Adsorption Mechanism of SO\textsubscript{2} on Transition Metal (Pd, Pt, Au, Fe, Co and Mo)-Modified InP\textsubscript{3} Monolayer

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Abstract: Using the first-principles theory, this study explored the electronic behavior and adsorption effect of SO\textsubscript{2} on an InP\textsubscript{3} monolayer doped with transition metal atoms (Pd, Pt, Au, Fe, Co and Mo). Through calculation and analysis, the optimum doping sites of TM dopants on the InP\textsubscript{3} monolayer were determined, and the adsorption processes of SO\textsubscript{2} by TM-InP\textsubscript{3} monolayers were simulated. In the adsorption process, all TM-InP\textsubscript{3} monolayers and SO\textsubscript{2} molecules were deformed to some extent. All adsorption was characterized as chemical adsorption, and SO\textsubscript{2} acted as an electron acceptor. Comparing $E_{\text{ad}}$ and $Q_{\text{ad}}$, the order of the SO\textsubscript{2} adsorption effect was Mo-InP\textsubscript{3} > Fe-InP\textsubscript{3} > Co-InP\textsubscript{3} > Pt-InP\textsubscript{3} > Pd-InP\textsubscript{3} > Au-InP\textsubscript{3}. Except for the Au atom, the other five TM atoms as dopants all enhanced the adsorption effect of InP\textsubscript{3} monolayers for SO\textsubscript{2}. Furthermore, the analysis of DCD and DOS further confirmed the above conclusions. Based on frontier orbital theory analysis, it is revealed that the adsorption of SO\textsubscript{2} reduces the conductivity of TM-InP\textsubscript{3} monolayers to different degrees, and it is concluded that Pd-InP\textsubscript{3}, Pt-InP\textsubscript{3}, Fe-InP\textsubscript{3} and Mo-InP\textsubscript{3} monolayers have great potential in the application of SO\textsubscript{2} resistive gas sensors. This study provides a theoretical basis for further research on TM-InP\textsubscript{3} as a SO\textsubscript{2} sensor.

Keywords: InP\textsubscript{3} monolayer; transition metal doping; SO\textsubscript{2} sensors; DFT

1. Introduction

Sulfur dioxide (SO\textsubscript{2}) is a corrosive, toxic and colorless gas but has a strong pungent smell. SO\textsubscript{2} is mainly produced by the combustion of sulfur, which comes from the industrial production process and automobile exhaust emissions [1–4]. A low concentration of SO\textsubscript{2} gas has many negative effects on the human body, such as skin burns, the stimulation of cardiopulmonary function and respiratory inflammation. A high concentration of SO\textsubscript{2} gas can directly lead to human death. Sulfate aerosol generated by SO\textsubscript{2} oxidation in the atmosphere plays an essential part in the formation of PM\textsubscript{2.5}, which is the chief culprit of smog weather. When SO\textsubscript{2} is dissolved in water, it forms sulfuric acid, which irritates the eyes and nasal mucosa [5–10]. SO\textsubscript{2} is closely associated with the formation of acid rain, which is one of the main air pollutants [11]. Therefore, the control of SO\textsubscript{2} concentration has aroused widespread concern, and it is particularly important to develop a gas sensor with high sensitivity to monitor SO\textsubscript{2}.

