sensing capabilities of Al- and P-doped WS₂ to NO, NO₂, and SO₂ were evaluated. Especially, we considered selectivity to target gases and dopant concentration. Molecular models of the adsorption systems were constructed, and density functional theory (DFT) was used to explore the adsorption behaviors of these gases from the perspective of binding energy, band structure, and density of states (DOS). The results suggested that doping atoms could increase the adsorption strength between gas molecules and substrate. Besides, the sensitivity of P-doped WS₂ to NO and NO₂ was hardly affected by CO₂ or H₂O. The sensitivity of Al-doped WS₂ to NO and SO₂ was also hard to be affected by CO₂ or H₂O. For NO detection, the WS₂ with 7.4% dopant concentration had better sensitive properties than that with a 3.7% dopant concentration. While for SO₂, the result was just the opposite. This work provided a comprehensive reference for choosing appropriate dopants (concentration) into 2D materials for sensing noxious gases.

Keywords: Gas-sensing performance, Binding energy, Gas adsorption property, Nitrogen oxides, Sulfur dioxide, Transition metal dichalcogenides, Density functional theory, Doped WS₂

Introduction

Nitrogen oxide and sulfur dioxide are widely used in industrial production. For example, nitric oxide (NO) could be used as the nitrogen source for doping processes in the semiconductor industry, and sulfur dioxide (SO₂) could be used to prevent grape from deterioration [1]. However, these gases are not only harmful but also could cause serious environmental problems, such as acid rain or photochemical smog [2, 3]. It is necessary to monitor the leakage of these gases in industrial applications. Among previous researches, metallic oxide gas sensors have been widely studied, but they have disadvantages of instability and limited working conditions [4]. Therefore, it is of considerable significance to find new materials to detect these gases [5]. To detect gas molecules effectively, the materials should have a large surface volume ratio and sufficient binding force to adsorb gas molecules [6, 7]. The discovery of graphene and rare gas sensing properties [8] has motivated researchers to put their attention towards 2D materials [9, 10].

Among 2D materials, transition metal disulfides (TMDs) have attracted a lot of concern in the gas sensing area because of their stable semiconducting properties and appropriate carrier mobility [11–13]. Especially as a typical kind of TMDs, WS₂ has various unique properties for sensing materials [14, 15], such as
excellent thermal stability, tunable band structure [16, 17], and low cost. However, pristine 2D WS\textsubscript{2} as a sensitive element has some disadvantages, such as weak adsorption with target gases, which cannot capture the gas molecules effectively [18]. In this case, doping is widely used in 2D materials to adjust the surface properties and binding force between materials and gas molecules and improve the adsorption and sensing capability of gases [19, 20]. Of course, different dopants have different effects on the sensing performance. Therefore, doped sensitive substrates must find suitable impurities to improve their sensing performance. For example, Pd-doped WS\textsubscript{2} has already shown their improvement over their pristine counterparts in gas sensing [6, 21]. Unfortunately, most previous studies about doped WS\textsubscript{2} as the sensitive element only focused on the binding strength and charge transfer between gas molecules and single-layer films. Adsorption selectivity to gases and the influence of doping concentration are often neglected. In this work, we comprehensively explored not only the binding strength and charge transfer but also the adsorption selectivity to target gases and the influence of doping concentrations.

Here, considering that Al and P atoms have a close covalent radius and similar electronic structure with S atoms, it is easier for them to replace S atoms and form stable covalent structure. Many previous studies have investigated materials with substitution doping of S atoms [22–25]. Therefore, this work explored the sensing performance of Al- and P-doped WS\textsubscript{2} with the help of DFT. The sensing properties of the doped systems with that of the undoped one were compared in terms of binding energy, band structure, and density of state. It proved that WS\textsubscript{2} doped with Al or P atoms had apparent advantages over the pristine WS\textsubscript{2} in detecting these gases. In addition to NO, NO\textsubscript{2}, and SO\textsubscript{2}, we considered CO\textsubscript{2} and H\textsubscript{2}O as disturbance gases to examine the selectivity of a doped substrate to the target gases. Two doping concentrations, 3.7% and 7.4%, were considered to estimate its influence on the sensitivity to gases. This work provides a comprehensive insight to select appropriate dopants (concentration) into 2D materials for sensing harmful gases.