In recent years, the discovery and preparation of graphene has triggered a wave of scholars’ research on two-dimensional (2D) materials. However, the zero-band-gap characteristic of graphene is an obstacle in some applications [12,13]. Therefore, in order to solve this problem, people have begun to explore new materials with better band-gap characteristics and graphene-like structures. Chemical sensors based on new 2D materials have been widely researched and applied in electrical equipment fault diagnosis and environmental gas monitoring, such as metal nitrides, transitional metal dichalcogenides, etc. [14–17]. New 2D materials containing main group III and V elements have become a hot
spot of research attention since the appearance of black phosphene materials [18,19]. The structural and bonding properties of novel 2D monolayers contained In sheet systems (such as InO and In$_2$O$_3$) have been researched by employing DFT, and they have been successfully synthesized [20,21]. The InP$_3$ monolayer is a new layered semiconductor material with a honeycomb structure. According to Ouyang et al., the electronic conductivity and electronic thermal conductivity of the InP$_3$ monolayer show marked anisotropy. At room temperature, the average lattice thermal conductivity of the InP$_3$ monolayer is about 0.63 W mK$^{-1}$, which is equivalent to that of classical thermoelectric materials [22]. Moreover, the InP$_3$ monolayer also has good optical properties, stable physical and chemical properties and high carrier mobility, which has great promise in the fields of battery materials, electronic/optical devices and gas sensors [23–26]. For example, Miao et al. found that the InP$_3$ monolayer shows semi-metallic and tunable magnetism in the case of hole doping, so it has a good application potential in electronic devices and photovoltaic devices [27]. Yi et al. proposed a new δ-InP$_3$ material and found that it has high carrier mobility and anisotropy. Through calculation, it was concluded that the δ-InP$_3$ monolayer is a N-based gas sensor with good reversibility and high selectivity and sensitivity [28]. Liao et al. investigated the adsorptive properties of Cr-InP$_3$ on H$_2$, C$_2$H$_2$ and CH$_4$ by density functional theory and discovered that Cr-InP$_3$ is a promising C$_2$H$_4$ sensor [29]. Therefore, the InP$_3$ monolayer is considered a base material for SO$_2$ adsorption.

As is well known, modifying and doping the base material with a transition metal (TM) can enhance electron mobility and promote the chemical activity of the base material, thus enhancing the gas adsorption capacity. The TM usually plays an essential role in improving the selectivity and sensitivity of nanomaterials to target gases [30–32]. In existing research, various doping atoms are used, but Pd, Pt, Au, Fe, Co and Mo as dopants have excellent doping and adsorption effects [33–38]. In our research, using density functional theory, we studied the electronic properties of an InP$_3$ monolayer doped with transition metals (Pd, Pt, Au, Fe, Co and Mo) and investigated the adsorption performance of SO$_2$ on the TM-modified InP$_3$ monolayer. The feasibilities of using TM-doped InP$_3$ monolayers as SO$_2$ gas sensors are proposed.

2. Computation Methods

In this study, the simulated computation was conducted in the Dmol$^3$ model of Materials Studio using the DFT method [39]. In order to obtain more reliable results, the Perdew–Burke–Ernzerhof (PBE) functional with high-precision generalized gradient approximation (GGA) was applied to calculate the electron exchange energy [40]. Tkatchenko and Scheffler’s (TS) method was adopted to correct the weak van der Waals forces between the TM-InP$_3$ monolayer and SO$_2$. The DFT-D method can be employed to compute the weak interaction between the base material and the adsorbed atoms, which makes the results more accurate [41]. Double numerical plus polarization (DNP) was used as the linear combination method of atomic orbits. DFT semi-core pseudopotential (DSPP) was selected to deal with the correlated effects of TM atoms [42]. An InP$_3$ monomer with lattice parameters of 14.9 Å × 14.9 Å × 24.1 Å was constructed, and its vacuum layer thickness was set to 20 Å. In the geometric optimization, we used a Monkhorst-Pack grid k-point mesh of 12 × 12 × 1 for Brillouin zone integration [43,44]. Moreover, the maximum force and displacement values were selected as 0.002 Ha/Å and 0.005 Å, and the energy tolerance accuracy was set at $1 \times 10^{-5}$ Ha. The self-consistent field tolerance (SCF) was $1 \times 10^{-6}$ Ha to make the calculation results more reliable [45,46].

To ascertain the most stable structure of the system under different doping conditions, the binding ($E_b$) energy of each system is usually computed by the below formula [47]:

$$E_b = E_{\text{TM-InP}_3} - E_{\text{InP}_3} - E_{\text{TM}}$$

(1)

$E_{\text{TM-InP}_3}$ and $E_{\text{InP}_3}$ represent the energy of the TM-InP$_3$ monolayer and the energy of the InP$_3$ monolayer, and $E_{\text{TM}}$ represents the energy of TM atoms [48].
Adsorption energy ($E_{ad}$) refers to the energy gained or lost by the system in the process of gas adsorption. It is an important indicator of adsorption difficulty. The calculation process is as follows [49]:

$$E_{ad} = E_{TM-InP_3/ SO_2} - E_{TM-InP_3} - E_{SO_2}$$ (2)

where $E_{TM-InP_3}$ and $E_{SO_2}$ denote the energy of TM-InP$_3$ and SO$_2$, respectively. $E_{TM-InP_3/ SO_2}$ represents the energy of the TM-InP$_3$/SO$_2$ system. An $E_{ad}$ less than 0 indicates that the adsorption process is exothermic, and if its absolute value is larger than 0.8 eV, it means that chemisorption occurs in the process [17,50].

Through Millikan population analysis, the charge transfer ($Q_t$) between the adsorbent surface and SO$_2$ can be known. The formula of $Q_t$ is as follows [51]:

$$Q_t = Q_{after} - Q_{before}$$ (3)

$Q_{before}$ and $Q_{after}$ denote the charge of SO$_2$ before and after adsorption. Negative $Q_t$ implies that electrons are transferred from the material to SO$_2$, and the adsorption material acts as an electron donor [52].

3. Results and Discussion

3.1. Structures of SO$_2$ and InP$_3$ Monolayer

The optimized SO$_2$ molecular model and its structural parameters are shown in Figure 1a. The SO$_2$ molecule has a symmetrical V-shaped structure, with the bond lengths of both S-O bonds being 1.480 Å and the bond angle of O-S-O being 120.031°. In this study, a two-dimensional InP$_3$ monolayer structure composed of 8 In atoms and 24 P atoms was adopted. Compared with an InP$_3$ multilayer system, a monolayer tends to have better semiconductor properties and carrier mobility. Its smaller band gap and better electrical conductivity are beneficial for its use as a gas sensing material. Therefore, in this work, the InP$_3$ monolayer was selected for doping and gas adsorption research [53–55]. The optimized InP$_3$ monolayer structure is shown in Figure 1b. Because the structure is symmetrical, there are two kinds of P atoms and two kinds of In atoms. In the InP$_3$ monolayer, the bond lengths of In-P and P-P are 2.531 Å and 2.236 Å, respectively, and the bond angles of P-In-P and P-P-P are 113.276° and 92.170°, respectively. The calculated energy band diagram of the InP$_3$ monolayer is shown in Figure 1c, and its band gap is 0.946 eV. The optimized structural data are in agreement with the data in References [43,56].

![Figure 1.](image-url)

Figure 1. (a) Structure of SO$_2$ and (b) structure and (c) energy band of InP$_3$ monolayer.

3.2. Analysis of TM Atom (Pd, Pt, Au, Fe, Co and Mo)-Doped InP$_3$ Monolayer

In this study, TM atoms were used to replace the atoms in the InP$_3$ monolayer. According to the above analysis of the InP$_3$ monolayer structure, it can be known that its structure
has symmetry. As shown in Figure 1b, P₁, P₂, In₁ or In₂ can be used as modification sites. Models of TM atom doping in intrinsic InP₃ through the above four possible sites were constructed, and the models were geometrically optimized. The binding energy (E_b) of each doping mode can be calculated by Equation (1). Through the analysis of each structure, the optimal doping sites and the binding energy (E_b) are shown in Table 1. The doping models are shown in Figure 2.

Table 1. Optimum doping sites and binding energies of TM-doped InP₃.

<table>
<thead>
<tr>
<th>Doping Sites</th>
<th>Pb-InP₃</th>
<th>Pt-InP₃</th>
<th>Au-InP₃</th>
<th>Fe-InP₃</th>
<th>Co-InP₃</th>
<th>Mo-InP₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_b (eV)</td>
<td>P₁</td>
<td>P₁</td>
<td>P₂</td>
<td>P₁</td>
<td>P₁</td>
<td>P₁</td>
</tr>
<tr>
<td></td>
<td>−4.410</td>
<td>−6.393</td>
<td>−3.767</td>
<td>−4.806</td>
<td>−5.180</td>
<td>−5.670</td>
</tr>
</tbody>
</table>

Figure 2. Structure and energy band of (a) Pd-InP₃, (b) Pt-InP₃, (c) Au-InP₃, (d) Fe-InP₃, (e) Co-InP₃ and (f) Mo-InP₃.