**Methods**

In this work, all first principle calculations were 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 pseudopotential) 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 as 4.9 Å to ensure enough accuracy. The Monkhorst-Pack k-points were 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 3 × 3 × 1 supercell containing 9 W atoms and 18 S atoms was established, as shown in Fig. 1a. For the models of doped WS\textsubscript{2}, an S atom was replaced by a P or Al atom [28], as shown in Fig. 1b–d. Then, a geometry optimization was given. After that, the gas molecule was set above the WS\textsubscript{2} plane to build the gas adsorption model. Three sites for the adsorbed gas molecule were

![Fig. 1](image-url) The 4 × 4 × 1 supercell model of a pristine WS\textsubscript{2}, b Al-doped WS\textsubscript{2}, and c P-doped WS\textsubscript{2} with the three adsorption sites marked. And the models of d NO, e NO\textsubscript{2}, and f SO\textsubscript{2} molecules. Yellow, light blue, dark red, violet, blue, and red balls represent S, W, Al, P, N, and O, respectively.
chosen. They were the top of S or dopant atoms (I), the top of the midpoint of the bond between the doped atom and the W or S atom (II), and the center of the hexagon structure (III), as shown in the Fig. 1a–c. After the geometry optimizations for every adsorption system, the geometric constructions with the most stable gas adsorption were found. The binding energy ($E_{\text{bind}}$) could reflect the interaction between the material and the adsorbed gas molecule and be calculated by the following function:

$$E_{\text{bind}} = E_{\text{tot}} - E_{\text{m}} - E_{\text{gas}}$$  \hspace{1cm} (1)

where $E_{\text{m}}$ represents the energy of the material without adsorbing gas molecules, $E_{\text{tot}}$ represents the total energy of the material and the gas molecules, and $E_{\text{gas}}$ represents the energy of the isolated gas molecule [29]. A more considerable absolute value of $E_{\text{bind}}$ represents a more potent interaction force between the material and gas molecules.

The formation energy ($E_{\text{fm}}$), which could reflect the difficulty to form a doping system, and the stability of the system was calculated by the function below:

$$E_{\text{fm}} = E_{\text{tot}} + E_{\text{s}} - E_{\text{m}} - E_{\text{dopant}}$$  \hspace{1cm} (2)

where $E_{\text{s}}$ is the total energy of the substituted S atom, and $E_{\text{dopant}}$ represents the total energy of the dopant atoms. A more significant value of $E_{\text{fm}}$ means more difficult to form the dopant system.

**Results and Discussion**

The adsorption positions have been shown in Fig. 1a–c, which was corresponding to pristine, Al-doped, and P-doped WS$_2$, respectively. In Fig. 1d–f the bond lengths of N=O, N=O, and S=O were 1.16 Å, 1.21 Å, and 1.46 Å, respectively. The bond length of W–S, Al–W, and P–W bond was around 2.43 Å, 2.86 Å, and 2.45 Å, respectively. After the geometric optimization, the energetically favorable site for each adsorbate has been used in the subsequent discussion. The binding energies of the 3.7% P- and Al-doped WS$_2$ system at the energetically favorable site were shown in Table 1. The binding energy of the pure WS$_2$ system was shown in Table S1. Then, according to the results of binding energy, the interaction between gas molecules and pure WS$_2$ was so weak that it was difficult for the substrate material to adsorb gas molecules stably. The binding energy of the NO-pristine WS$_2$ system was even positive. However, the introduction of dopant could significantly enhance the adsorption strength between gas and WS$_2$, especially for WS$_2$ doped by Al atom. Among all the doping cases, the adsorption strength was the smallest, while SO$_2$ adsorbed on P–WS$_2$. Besides, apart from Al and P, other elements in the same period or family with S, such as O, Si, Cl, or Se, were also considered. The case of Fe-doped W-substituted WS$_2$ was shown in Fig. S1, while WS$_2$ systems with these dopants had either poor stability (high $E_{\text{fm}}$) or weak interaction with gas molecules. Considering this, these dopants were not involved in the subsequent studies. The energetically favorable sites (the lowest negative binding energy) of NO, NO$_2$, and SO$_2$ molecules adsorbed on the doped WS$_2$ were shown in Fig. S2, S3, and S4, respectively.