As can be observed in Table 1, the preferred doping sites of Pd, Pt, Fe, Co and Mo dopants are P₁ sites, while only the Au dopant is suitable for doping at the P₂ site. The E_b of the Pt-InP₃ monolayer is −6.393 eV, and the absolute value of E_b is the highest, while that of the Au-InP₃ monolayer is only −3.767 eV, and the absolute value of E_b is the lowest. The binding energies of the other four doping structures lie between those of Pt-InP₃ and Au-InP₃. This shows that the Pt dopant has the strongest binding ability with the InP₃ monolayer, and the doping structure is the most stable. On the contrary, the binding ability of Au to InP₃ is weak compared with the other five doping systems. It can be noted in Figure 2 that all six doping systems are deformed to some extent. By observing the energy band diagrams of the six systems, it can be found that, compared with intrinsic InP₃, the band gap of the InP₃ monolayer doped with metal atoms decreases from the initial 0.946 eV to 0 in Pb-InP₃, 0 in Pt-InP₃, 0.485 eV in Au-InP₃, 0.412 eV in Fe-InP₃, 0.837 eV in Co-InP₃ and 0.109 eV in Mo-InP₃. The reduction in the band gap means that electrons can easily complete the transfer from the valence band to the conduction band, which indicates that doping with the six metal atoms enhances the conductivity of the system. It is worth noting that after Pd and Pt dopants are doped into InP₃ monolayers, their band gaps are 0. This is
because Pd and Pt dopants induce the impurity state of the Pd-InP$_3$ monolayer and Pt-InP$_3$ monolayer, which results in strong N-type doping of InP$_3$. This behavior is similar to that of Au doping in the MoTe$_2$ system [57].

Figure 3 shows the density of states (TDOS and PDOS) of the six doping systems, which is used to analyze the electronic behavior of TM-InP$_3$ systems. Compared with the TDOS of intrinsic InP$_3$, the TDOS of the six TM-InP$_3$ systems all moved to low energy levels, which indicates that the conductivity of the six systems all increased, which is identical to the above conclusion of the energy band analysis. It can be found that the spin-down and spin-up of the TDOS of Fe-InP$_3$ and Mo-InP$_3$ systems are asymmetric, which indicates that the use of two dopants makes the InP$_3$ monolayer become magnetic. By analyzing the PDOS of the above two systems, it can be found that the Fe-3d orbit and Mo-4d orbit have high values near the Fermi level, which means that the electronic behaviors of Fe atoms and Mo atoms affect the magnetic transformation of the two systems. In TDOS, both Pd and Pt dopants contribute greatly to the TDOS at around $-2.8$ eV, and the value of the Au dopant is larger at around $-3.5$ eV. For Fe-InP$_3$, Co-InP$_3$ and Mo-InP$_3$ systems, the contributions of doped atoms to the TDOS of the system are mainly close to the Fermi level. In the PDOS diagram, the orbitals of the six doped atoms (Pd-3d, Pt-5d, Au-5d, Fe-3d, Co-3d and Mo-4d) markedly overlap with the In-5p and P-3p orbitals of InP$_3$, which implies that there are stable chemical bonds between TM atoms and InP$_3$ monolayers, and the overlap of Pt-InP$_3$ and Mo-InP$_3$ systems is the most pronounced. The above analysis shows that TM dopants can stably exist in InP$_3$ monolayers.

Figure 3. DOS of (a) Pd-InP$_3$, (b) Pt-InP$_3$, (c) Au-InP$_3$, (d) Fe-InP$_3$, (e) Co-InP$_3$ and (f) Mo-InP$_3$. 
3.3. Analysis of Adsorption Behaviors of \( \text{SO}_2 \) on TM-InP\(_3\) Monolayers

Next, the adsorption behaviors of \( \text{SO}_2 \) on TM-InP\(_3\) monolayers were analyzed. The gas molecules approach the TM-InP\(_3\) monolayer in different forms. After optimization, the adsorption energy \((E_{\text{ad}})\) was calculated by Equation (2), and the most stable adsorption structure was found. Table 2 presents the parameters and Millikan charge transfer of six optimal adsorption models. Figure 4 shows the optimized adsorption models and their deformation charge density (DCD). Table 3 lists the adsorption parameters of the intrinsic InP\(_3\) monolayer for \( \text{SO}_2 \) \((E_{\text{ad}}\) and \(Q_t\) in these data are derived from previous research results of Liao et al. [43]).

### Table 2. Characteristic parameters of \( \text{SO}_2 \) adsorption on TM-InP\(_3\) monolayers.

<table>
<thead>
<tr>
<th>Structure</th>
<th>The Length of Bond (Å)</th>
<th>Bond Angle (°)</th>
<th>Adsorption Distance (Å)</th>
<th>Atom</th>
<th>Mulliken Charge (e)</th>
<th>(Q_t) (e)</th>
<th>Ead (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-InP(_3)/SO(_2)</td>
<td>1.563</td>
<td>O(_1)-S-O(_2)</td>
<td>113.199</td>
<td>2.430</td>
<td>S</td>
<td>0.427</td>
<td>−0.420</td>
</tr>
<tr>
<td>S-O(_2)</td>
<td>1.564</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.409</td>
<td></td>
</tr>
<tr>
<td>Pt-InP(_3)/SO(_2)</td>
<td>1.556</td>
<td>O(_1)-S-O(_2)</td>
<td>111.696</td>
<td>2.403</td>
<td>S</td>
<td>0.416</td>
<td>−0.438</td>
</tr>
<tr>
<td>Au-InP(_3)/SO(_2)</td>
<td>1.576</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.440</td>
<td></td>
</tr>
<tr>
<td>Fe-InP(_3)/SO(_2)</td>
<td>1.486</td>
<td>O(_1)-S-O(_2)</td>
<td>114.541</td>
<td>4.209</td>
<td>S</td>
<td>0.372</td>
<td>−0.341</td>
</tr>
<tr>
<td>Co-InP(_3)/SO(_2)</td>
<td>1.558</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.429</td>
<td></td>
</tr>
<tr>
<td>Mo-InP(_3)/SO(_2)</td>
<td>1.566</td>
<td>O(_1)-S-O(_2)</td>
<td>110.233</td>
<td>2.123</td>
<td>S</td>
<td>0.436</td>
<td>−0.539</td>
</tr>
<tr>
<td>S-O(_2)</td>
<td>1.583</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−0.456</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3. Parameters of \( \text{SO}_2 \) adsorption by intrinsic InP\(_3\) monolayer.

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{\text{ad}}) (eV)</th>
<th>(Q_t) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP(_3)/SO(_2)</td>
<td>−1.050</td>
<td>−0.545</td>
</tr>
</tbody>
</table>