The band structures of pristine and Al- and P-doped monolayer WS$_2$ were presented in Fig. 2. The projective density of states (PDOS) results was shown in Fig. S5. The monolayer 2H WS$_2$ is a semiconductor with a direct bandgap at the Γ point. For WS$_2$ doped with Al atom, the impurity introduced interface states into the bandgap region of monolayer 2H WS$_2$. What’s more, the presence of metal atom forms the Schottky barrier with the Fermi level pinned in the surface region of the semiconductor. The pinning position is within 0.2 eV to the Fermi level of the first semiconductor [5]. Metal properties are brought by metal dopants [30]. At the same time, the P atom introduced energy bands mixed with the conduction and valance band of WS$_2$. Band structures of doped WS$_2$ after gas adsorption were shown in Fig. S6. Consequently, in the cases of NO on Al-doped WS$_2$, NO on P-doped WS$_2$, and SO$_2$ on Al-doped WS$_2$, the bandgap width of material had an evident change after the gas molecules were adsorbed. Previous studies have shown that a narrowed bandgap means lower kinetic stability, higher chemical activity, and a more natural electron transition from the valence band to the conduction band [31, 32]. Thus, after gas adsorption, evident bandgap changes of doped materials made them possible to be sensitive substrates to detect the existence of gas molecules.

Based on the charge transfer between gas molecules and substrate materials, the detection of gas can be completed by gas sensors. According to the traditional charge transfer theory, the mechanism of the charge transfer process between gas and WS$_2$ was shown in Fig. 3. LUMO is the

| Substrate | Gas   | Binding energy (eV) | Substrate | Gas   | Binding energy (eV) |
|-----------|-------|---------------------|-----------|-------|---------------------|
| P-WS$_2$  | NO    | −0.87               | Al-WS$_2$ | NO    | −1.76               |
|           | NO$_2$| −1.27               |           | NO$_2$| −3.16               |
|           | SO$_2$| −0.29               |           | SO$_2$| −2.12               |
lowest unoccupied molecule orbital, while HOMO is the highest occupied molecule orbital. \( E_f \) is the Fermi level of the substrate. If \( E_f \) is between LUMO and HOMO, there will be no charge transfer according to the traditional theory. Then, Zhou et al. added that the charge transfer mechanism would be decided by the orbital mixing of LUMO and HOMO with the substrate material if \( E_f \) lies between LUMO and HOMO, as shown in Fig. 3a [5]. If the LUMO is lower than the Fermi level of WS\(_2\), electrons will flow from WS\(_2\) to gas molecule shown in Fig. 3b [7]. After achieving the equilibrium state, the \( E_f \) of the adsorption system is the same as LUMO. Conversely, if the HOMO is higher than the Fermi level of WS\(_2\), electrons will flow from gas molecules to WS\(_2\) shown in Fig. 3c [5].

The \( E_f \) of the adsorption system is the same as LUMO under the equilibrium state. The LUMO and HOMO iso-surfaces of NO, NO\(_2\), and SO\(_2\) molecule orbital were shown in Fig. 4, a–c respectively. The energy of LUMO and HOMO and \( E_f \) of WS\(_2\) were presented in Table S2.

According to the table, \( E_f \) lied between LUMO and HOMO in the Al- and P-doped adsorption systems. Hence, it is necessary to explore the orbital mixing between the LUMO and HOMO of gas molecules and the substrate material.

DOS was employed to discuss further the electron distribution and orbital mixing in the adsorption system, which depended on the interaction between gases and substrates. Figure 5 presents the DOS of gases, dopants, S, and W atoms. Black and red lines were the DOS curves of gases and dopants, respectively. And blue and olive lines were those of S and W atoms, respectively. After gas adsorption, due to the orbital interaction, the electron redistribution occurred in the whole system, which would lead to the overlaps of DOS peaks between the gas and substrate material. The overlaps of DOS peaks meant the mixing between molecular orbitals, proving the existence of an interaction between gas and sensing materials [33]. The mixing of molecular orbitals was helpful to charge transfer so that it can augment the adsorption interaction between gas and material surface [34–36]. Hence, the mixing between molecular orbitals was compared to evaluate the adsorption effects of gas molecules. In Fig. 5a, the orbital mixing between NO molecule and Al atom was at \(-12.62\) and \(-8.11\) eV. And the orbital mixing between NO molecule and Al, S, and W atoms was at 2.02 eV. In Fig. 5b, the orbital mixing between NO\(_2\) molecule and Al atom was at \(-19.60\), \(-11.60\), and \(-8.44\) eV. And the orbital mixing between NO\(_2\) molecule and Al, S, and W atoms was at 2.02 eV. In Fig. 5c, the orbital mixing between SO\(_2\) molecule and Al atom was at \(-12.09\) eV. The orbital mixing between SO\(_2\) molecule and Al and S atoms was at \(-8.27\) eV. The orbital mixing between SO\(_2\) molecule and Al, S, and W atoms was at 1.75 eV. In Fig. 5d, the orbital mixture between NO molecule and P atom was at \(-12.21\) eV. And the orbital mixing between NO molecule and P, S, and W atoms was at \(-10\) eV. In Fig. 5e, the orbital mixture between NO\(_2\) molecule and P atom was at \(-12.63\) eV. And the orbital mixing between NO\(_2\) molecule and P, S, and W atoms was at \(-9.66\) and \(-5.51\) eV. In Fig. 5f, the orbital mixing between SO\(_2\) molecule and S atoms was at \(-9.25\) eV. From the above results, it can be found that the presence of impurities results in more orbital mixing. Moreover, the orbital mixing in the systems with Al
atom doped is more than that in the systems with P atom doped, indicating stronger interaction between gas molecules and substrate in Al-doped systems that agreed well with the binding energy results. To sum up, the introduction of impurities can provide more activated peaks in the whole band, thus increasing the possibility of orbital mixing between the substrate and gas molecules.