By analyzing the experimental data, it was found that the \(E_{\text{ad}}\) of the adsorption model with the largest absolute value in the Au-InP\(_3\)/SO\(_2\) system was \(-1.033\) eV, which is close to the \(E_{\text{ad}}\) of the InP\(_3\)/SO\(_2\) system in Table 3 \((E_{\text{ad}} = −1.050\) eV). The adsorption model in Figure 4c was observed, and it was found that the \( \text{SO}_2 \) molecule was far away from the Au dopant but close to a P atom on the InP\(_3\) monolayer. It is speculated that the Au dopant has no significant effect on the adsorption of \( \text{SO}_2 \) by the InP\(_3\) monolayer. In the above five adsorption systems (except for the Au-InP\(_3\)/SO\(_2\) system), the adsorption energy ranged from \(-1.635\) eV to \(-2.800\) eV, which are markedly improved compared with the adsorption energy of \( \text{SO}_2 \) using the intrinsic InP\(_3\) monolayer. The range of \(Q_t\) was \(-0.420\) e to \(-0.539\) e. The adsorption effect was ranked as Mo-InP\(_3\)/SO\(_2\) > Fe-InP\(_3\)/SO\(_2\) > Co-InP\(_3\)/SO\(_2\) > Pt-InP\(_3\)/SO\(_2\) > Pd-InP\(_3\)/SO\(_2\). The above data show that the adsorption processes of the five TM-InP\(_3\)/SO\(_2\) systems are all chemical adsorption, and negative \(Q_t\) means that \( \text{SO}_2 \) molecules act as electron acceptors and accept the electron transferred from TM-InP\(_3\) monolayers. After the adsorption process, the S-O bonds of \( \text{SO}_2 \) molecules in five systems (except for the Au-InP\(_3\)/SO\(_2\) system) are lengthened to different degrees, and the O-S-O bond angles are decreased to different degrees. It can be observed in Figure 4 that TM-InP\(_3\) monolayers with adsorbed \( \text{SO}_2 \) have pronounced geometric deformation. In particular, as can be seen from Figure 4e, the position of Co has moved considerably, and
the Co-In bond has been extended from 2.615 Å to 2.920 Å after adsorption. The Co atom has captured the SO$_2$ molecule through the S atom. The adsorption distance is 2.170 Å, and it is presumed that a Co-S bond with the same length is formed between them. Similarly, in the InP$_3$ monolayer system with Pd, Pt, Fe and Mo as dopants, SO$_2$ molecules were captured by doped atoms, forming a Pd-S bond of 2.430 Å, a Pt-S bond of 2.403 Å, an Fe-S bond of 2.059 Å and a Mo-S bond of 2.123 Å, respectively. Through the above analysis, it is speculated that it is precisely because of the good catalytic properties of Pd, Pt, Fe, Co and Mo atoms that SO$_2$ molecules are activated in the adsorption process.

Next, the interactions between SO$_2$ and TM-InP$_3$ monolayers were further verified by DCD. In Pd-InP$_3$, Pt-InP$_3$ and Mo-InP$_3$ adsorption systems, the electron depletion regions are mainly concentrated on TM-doped atoms, while in Fe-InP$_3$ and Co-InP$_3$ adsorption systems, the electron aggregation areas are around TM dopants. From the DCD diagrams of the above five systems, we can see that there is a pronounced overlap between the

electron depletion regions and the electron aggregation regions, which means that there are strong interactions between SO$_2$ and TM-InP$_3$ and the formation of new chemical bonds. However, for the Au-InP$_3$ adsorption system, there is no apparent continuous electron region between Au and SO$_2$ molecules, which implies that there is no significant charge transfer and no stable chemical bond formation between the SO$_2$ molecule and Au.

The DOS of the adsorption systems was analyzed to further explore the electronic behaviors of SO$_2$ molecules adsorbed by TM-InP$_3$ monolayers. It can be seen in Figure 5 that in Pd-InP$_3$, Pt-InP$_3$, Fe-InP$_3$ and Mo-InP$_3$ systems, after SO$_2$ was adsorbed, the TDOS of the systems moved considerably to the right, which means that the conductivity of the systems decreased. However, the TDOS of Au-InP$_3$ and Co-InP$_3$ systems did not show notable displacement, and the conductivity of the systems changed little after gas adsorption. Before and after SO$_2$ adsorption, the $\alpha$-spin and $\beta$-spin of Fe-InP$_3$ and Mo-InP$_3$ monolayers were highly asymmetric near the Fermi level, which indicates that the two systems that adsorbed SO$_2$ still had magnetism. In all TM-InP$_3$/SO$_2$ systems, a number of new peaks appeared between $-6$ eV and $-8$ eV, which are attributed to SO$_2$ after its adsorption. The appearance of a new peak means that SO$_2$ molecules are activated by TM-InP$_3$ monolayers, and it is speculated that this is mainly caused by orbital hybridization between TM atoms and SO$_2$.