To further evaluate the sensing potential of the Al- and P-doped WS$_2$, CO$_2$ and H$_2$O were also considered for testing the selectivity of Al- and P-doped WS$_2$ to target gas. Similar to NO, NO$_2$, or SO$_2$ adsorption, the most stable adsorption site among three sites with high geometric symmetry on WS$_2$ was shown in Fig. S7(a), (b), (c) and (d). The binding energy results were presented in Table S3, and band structure results were shown in Fig. S7(e), (f), (g) and (h). The bond length of C=O in isolated CO$_2$ and O–H in isolated H$_2$O was 1.175 Å and 0.971 Å, respectively. They did not change much after gas adsorbed on the doped WS$_2$ except for H$_2$O adsorbed on Al-WS$_2$. That indicated the interaction between the H$_2$O molecule and Al-doped WS$_2$ was the strongest. According to Table 2, the calculated binding energy of H$_2$O on Al-WS$_2$ was $-1.69$ eV.
All these results pointed to a possibility that the Al-doped WS₂ would have poor selectivity to target gas under the existence of H₂O. To further confirm this point, the DOS analysis was carried out, shown in Fig. 6. For Fig. 6b, in the group of H₂O on Al-WS₂, the overlaps of DOS peaks between the gas and substrate material near $E_f$ (0 eV) were much more apparent than the other three. That proved a strong interaction and more possibility of charge transfer between H₂O molecule and Al-WS₂. Besides, more orbital mixing between the H₂O molecule and Al atom could be found, which provided more evidence for the interaction. From these, we could conclude that the Al-doped WS₂ as sensing material would be easily affected by H₂O. The binding energy was $-0.18$ and $-0.27$ eV with CO₂ and H₂O adsorbing on P-doped WS₂, respectively. These results were less than the binding energy of NO ($-0.87$ eV) and NO₂ ($-1.27$ eV) but very close to the binding energy of SO₂ ($-0.29$ eV) on P-doped WS₂. In Fig. 6c, the orbital mixing between CO₂ molecule and P atom was at $-12.63$ and $-9.66$ eV. In Fig. 6d, the orbital mixture between H₂O molecule and S atoms was at $-9.25$ eV. Therefore, the sensitivity of P-doped WS₂ to SO₂ was easily effected in the presence of CO₂ or H₂O when binding energy and orbital mixing were taken into consideration simultaneously.

The single-atom doping (3.7% doping concentration) was discussed in the above parts. Considering that different doping concentrations had an impact on the sensing

| Substrate | Gas    | Binding energy (eV) | Substrate | Gas    | Binding energy (eV) |
|-----------|--------|---------------------|-----------|--------|---------------------|
| Al-WS₂    | CO₂    | $-0.19$             | P-WS₂    | CO₂    | $-0.18$             |
|           | H₂O    | $-1.69$             |           | H₂O    | $-0.27$             |

Fig. 6 DOS of a CO₂, Al, S, and W atoms; b H₂O, Al, S, and W atoms; c CO₂, P, S, and W atoms; and d H₂O, P, S, and W atoms
performance, the case of diatomic doping (7.4% doping concentration) was also discussed in the $3 \times 3$ WS$_2$ model. S atoms were still replaced by doping atoms. There were four situations for doping locations shown in Fig. S8. For the Al-doped WS$_2$, they were named as 2Al-1, 2Al-2, 2Al-3, and 2Al-4, respectively. For the P-doped WS$_2$, they were named as 2P-1, 2P-2, 2P-3, and 2P-4, respectively. Then, the formation energy of each doping system was calculated to evaluate the difficulty of forming these structures. The lower the formation of energy is, the easier the formation of configuration is. The results of the formation of energy were shown in Table S4. The 2Al-1 structure was chosen since it has the lowest formation energy among the four cases. Similarly, 2P-1 and 2P-3 were both chosen since they have adjacent formation energies.