Therefore, the PDOSs of the six systems were thoroughly analyzed. Taking the Pd-InP$_3$/SO$_2$ system as an example, Pd-4d, S-2p and O-2p orbitals markedly overlap between $-8$ eV and $2$ eV, so there is an intense hybridization phenomenon between them, which contributes to the formation of stable chemical bonds. This confirms our previous assumption. Similarly, in Pt-InP$_3$/SO$_2$, Fe-InP$_3$/SO$_2$, Co-InP$_3$/SO$_2$ and Mo-InP$_3$/SO$_2$ systems, the atomic orbits of TM atoms overlap with those of SO$_2$ in a large range, and the orbitals of SO$_2$ and TM atoms are highly hybridized. For the Au-InP$_3$/SO$_2$ system, we found that the Au-5d, S-3p and O-2p orbitals only slightly overlap from $-4$ eV to $-2$ eV, so it is speculated that there is no stable chemical bond between SO$_2$ molecules and Au atoms. Combined with the previous discussion, it can be inferred that using Au as the dopant does not enhance the adsorption properties of the InP$_3$ monolayer for SO$_2$, and its adsorption effect is similar to that of the intrinsic InP$_3$ monolayer. These phenomena indicate that, apart from the Au-InP$_3$/SO$_2$ system, there are new bonds between SO$_2$ and TM atoms, which gives SO$_2$ excellent chemisorption effects on TM-InP$_3$ monolayers and greatly affects the electronic behavior of intrinsic materials. In other words, the doping of five kinds of TM atoms (except for Au atoms) provides InP$_3$ monolayers with better adsorption stability for SO$_2$.

### 3.4. Frontier Orbital Theory and Gas Sensing Mechanism Analysis

The change in conductivity in TM-InP$_3$ monolayers caused by SO$_2$ adsorption was further studied, and the possibility of using them as SO$_2$ resistive sensing materials was explored. On the basis of frontier molecular orbital (FMO) theory, the LUMO and HOMO of the systems were calculated, and the energy between them is the band gap. From the previous analysis of the energy band diagram, it is known that a wider band gap means that it has lower conductivity. It can be found in Figure 6 that the LUMO and HOMO of TM (Pd, Pt, Fe, Co and Mo)-InP$_3$ systems after gas adsorption changed compared with those before gas adsorption, which implies that the gas adsorption process redistributes the electrons of the system. However, for the Au-InP$_3$ system, HOMO and LUMO did not markedly change before and after adsorption, which means that the adsorption process had little effect on the electronic behavior of the material. This shows again that the doping of Au did not improve the adsorption effect of SO$_2$, which is consistent with the previous conclusion. In the six TM-InP$_3$ systems, the adsorption of SO$_2$ changed the conductivity of the InP$_3$ monolayer to different degrees. For Pd-InP$_3$ and Pt-InP$_3$ monolayers, after adsorption, their band gaps increased to $0.330$ eV and $0.148$ eV, respectively, and their conductivity decreased. The adsorption of SO$_2$ made the two monolayers behave as semiconductors [57]. Both of them are potential choices as SO$_2$ sensor materials. For the Au-InP$_3$ monolayer, its band gap only
increased by 0.022 eV. Combined with previous research on its adsorption performance, it is concluded that it is not a suitable SO\textsubscript{2} sensor. Similarly, for the Co-InP\textsubscript{3} monolayer, although it has an excellent adsorption effect on SO\textsubscript{2}, its energy band changed little, only increasing by 0.024 eV, so it is not suitable as a material for detecting SO\textsubscript{2}. However, for Fe-InP\textsubscript{3} and Mo-InP\textsubscript{3} monolayers, the absorption of SO\textsubscript{2} made their band gaps almost double, so the conductivity decreased significantly. This provides us with two potential choices for the research of ideal SO\textsubscript{2} resistive sensor materials.