According to band structure results (Fig. S6), Al-doped WS$_2$ had excellent adsorption performance to NO and SO$_2$ when the doping concentration was 3.7%. And P-doped WS$_2$ had superior adsorption performance to NO than NO$_2$ and SO$_2$. Therefore, for Al-doped WS$_2$, only NO and SO$_2$ were considered when the doping concentration was 7.4%. For P-doped WS$_2$, only NO was considered. Based on this, the influence of doping concentration on adsorption performance was explored. The most stable adsorption structures were shown in Fig. S9 and showed the binding energy results were shown in Table S5. DOS of these systems were presented in Fig. 7. In Fig. 7a, the orbital mixing between NO molecule and Al atoms was at $-6.51$, $-3.25$, and $-0.75$ eV, respectively. The orbital mixing between NO molecule and S, as well as W atoms, was at 1.78 eV. In Fig. 7b, the orbital mixing between SO$_2$ molecule and S atoms was at $-19.69$ eV. The orbital mixing between SO$_2$ molecule and S, as well as Al atoms, was at $-10.91$ eV. In Fig. 7c, the orbital mixing between NO molecule and P atoms was at $-7.67$ eV. The orbital mixing was at $-0.86$ eV between NO molecule and P as well as W atoms. The orbital mixing was at $-2.39$ eV between NO molecule and P, S, as well as W atoms. In Fig. 7d, the orbital mixing between NO molecule and W atoms was at $-12.55$ and $-0.76$ eV, respectively. Comparing Fig. 7a with Fig. 5a, it can be observed that the orbital mixing and binding energy strengthened, which indicated 7.4% Al-doping concentration induced greater NO adsorption performance than 3.7%. Comparing Fig. 7b with Fig. 5c, the orbital mixing and binding energy weakened, suggesting 7.4% Al-doping concentration caused poorer SO$_2$ adsorption performance than 3.7%. And the negative binding energy of the 2P-1 system was lower than that of 2P-3, according to Table S5. Hence, the adsorption performance of the 2P-3 system was poorer than the 2P-1 one, from the perspective of binding energy and orbital mixing, then, comparing the 2P-1 structure with Fig. 5d. Comparing Fig. 7c with Fig. 5d, the orbital mixing and binding energy were strengthened and that indicated 7.4% P-doping concentration can be brought better NO adsorption performance than 3.7%. To sum up, it could be observed that the influence of different doping concentrations on the sensing performance of P-doped WS$_2$ was less than that of Al-doped WS$_2$. 

![Fig. 7](image-url) DOS of a NO, 2Al-1, S, and W atoms; b SO$_2$, 2Al-1, S, and W atoms; c NO, 2P-1, S, and W atoms; and d NO, 2P-3, S, and W atoms. e Binding energies of all the adsorption systems.
On the other hand, the binding energies of all the adsorption systems were shown in the form of a columnar graph in Fig. 7e. According to Fig. 7e, both concentrations of 3.7% and 7.4% doping could enhance the adsorption strength of the system compared with the pure WS₂ system. For the systems doped with two P atoms, 7.4% doping improved the adsorption strength of more than 3.7% doping, especially for NO gas adsorbing. For the systems doped with two Al atoms, the adsorption strength to NO gas increased. While the adsorption strength to SO₂ or NO₂ decreased, and that in the cases with SO₂ decreased more than the cases with NO₂. Overall, the increase of doping concentration had a greater influence on the adsorption strength of Al-doped systems than P-doped ones.

**Conclusion**

In this work, using first principles, theoretical calculations were carried out to evaluate the influence of Al and P dopants and their doping concentration on the sensitive performance of WS₂ towards NO, NO₂, and SO₂ molecule. The work also explored the selectivity towards target gases in the presence of CO₂ and H₂O gases. For the band structure after gas adsorption, the change of bandgap and low levels near the Fermi level meant doped WS₂ had great potential to be used as a resistance type gas sensor toward NO or SO₂. According to the binding energy results, both Al- and P-doped WS₂ had lower negative binding energy to gas molecules than the pristine WS₂, indicating the improvement of adsorption strength because of the presence of impurity. DOS showed that the impurity could generate more activated peaks and significantly stimulate the orbital mixing between gas and substrate to enhance the sensitivity of the substrate material. Therefore, there were more charge transfer and stronger binding interaction between gas molecules and doped WS₂ material. Besides, the sensitivity of P-doped WS₂ to NO and NO₂ was almost impossible to be affected by CO₂ and H₂O, while that to SO₂ would be changed in the presence of CO₂ or H₂O. The sensitivity of Al-doped WS₂ to NO was easily affected by H₂O but hard to be influenced by CO₂. However, the sensitivity of Al-doped WS₂ to NO and SO₂ was hard to be affected by CO₂ and H₂O. For NO detection, the Al- and P-doped WS₂ with a 7.4% dopant concentration had better sensitive properties than that with a 3.7% dopant concentration. While for SO₂ sensing, Al-doped WS₂ with a dopant concentration of 7.4% had a more pronounced weakening responsive performance than that with a 3.7% dopant concentration. The influence of doping concentration on the sensing performance of P-doped WS₂ was smaller than that of Al-doped WS₂. Therefore, our comprehensive calculations could provide doped two-dimensional materials with a valuable reference for sensing noxious gases.

**Supplementary information**

**Additional file 1: Fig. S1.** The 4 × 4 × 1 supercell model of Fe-doped WS₂ with the three adsorption sites marked. **Fig. S2.** The most stable adsorption model for NO adsorption on (a) Al-doped WS₂, (b) P-doped WS₂, (c) Fe-doped WS₂. Yellow, light blue, dark red, violet, purple, blue, and red balls represent S, W, Al, P, Fe, and O, respectively, the same below. The length of the N-O bonds in these models is marked in the figures.

**Fig. S3.** The most stable adsorption models of NO₂ adsorbed on (a) Al-doped WS₂, (b) P-doped WS₂, (c) Fe-doped WS₂. The length of the S-O bond after adsorption is marked in the figure. **Fig. S4.** The most stable adsorption models for SO₂ adsorbed on (a) Al-doped WS₂, (b) P-doped WS₂, (c) Fe-doped WS₂. The length of the S-O bond after adsorption is marked in the figure. **Fig. S5.** Projective density of states (PDOS) of (a) pristine WS₂, (b) Al-doped WS₂, (c) P-doped WS₂, (d) Fe-doped WS₂. Band structure of (a) Al-WS₂ with NO (b) Al-WS₂ with NO₂ (c) Al-WS₂ with SO₂ (d) P-WS₂ with NO (e) P-WS₂ with NO₂ (f) P-WS₂ with SO₂. Structural models and band structures for the Al-doped WS₂ with the most stable adsorption of (a) and (e) CO₂ molecule (b) and (f) H₂O molecule adsorbed; the P-doped WS₂ with (c) and (g) CO₂ molecule (d) and (h) H₂O molecule adsorbed. **Fig. S8.** Schematic diagrams for the four cases of 2Al or 2P atoms doped WS₂: (a) 2Al-WS₂-1 (b) 2Al-WS₂-2 (c) 2Al-WS₂-3 (d) 2Al-WS₂-4 (e) 2P-WS₂-1 (f) 2P-WS₂-2 (g) 2P-WS₂-3 (h) 2P-WS₂-4. **Fig. S9.** Models of the 2Al-doped WS₂-1 with the most stable adsorption with (a) NO molecule adsorbed and (b) SO₂ molecule adsorbed; the 2P-doped WS₂-1 with (c) NO molecule adsorbed and the 2P-doped WS₂-3 with (d) H₂O molecule adsorbed. **Table S1.** The Ebind results of the three gases adsorbed on this pristine or doped WS₂ on the different sites. **Table S2.** LOMO and HOMO of gases and E₁ of WS₂. **Table S3.** The Ebind results of CO₂ or H₂O gas molecules adsorbed on Al- or P-doped WS₂ on the different sites. **Table S4.** The Ebind results of NO or SO₂ gas molecules adsorbed on these two Al- or P-atoms-doped WS₂ on the different sites.

**Abbreviations**

2D: Two dimensional; TMDs: Transition metal disulfides; DFT: Density functional theory; LDA: Local density approximation; DNP: Double numerical plus polarization; DOS: Density of states; PDOS: Partial density of states; LUMO: Lowest unoccupied molecular orbital; HOMO: Highest occupied molecular orbital

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**Authors’ Contributions**

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

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**Availability of Data and Materials**

All data are fully available without restriction.

**Competing Interests**

The authors declare that they have no competing interests.

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