Figure 5. DOS of (a) Pd-InP\textsubscript{3}/SO\textsubscript{2}, (b) Pt-InP\textsubscript{3}/SO\textsubscript{2}, (c) Au-InP\textsubscript{3}/SO\textsubscript{2}, (d) Fe-InP\textsubscript{3}/SO\textsubscript{2}, (e) Co-InP\textsubscript{3}/SO\textsubscript{2} and (f) Mo-InP\textsubscript{3}/SO\textsubscript{2}.
3.5. Recovery Time Analysis

Recovery time refers to the time required for gas to desorb from the adsorption material, and it is an essential index for judging the gas sensing performance of the material. It is calculated by the following formula:

\[ \tau = \frac{1}{a} e^{\left(-\frac{E_a}{K_B T}\right)} \]  

where \( a \) is the attempt frequency, which is a constant with a value of \( 10^{12} \) s\(^{-1} \) [58,59]. \( K_B \) is the Boltzmann constant \( (8.62 \times 10^{-5} \text{ eV/K}) \), and \( T \) is the ambient temperature. \( E_a \) represents the energy barrier to be overcome in the desorption process, which is often displaced by \( E_{ad} \). The desorption time of \( \text{SO}_2 \) on the six kinds of adsorption materials at three different temperatures (298 K, 498 K and 698 K) was calculated and is shown in

Figure 6. HOMO and LUMO distributions of TM-InP\(_3\) monolayers and TM-InP\(_3\)/SO\(_2\) systems, (a) TM = Pd, Pt, Au, (b) TM = Fe, Co, Mo.
Figure 7. At room temperature (298 K), the desorption time of SO$_2$ on Au-InP$_3$ was the shortest. For Pd-InP$_3$, Pt-InP$_3$, Co-InP$_3$ and Fe-InP$_3$ monolayers, the desorption time of SO$_2$ at room temperature was very long, but the recovery time was significantly shortened when the temperature rose to 698 K. Their minimum value was only 0.63 s (Pd-InP$_3$), and the recovery time of the maximum Fe-InP$_3$ was 7.4 h. They had stable adsorption performance for SO$_2$ at room temperature and a short recovery time at high temperature, which means that they can be used as gas sensors many times and recycled. For the Mo-InP$_3$ monolayer, even at the high temperature of 698 K, it still took about 5 years for SO$_2$ to be released from the material surface. This means that the Mo-InP$_3$ monolayer has a strong ability to remove SO$_2$. Therefore, the Mo-InP$_3$ monolayer can be developed into a disposable SO$_2$ resistance sensor with a scavenger function, which can detect and remove SO$_2$.

![Figure 7. Recovery time of TM-InP$_3$ monolayers toward SO$_2$.](image)

4. Conclusions

All of the research in this paper is based on the first-principles theory. The effects of TM (Pd, Pt, Au, Fe, Co and Mo) dopants on the configuration and electronic behavior of InP$_3$ monolayers were studied. Through the analysis of DCD, DOS and frontier orbital theory, the adsorption characteristics, electronic behavior and sensing mechanism of SO$_2$ on TM-InP$_3$ monolayers were explored. The main conclusions are as follows:

1. Pd, Pt, Fe, Co and Mo atoms are more inclined to replace the P atom at the P$_1$ site in the InP$_3$ monolayer, while Au atoms are more inclined to replace the P$_2$ atom. Orbital hybridization makes the dopant form stable TM-P bonds and TM-In bonds with the intrinsic InP$_3$ monolayer.
2. The adsorption of SO$_2$ on TM-InP$_3$ monolayers was characterized as chemical adsorption, and SO$_2$ showed electron acceptance behavior.
3. Combined with the analysis of $E_{ad}$ and $Q_t$ of six adsorption systems, the adsorption effect of TM-InP$_3$ monolayers for SO$_2$ was in the following order: Mo-InP$_3$ > Fe-InP$_3$
except for the Au atom, the other five TM atoms as InP$_3$ dopants significantly enhanced the adsorption effect of the InP$_3$ monolayer for SO$_2$, and considerable orbital hybridization and stable chemical bonds were formed between dopants and SO$_2$.

4. The adsorption of SO$_2$ resulted in a change in the conductivity of TM-InP$_3$ monolayers to different degrees. Combined with the adsorption effect of the six systems for SO$_2$, this shows that Pd-InP$_3$, Pt-InP$_3$, Fe-InP$_3$ and Mo-InP$_3$ monolayers have great potential to be used as resistive SO$_2$ sensors, among which Fe-InP$_3$ and Mo-InP$_3$ are the most promising SO$_2$ sensor candidates.

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